

DEFORMATION AND METAMORPHISM OF THE
~~PYRITIC~~ ^{PYRITIC} SAN DIONISIO ORE BODY.
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by

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ABSTRACT

At the present time massive stratiform sulphide deposits are widely regarded as having an exhalative-sedimentary origin. The applicability of this view to the Rio Tinto deposits has been tested by investigating whether or not there is evidence in the essentially pyritic San Dionisio ore body of the regional metamorphic and tectonic activity. The stratigraphic conformity and the shape of the lode suggest that its present configuration may have been derived by folding during the first phase of deformation which affected the volcanic and sedimentary country rocks.

The granular structure of the massive ore has been systematised by distinguishing several microstructural assemblages. Almost every type of microstructure is characterised by the presence of euhedral compositional zoning in the component pyrite grains. By examining possible modes of recrystallisation in the natural environment it has been shown that the zoning is not a metamorphic feature, but records the transient grain shapes during the primary depositional history of the lode. The main grain size and shape characteristics of the pyrite aggregates are defined independently by zone structures and represent primary growth fabrics which were not detectably modified by recrystallisation. The instability of the compositional zoning under metamorphic conditions permitting volume diffusion in the pyrite lattice was demonstrated in a series of week-long experiments in which the natural ore was recrystallised in the solid state at temperatures between 600°C and 700°C.

From the morphology of the lode contacts and of internal primary marker surfaces it is argued that if the lode has been folded there should be evidence of observable displacements spaced at distances in the order of a few grain diameters or less. Except for fine grained pyrite ellipses, which originated from amorphous spherical precipitates and were distorted in a non-crystalline state, there is no record in the microstructure of the ore that the initial growth fabrics were

deformed during the regional folding. Primary growth structures in the pyrite aggregates are shown to have retained their original forms, and the structure, distribution and arrangement of primary intragranular zones is found to be inconsistent with the predicted effects of cataclastic deformation and mechanical and diffusional plastic deformation. Slickensides were apparently produced during an elastic deformation involving cyclic movements along isolated fracture planes. Friable zones of ore along the axis of the main syncline are re-interpreted in terms of leaching activity for which there is also considerable evidence in the microstructure of the pyrite aggregates.

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CHAPTER 1

INTRODUCTION

Massive, stratiform sulphide deposits have world-wide occurrence but their main features and possible modes of origin have probably received most attention in Canada, the Soviet Union, Japan, the U.S., Spain, Norway, Germany and Australia (see for example Stanton, 1960; Zavaritsky, 1950; Nishio, 1940; Kinkel et al., 1956; Williams, 1962; Vokes, 1963; Ramdohr, 1953; Solomon, 1965). Stratiform sulphide deposits are characterised by a simple mineralogy and by structural conformity with the local stratigraphic or tectonic environment. The mineral assemblages are dominated by pyrite, pyrrhotite, chalcopyrite, sphalerite and galena. Many ore bodies are essentially pyritic and among these the deposits in southern Spain are outstanding examples.

Early appraisals of the composition, structure and geological environment of stratiform pyrite deposits favoured an epigenetic, hydrothermal replacement origin (see for example Williams, 1934; Stickney, 1915). Subsequently, a possible genetic connection between the deposition of the ores and their volcanic host rocks has become widely recognised, and at present there are many stratiform ores for which it is commonly accepted that their origin can be regarded as essentially syngenetic and closely associated with the regional volcanism (see e.g. Zavaritsky, 1943; Tvalchrelidze and Buadze, 1967; Imai, 1960; Hutchinson, 1965; Kinkel, 1966; Williams, 1962; Higashimoto, 1960). The main relationships involved in the contemporaneous deposition of sulphides and volcanics were outlined by Oftedahl (1958) in his theory of exhalative-sedimentary ore genesis. The spatial propinquity of ore deposits and volcanic host rocks forms the basis of this theory. Kinkel (1966) and Hutchinson (1965) have also attempted to substantiate the volcanic origin of many ancient stratiform deposits by pointing out their

similarity to younger deposits whose volcanic associations are either evident at present or can be adduced with much greater certainty. These arguments have led Kinkel (1962, 1966) to believe that the Rio Tinto, La Zarza and Tharsis deposits in southern Spain are closely related to the volcanic activity associated with the deposition of the underlying host rocks. Just previously to this Williams (1962) had reviewed his earlier ideas on the origin of the Rio Tinto ores and arrived at a similar conclusion.

The volcanic origin of many stratiform deposits occurring in folded and metamorphosed country rocks has frequently been confirmed by reports that the sulphide ores show evidence of deformation. For example, slickensides (Zavaritsky, 1950), elongate sulphide grains (Page, 1963; Vokes, 1963; Kanehira, 1959), small scale folds and flowage structures (Solomon, 1965; Vokes, 1963; Kalliokoski, 1965) and cataclastic structures (Hutchinson, 1965; Domarev, 1956) have been taken to indicate that the sulphide ores were involved in a regional tectonic (folding) event. Emplacement of stratiform deposits earlier than the regional tectonic/metamorphic activity has also been inferred from reports of evidence that the sulphide ores have been recrystallised. The main features adduced in support of recrystallisation are the development of euhedral pyrite crystals (Stanton, 1960; Vokes, 1963; Kalliokoski, 1965), the development of polygonal grain boundary configurations in polycrystalline aggregates (Stanton, 1964), a decreasing incidence of colloform structures with increasing metamorphic grade (Zavaritsky, 1943; Yamaoka, 1962), an increase in grain size with increasing metamorphic grade (Hutchinson, 1965; Vokes, 1962; King, 1959) and an increase in the volume ratio pyrite:pyrrhotite with increasing metamorphic grade (Hutchinson, 1965).

In contrast to prevalent views (see for example Hutchinson, 1965; Sharpe, 1965) on the origin of the Canadian deposits, Boyle and Davis (1964) and Boyle (1965) claim that the stratiform ores in the New Brunswick district are epigenetic. This

conclusion is largely based on the mineralogical identity between the stratiform deposits and coexisting vein deposits which undoubtedly post-date the regional folding. Boyle (1965) also notes that the Larder U deposit in New Brunswick is discordant with the stratigraphic succession. His maps indicate that this ore body is parallel to the regional cleavage, thus implying that its emplacement was controlled by, and therefore post-dates the main folding event in the region. Campbell and Irvine (1960) described a similar relationship for several stratiform deposits in British Columbia. Suffel (1965) has also acknowledged the discrepancy that arises where the structure of supposedly exhalative-sedimentary ore bodies is controlled by tectonic features. However, he points out that this relationship may be explicable in terms of remobilisation. Hanson (1920) considered that stratiform deposits parallel to the regional cleavage were post-tectonic, and therefore of epigenetic origin.

In addition to the criticism raised by Boyle, there are other aspects of the exhalative-sedimentary theory which suggests that this mode of origin is not applicable to all stratiform sulphide deposits. For example, Davidson (1963) has questioned the adequacy of volcanic exhalations in providing the required composition and amount of sulphide material found in natural deposits. Worthington (1965) pointed out that several stratiform ores in the southern Appalachians occur in a clastic sedimentary succession where volcanics, and thus the immediate source of the sulphides, are either absent or a very minor part of the sequence. Byers (1960) reports that the steep-dipping Coronation and Birch Lake deposits in Canada show vertical compositional zoning; this feature strongly suggests that the lodes were originally emplaced in their present orientation. Finally, it is worthwhile pointing out that two modes of origin are currently attributed to the massive pyritic ores in the Ural and Caucasus Mountains (see for example Tvalchrelidze and Buadze, 1967; Yakovlev, Zarayskiy and Starostin, 1966). Some deposits are believed to form in close association with effusive volcanic activity, whilst others are

thought to originate by hydrothermal metasomatism related to comparatively deep-seated intrusions, which in turn are connected with the same magma source as the surface volcanism. A sub-volcanic origin for stratiform ores might account for the spatial relationship between the sulphide deposits and their volcanic host rocks, and at the same time provide an explanation for the emplacement of the sulphides in strata which are already folded or tilted.

An exhalative-sedimentary origin has been attributed to several of the massive pyrite deposits in southern Spain on the basis of their occurrence near the top of a succession of volcanic host rocks. Other implications of this origin have not been examined, though Hutchings (1963) reports that the La Ratera deposit is locally conformable with the regional slaty cleavage and Kinkel (1962) claims that the Rio Tinto deposits show evidence of cataclastic deformation. In comparison to the North American, Norwegian, Russian and Japanese deposits there has been no serious attempt to test the exhalative-sedimentary origin of the Spanish ores by investigating the deformation and metamorphic effects which the deposits should have been subjected to during the Hercynian orogeny.

The object of this study is to clarify the origin of the Rio Tinto deposits, and in particular the San Dionisio lode, by a direct examination of the metamorphic and structural implications of genetic theories based on primary deposition of the sulphides in a flat-lying horizon.

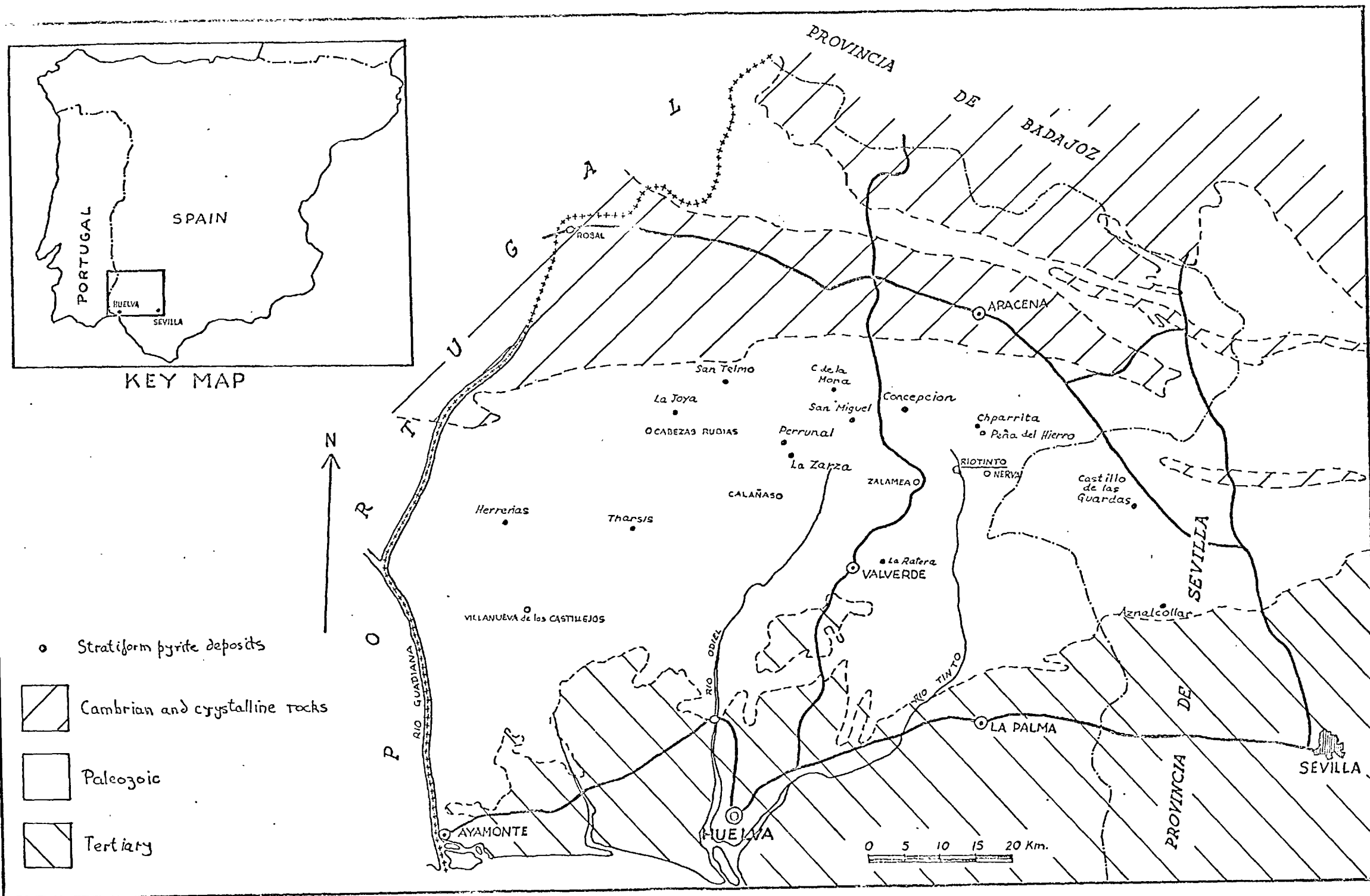


Figure 2.1 Regional location map showing the distribution of the stratiform pyrite deposits in the Paleozoic geosyncline of south-west Spain.

CHAPTER 2

LOCAL AND REGIONAL GEOLOGY OF THE RIO TINTO AREA

2.1 Regional Geological Environment

The Rio Tinto deposits, situated approximately 65 kms. north-west of Sevilla, are the best known ore bodies in the south of the Iberian Peninsula. The stratigraphy of the western part of this region, especially in Portugal, has been extensively studied by McGillavry and his co-workers, and although the detailed succession in the Province of Huelva is less clearly known, important generalisations can be made.

The regional geology is shown in fig. 2.1. Pre-Cambrian and Cambrian gneisses, schists and other relatively high grade metamorphic rocks outcrop in the north of the area, and are separated from a zone of Tertiary deposits to the south of **the** River Guadalquivir, by an extensive belt of Paleozoic rocks (D. Williams, 1934, p. 595). The latter are mainly Devonian to Carboniferous in age, and apart from occasional strata indicative of shallow water deposition, they consist chiefly of: (1) a lower series of rocks belonging to a volcanic facies, and (2) an upper sequence of rocks belonging to a non-volcanic, deepwater, clastic facies. The Paleozoic rocks, which according to McGillavry (1962) represent a eugeosynclinal sequence, are intruded by essentially concordant granites in the north, and have been subjected to extensive Hercynian folding and to regional metamorphism producing mineral assemblages indicative of the lower greenschist facies. A large number of conformable, pyritic deposits, typified by those at Rio Tinto, are confined exclusively to this belt of Paleozoic rocks (fig. 2.1).

Several of the pyritic deposits of south-west Spain and Portugal have now been studied. Although only a few of these studies are published, a large volume of descriptive

information, in the form of unpublished theses, was available at the time the present investigation was carried out. It is not within the scope of this thesis to summarise the vast accumulation of data collected in earlier studies, and thereby to demonstrate the essential similarity of the pyrite deposits throughout the ore-bearing zone, because to some extent this conspectus has been attempted previously. For example, it is evident from such comparisons as those published by Edge (1926), Finlayson (1910), and Kinkel (1962) that the broad regional setting and megascopic features of the Rio Tinto ore bodies are duplicated in other well known deposits of the Province, though in detail differences are apparent. The information contained in several unpublished theses (Barringer, 1954; Apps, 1961; Seaward & Rexworthy, 1963; Hutchings, 1963; Elliott, 1966) and in "Pyritas de Huelva" (Pinedo Vara, 1963) indicates that similar comparisons can be extended to the entire ore-bearing zone, including the lesser known and smaller deposits of the Province of Huelva.

The evidence drawn on in proposing the essentially uniform character of these deposits is entirely descriptive and non-genetic. The number of theories promulgated in the past to account for the origin of one or more of the deposits bears no relation to variations in the type of the deposit, and is purely the result of changing interpretations of an essentially constant assemblage of facts. Indeed, it is probably safe to venture the statement that at present it is principally because of the uniformity of the ore-bearing zone that a large body of opinion would concur with the views of D. Williams (1962) and Kinkel (1962) in assigning a single origin (i.e. volcanic-exhalative) to all the deposits in the region.

2.2 Local Geological Environment

At Rio Tinto a number of tabular to complexly shaped, almost monomineralic pyrite ore bodies lie, broadly speaking,

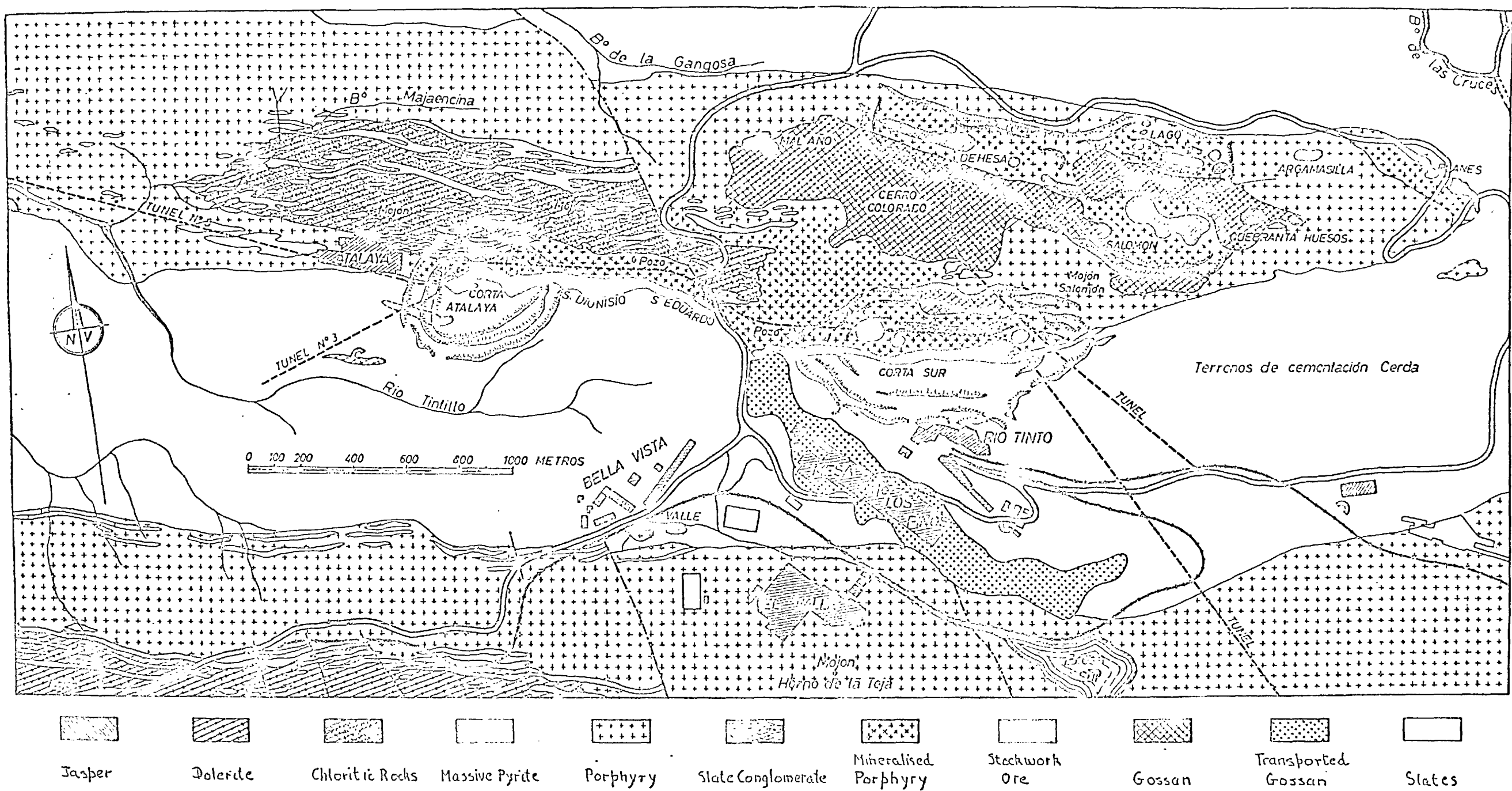


Figure 2.2 Geological map of the Rio Tinto area (compiled by Williams, 1934).

on an otherwise conformable contact between a heterogeneous succession of underlying volcanic rocks and an overlying sequence of quartz-rich, clastic sediments (fig. 2.2) which have been assigned to the Viséan stage of the Lower Carboniferous (Gonzalo y Tarin, 1888, p. 663). The principal ore bodies are grouped on the southern flank, the eastern nose and the north-eastern "roof" of a regional, east-west trending anticline, the core of which is occupied by volcanic rocks (D. Williams, 1934, Plate 26). Similar ore bodies are also found, probably on the same contact, a few miles to the north of Rio Tinto (e.g. Peña de Hierro, Chaparrita, and San Miguel; see Apps. 1961).

The San Dionisio ore body is the largest of the Rio Tinto group of deposits, being some 1000 m. long, and when unfolded, having an estimated thickness of 25 to 100 m. and a maximum width of at least 550 m. The lode is continuous on its upper levels with a small deposit (the Eduardo Mass) in the east, and the latter in turn is separated from the next largest ore body in the group (South Lode) by a prominent fault zone (the Eduardo Fault). All three of these deposits occur on the southern flank of the main anticlinal structure in the mine area (fig. 2.2).

2.3 The Stratigraphic Succession at Rio Tinto

Before proceeding with a detailed description of the individual rock units in the immediate vicinity of the San Dionisio ore body, it is important to outline the general character of the stratigraphic succession in the mine area. It is now well established (D. Williams, 1962; Kinkel, 1962) that at Rio Tinto, La Zarza, Tharsis and probably several of the other deposits in the Province, the stratigraphic sequence can be divided into two main formations.

The upper formation consists principally of pelitic sediments. The lower formation consists of a heterogeneous sequence of volcanic rocks, composed mainly of lavas, which

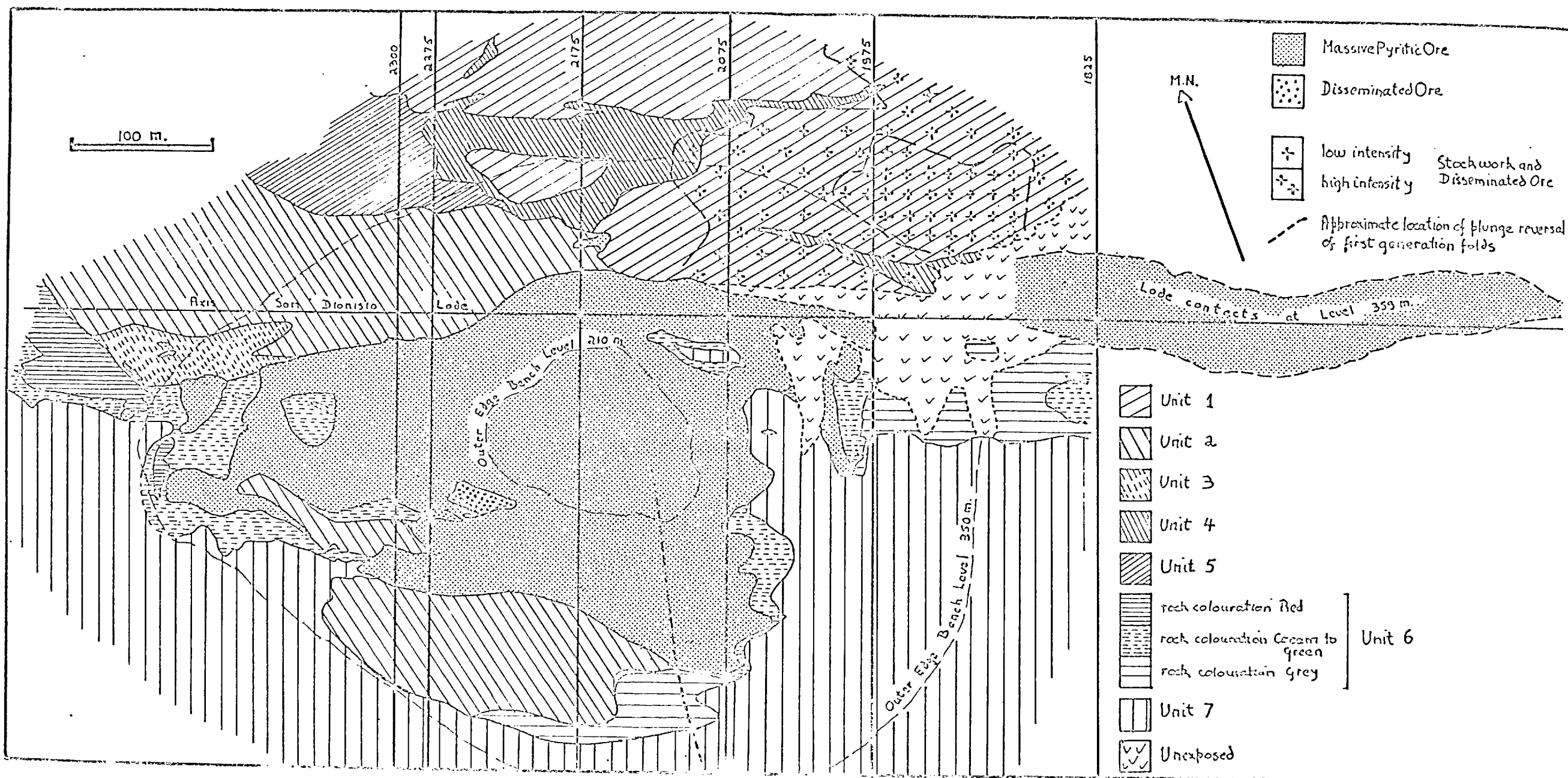


Figure 2.3 Geological map of the immediate area of the San Dionisio ore body (Atalaya opencast).

passes upwards gradationally into a zone of fine grained, tuffaceous or fragmental pyroclastic rocks. Most of the massive sulphide ore bodies lie within, or near to, this zone of pyroclastic deposits.

Although many descriptions of the igneous rocks (excluding the granites in the north) were biased towards the then prevalent view that these rocks were intrusive (e.g. Finlayson, 1910; G. Williams, 1932, D. Williams, 1934), a number of investigators (e.g. Fourmarier, 1928; Collins, 1922) suggested a volcanic origin for several or all of the igneous rocks. Within recent years new evidence has been brought forward in support of the volcanic affinities of these rocks, and it can now be safely said that an extrusive origin is widely accepted (D. Williams, 1962; Kinkel, 1962). Some additional observations presented by Elliott (1966), and the descriptions that follow, corroborate the volcanic origin of the igneous rocks at Rio Tinto.

Rock Type Descriptions: In the footwall succession immediately below the San Dionisio ore body, five mappable rock units are recognisable (see fig. 2.3). Although some of these have been given specific names in the past, this practice will not be adhered to here. For descriptive purposes the units are numbered 1, 2, 3, 4 and 5.

Unit 1 consists of fine grained rocks, often massive and green coloured in the field. They are dominantly composed of approximately equal amounts of micaceous minerals and quartz, the latter occasionally occurring as large grains or as relatively coarse grained aggregates. Quartz veins and stock-work ore are almost entirely restricted to this unit, which immediately underlies the ore body along the entire eastern two-thirds of the northern flank of the main synclinal structure (fig. 2.3).

Unit 2 is characterised by rocks having a porphyritic fabric. Phenocrysts, mainly of quartz, and less frequently of plagioclase and alkali feldspar, occur together with a few

grains of calcite, in a matrix of quartz and micaceous minerals. The feldspar phenocrysts often tend to develop euhedral shapes, whereas the phenocrystic quartz is generally rounded, weakly to strongly embayed and often exhibits secondary growth fringes. Rocks of this unit directly underlie the ore body in the north-western sector of the opencast, along the southern flank of the main synclinal structure, and in the southern anticline (fig. 2.3).

Unit 3 consists predominantly of rocks mineralogically similar to those of unit 2, but which have a distinctly less marked porphyritic fabric. Interbanded with these rocks, and characteristic of this unit, are lenses of pelitic material.

Unit 4 is characterised by fine grained, megascopically banded rocks, consisting of intercalations (in the order of 1 - 10 cms. thick) of pelitic and psammitic material. The mineralogy of these rocks is dominated by quartz and micaceous minerals.

Unit 5 consists of conglomeratic rocks (the "slate-conglomerate" described by D. Williams, 1934, p. 599) in which rounded to ellipsoidal, fine grained, quartzitic pebbles (in the order of 0.25 - 10 cms. in diameter) are contained in a pelitic matrix of quartz and micaceous minerals.

Apart from their association with rock types such as those having a glassy texture, a tuffaceous nature, a graded-bedded or a flow-banded structure, the main field evidence for the volcanic origin of the rock types of units 1 to 5 is the total absence of intrusive contacts. In addition, and in spite of the probable modification of primary textures caused both by shearing and the widespread replacement of earlier minerals by chlorite, calcite, epidote and mica, there is mineralogical and microstructural evidence of the volcanic nature of these units. For example, the overall fabric and the habit of phenocrysts in unit 2 suggests that this rock type was initially a flow or a tuff. In unit 1 the unusually large grains occasionally found in the fine grained matrix

may be satisfactorily interpreted as phenocrysts; moreover, the massive and highly coherent nature of this rock suggests that it has an extrusive volcanic origin. Especially when considered in the wider context of the overall stratigraphic succession, there seems little doubt that the rock types of units 1 to 5 were derived either directly or indirectly from a volcanic provenance. Rock types identical to units 1 and 2 underlie a large part of the La Zarza deposit.

Two rock units occur above the San Dionisio ore body. The lower of these (unit 6, see fig. 2.3) is characteristic of the junction between the main volcanic and non-volcanic sequences, and appears to be more or less continuous on a regional scale. The rocks comprising this unit are psammpelitic, and sometimes megascopically banded; they are less fissile than the overlying slates and show predominantly lateral colour variations through red, yellow, cream and green to grey (fig. 2.3). These rocks are composed of quartz, chlorite and micaceous minerals. Thin calcite-rich bands (ca. 1 - 5 cms. thick) occur as sporadic intercalations in the reddish coloured psammpelites in the west of the opencast. On the 29th. floor, in the underground workings to the east, an apparently fragmental rock type immediately overlies the ore body, as a lens in unit 6. This rock contains unusually large (ca. 1 - 2 mm. in diameter) single grains and aggregates of quartz set in a micaceous groundmass; it is the only member of unit 6 which can, with reasonable certainty, be ascribed to a volcanic provenance. The fine grained rocks comprising the bulk of the unit are also thought to have a volcanic origin (D. Williams, 1962).

Bands of jasper (0.5-1 m. thick) and of dense black pelitic rocks (1-20 cms. thick) are occasionally found at the base of unit 6. These dense black pelitic bands have generally been referred to, both at Rio Tinto and elsewhere in the Province, (see Kinkel, 1962, p.1072) as carbonaceous shales. Analyses of two typical samples of this rock (taken from immediately above the San

Dionisio lode) show an average carbon tenor of 0.83%, a value which is little different from the 0.62% carbon content reported by D. Williams (1934, p. 599) for the grey-black shales comprising the main pelitic formation overlying the ore bodies. The intense black colour of these slates may be due to disseminations of finely particulate sulphide, and claims that they indicate reducing conditions of deposition must therefore be regarded with caution.

The upper stratigraphic unit at Rio Tinto (unit 7, see fig. 2.3) consists of grey to black, dominantly pelitic rocks. Intercalations of psammitic material are of common, though local occurrence in the slate succession. The mineralogy of this unit is dominated by quartz, chlorite and micaceous minerals.

2.4 Composition and Stratigraphic Relationships of the San Dionisio Ore Body.

The San Dionisio ore body lies between the main volcanic succession and the overlying unit 6, and can be satisfactorily regarded as an integral part of the bedded succession. A generalised statement of this type can be extended to apply to the La Zarza deposit and probably also to most of the pyrite deposits in the Province. The upper contact of the San Dionisio ore body displays complete stratigraphic conformity on a mappable scale (fig. 2.3). Its lower contact is locally unconformable (i.e. at the boundaries between units 2 and 3 and units 2 and 1; see fig. 2.3), and although this may indicate a real stratigraphic or structural discontinuity, it is more probably a reflection of the manifestly lenticular and interfingering arrangement of the various rock units in the volcanic succession. The conformable nature of the direct contact between unit 6 and the underlying volcanic succession, a feature which can be observed to the west of the ore body, is indicative of the absence of a stratigraphic discontinuity at

the base of the latter. Small scale cross-cutting relationships between the ore body contact and bedding in the overlying and underlying sediments have not been observed.

Megascopically, the ore body is remarkably homogeneous. It consists almost entirely of massive pyritic ore, containing in the order of 5% of sphalerite and chalcopyrite combined, together with minor amounts of galena, arsenopyrite and tetrahedrite; in addition, Bateman (1927, p. 587) lists a group of rare sulphides, arsenides and selenides. A number of secondary minerals are also reported by Bateman (1927, p. 591) and D. Williams (1934, p. 634). Assay results show that whereas there is little regularity in the distribution of Pb-Zn values, the primary copper content of the ore body exhibits a consistent increase towards its base, reaching the highest values adjacent to the heavily stockworked footwall rocks (D. Williams, 1934, p. 620 - 3). Sub-units within the ore body cannot be distinguished since, except in local marginal areas field observations do not permit the recognition or delimitation of zones or bands of ore which are mineralogically or texturally distinct (see sect. 3.1).

Isolated in the eastern half of the northern limb of the main ore body syncline, a number of volcanic/sedimentary "horses" were encountered in the old min workings (D. Williams, 1934, p. 624 - 5). These bodies, which were remarkably extensive and regular, had a plate-like form and their orientation was approximately conformable with that of the ore body contacts. A rock type identical to that of unit 2, described above, made up a large part of these "horses" and was frequently intercalated with bands of pelitic material or a rock type similar to that in unit 6.

The upper contact of the ore body is almost always quite abrupt, though local transitional boundaries have been reported by some investigators (e.g. D. Williams, 1934, p. 613). Disseminated mineralisation in the hanging wall rocks is

extremely sparse. On the 18th., 19th. and 20th levels, at the crest of the southern anticline, a stockwork ore has been observed in unit 6.

The lower contact of the lode shows various degrees of definition which can be largely correlated with the state of mineralisation of the adjacent wall rocks. Wherever the foot-wall volcanics are unmineralised (e.g. in the western one-third of the opencast, see fig. 2.3) the contact is sharply defined. Where the footwall rocks contain much disseminated mineralisation the contact tends to become gradational, though locally it is sharply defined. As the zone of stockwork and intensely mineralised volcanics is approached, the gradational nature of the contact becomes increasingly marked.

The stockwork ore (D. Williams, 1934, p. 627) appears as a complex, three dimensional network of essentially sulphide-bearing veins with an average thickness of approximately 2 - 3 cms. The orientation of the veins cannot be related to any immediately obvious pattern. Vein walls are sharply defined and, not uncommonly, they can be matched; the rock material between individual veins is mineralised. The incidence of stockwork veins and the intensity of disseminated mineralisation decreases with depth below the ore body and, in addition, it shows a lateral variation (fig. 2.3). Sulphide minerals in the zone of stockwork and disseminated mineralisation are relatively richer in copper than those in the overlying massive ore (D. Williams, 1934, p. 623).

Wall rock alteration is a prominent feature of the San Dionisio ore body and is remarkable for its lack of regular distribution. In some areas perfectly fresh hanging wall rocks extend up to the ore body contact, whereas in other places thin veneers of heavily bleached, fine grained rocks intervene along the contact and may rapidly expand up to thicknesses in the order of 5 - 10 m. Apart from heavily chloritised rocks, which occur within and extend to the north

of the stockwork ore zone (D. Williams, 1934, p. 603), the foot wall volcanics show no alteration which can be related to the proximity of the ore body.

2.5 The Regional and Local Structural Environment

Although the regional aspects of the tectonic history of south-east Spain and Portugal have been known for a long time, the detailed geometric and time relationships have not been appreciated until recently, and then only in a few, relatively small areas. The pioneering geological studies of Gonzalo y Tarin (1888) demonstrated the major importance of a system of east-west trending folds, plunging gently towards the east and west; these folds determine, and their orientation can be inferred from, the regional outcrop pattern of mappable stratigraphic units.

Subsequent, though areally less extensive surveys (e.g. D. Williams, 1934; G. Williams, 1933) confirmed the general picture established by Gonzalo y Tarin. More recently, Bard (1965), Rambaud Perez (1963) and Febrel Molinero (1965) have succeeded in recognising different tectonic events in the overall structural history of the area, and have attempted to date and work out the geometry of the different fold systems.

A summary of the present state of knowledge of the structural history of this part of the Iberian Peninsula is given below:

- (1) All the deformation can be ascribed to two periods of folding and a final phase of faulting.
- (2) Ubiquitous, first generation E.-W. folds are represented both by large and small scale, open to isoclinal structures, overturned generally to the south, with frequent and often strong plunge changes. These folds correspond to the structures recognised by Gonzalo y Tarin and, as further noted by him, comprise the most

prominent fold system in the Province. These first generation folds are accompanied by an axial plane slaty cleavage.

- (3) Second generation folds are characterised by their style, their relatively small scale (wave-lengths measured in the order of centimetres or metres) and by their localised occurrence; they are usually absent from the more competent rock types. Folds belonging to this system are accompanied by an axial plane fracture cleavage (the existence of which was occasionally recognised by earlier workers - e.g. G. Williams, 1933, p. 24) and generally appear to have a moderate dip to the south and an east-west strike. (See, for example, Febrel Molinero, 1965).
- (4) All folding movements occurred during the Hercynian orogeny (G. Williams, 1933, p. 5; Bard, 1965, p. 336).
- (5) Regional metamorphism was contemporaneous with the first period of folding (Bard, 1965, p. 323).
- (6) Extensive faulting occurred after all fold movements, and has been dated as late Hercynian (Bard, 1965, p. 323).

At Rio Tinto the first comprehensive geological survey by D. Williams (1934), established the existence of major east-west trending folds and revealed the structural continuity of the area with that of the rest of the Province. Subsequent work in the area confirmed these findings, and Rambaud Perez (1963, p. 88 - 91) went a step further in partly describing the geometry of the major fold system.

The investigations described in this thesis were thus commenced in the light of a fairly thorough background knowledge of the local and regional setting. Most importantly, the broad structural relationships of the various Rio Tinto ore bodies were known or could easily be deduced - i.e. the ore bodies were distributed along an important stratigraphic

boundary, the three-dimensional form of the latter defining a major east-west trending and easterly plunging anticline or anticlinorium (see Rambaud Perez, 1963, fig. on p. 93).

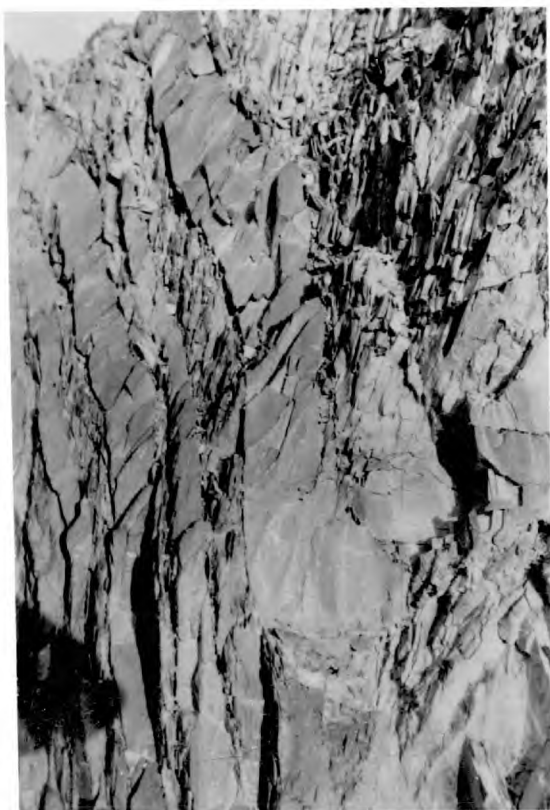
The San Dionisio ore body was mapped in three dimensions by D. Williams (Mines Plans, 1928 - 32) who recognised its continuous distribution in the form of a syncline and part of an adjacent anticline (see fig. 2.8). The broad scale conformity of the ore body was evident from its confinement to the boundary between the underlying volcanic sequence and the overlying non-volcanic sequence. The detailed nature of the conformity relationship was, however, not known and since the occurrence of any cross-cutting features may have important implications concerning either ore migration during deformation or a primary replacement process, it was decided to evaluate as closely as possible the degree of conformity of the ore body contact with respect to the orientation of bedding in the immediately surrounding country rocks.

The limitations of surface mapping in this endeavour are directly related to the closeness to the ore body of mappable stratigraphic units. It was therefore proposed to carry out a structural analysis of the ore body contact and the country rocks, in the hope that a correlation of these analyses would provide a more detailed picture of the conformity relationships.

2.6 Structural Relations in the Metasediments in the Immediate Vicinity of the San Dionisio Ore Body

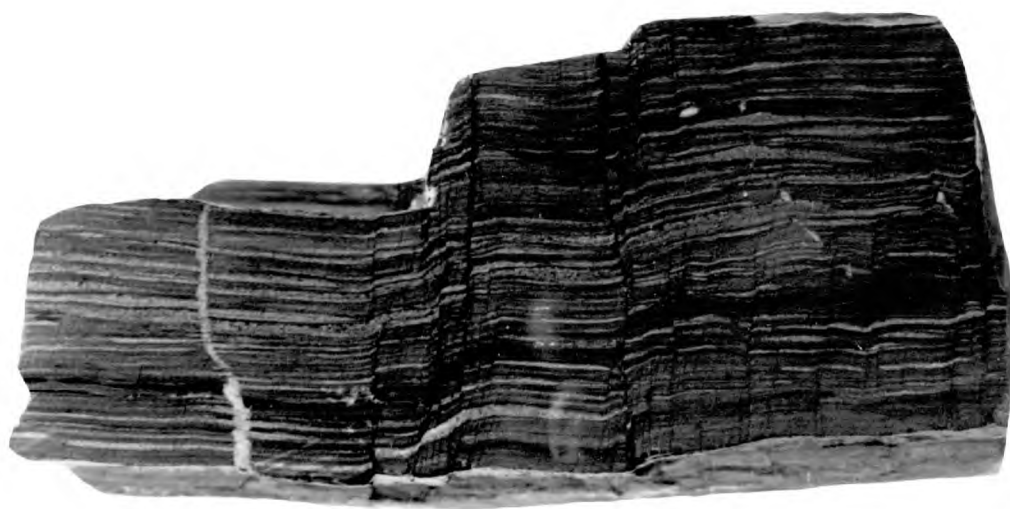
The structural history which has been established for the area in the immediate precincts of the San Dionisio ore body is applicable to a large part of the surrounding region, and involves two successive folding phases and a final period of faulting.

First generation folds are most commonly observed as



2·1

1 m



2·2

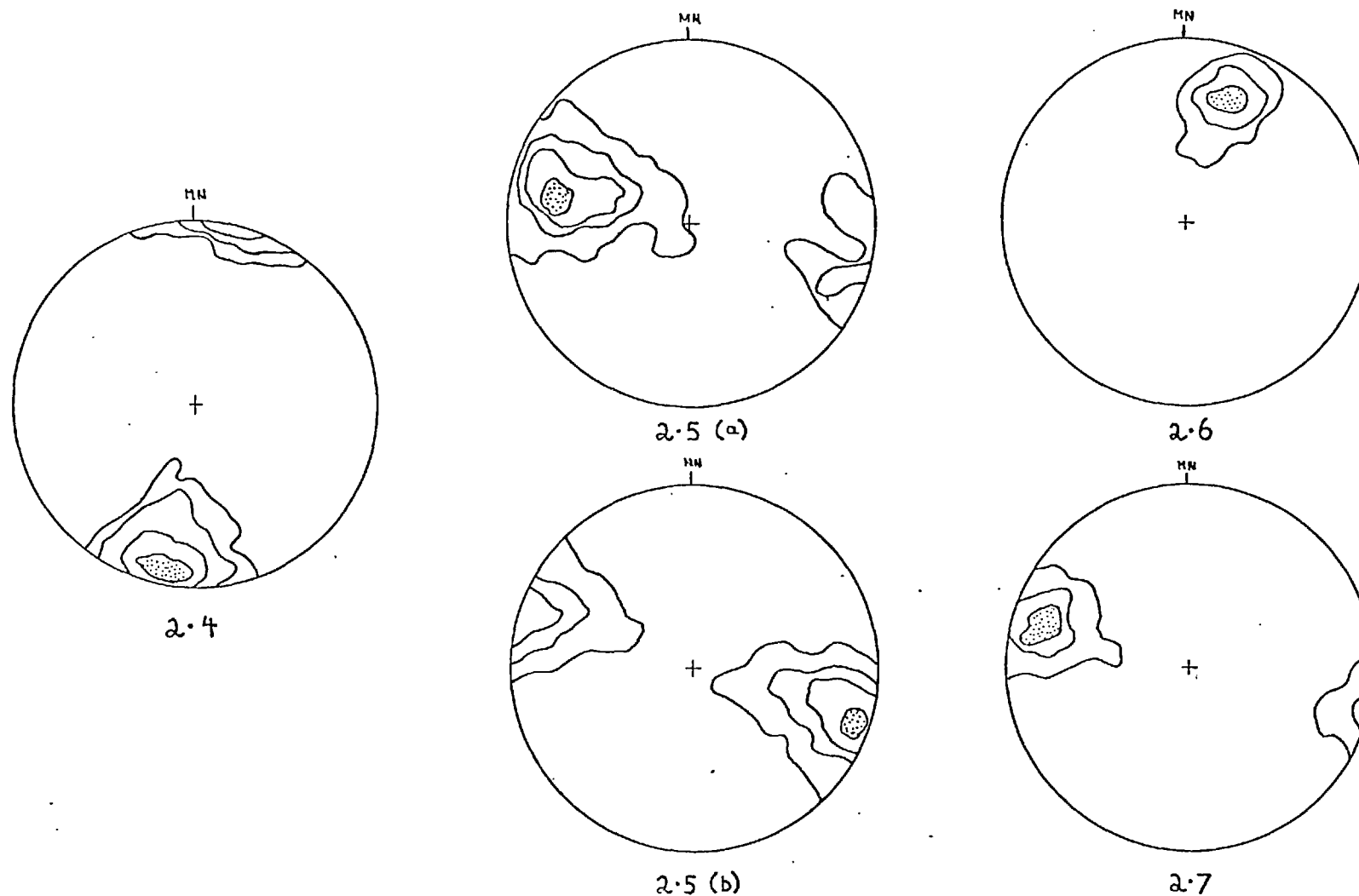
2 cm

Plate 2.1

First generation fold in the fine grained clastic sediments (unit 7) overlying the ore body. The regional slaty cleavage (S_1) trends vertically in the illustration and is parallel to the axial plane of the syncline in the less competent layers.

Plate 2.2

Second generation folds in the fine grained sediments (unit 6) immediately overlying the ore body. The fold profiles are asymmetrical and their axial plane is defined by a fracture cleavage (S_2) which trends vertically in the illustration.



Equal area, lower hemisphere, stereographic projections.
Orientation of cleavages and fold axes in the pelitic rocks
overlying the San Dionisio lode.

Figure 2.4 550 poles to slaty cleavage (S_1). Contours 1, 3, 10, 28 p.c. per one p.c. area.

Figure 2.5(a) 143 first generation fold axes (bedding/ S_1 intersections) in the rocks overlying the western one third of the lode. Contours 1, 4, 7, 11 p.c. per one p.c. area.

Figure 2.5(b) 221 first generation fold axes in the rocks overlying the eastern two thirds of the lode. Contours 1, 3, 7, 11 p.c. per one p.c. area

Figure 2.6 45 poles to fracture cleavage (S_2). Contours 1, 2, 5 p.c. per one p.c. area.

Figure 2.7 146 second generation fold axes (S_1/S_2 intersections). Contours 2, 10, 20 p.c. per one p.c. area.

minor structures in units 6 and 7 (where small scale bedded units show frequent and regular repetition) and are rarely observed in the volcanic sequence underlying the ore body, where manifestations of bedding are confined almost entirely to the mappable boundaries of units 1 to 5. These structures deform bedding and have an axial plane, slaty cleavage (denoted S_1), which shows less penetrative characteristics in the more competent volcanics and quartzitic beds. Fold profiles tend to be tight to isoclinal in all rock types (Plate 2.1), though relatively open folds occur locally. The geometry of small scale, first generation structures can be correlated with the orientation of major folds of bedding as defined by the outcrop pattern of mappable stratigraphic units.

Axial planes of first phase folds show a high degree of preferred orientation (fig. 2.4), with a statistical strike east-west and a dip of 80° north (see also, Rambaud Perez, 1963, p. 89 - 90).

The orientation of first generation fold axes (determined by measurement of the orientation of bedding- S_1 intersections) is plotted on stereographic projections in figs. 2.5 (a) and (b). The predominantly west-plunging orientations shown in fig. 2.5 (a) were collected in the western half of the opencast mine, mainly from the pelitic rocks overlying the ore body.

The predominantly east-plunging orientations shown in fig. 2.5 (b) were collected from the rocks overlying the lode in the eastern half of the opencast mine, and in the rocks exposed at the surface immediately above the underground workings. From these orientation diagrams it is evident that the first generation fold axes show a marked plunge reversal at approximately one third of the distance along the lode from its western extremity.

It seems reasonable to expect a change in some aspects of the structural pattern of first phase folds across the boundary between the relatively incompetent pelitic rocks overlying the

ore body and the more competent, underlying volcanics. This question is difficult to assess directly, however, since suitable markers of the deformation (i.e. small scale bedding) are rarely observed in the volcanics. Where small scale bedding does occur first generation folds are developed on the same scale as in the pelitic rocks of unit 7.

The stockwork veins in the north face of Corta Atalaya were studied in order to clarify the time relationship between their emplacement and the deformation of the volcanics. Apart from extremely rare occurrences where the stockwork veins have complexly curved shapes, there is no indication of regular fold structures defined by the sulphide veins. The configuration of many veins is gently undulose, but throughout the stockwork zone there are numerous instances where single veins extend over distances of several metres with approximately the same orientation. On the scale of more than a single bench wall gentle warps may exist, but would be difficult to distinguish from curved orientations which are a part of the original vein system. An unusual modification of the stockwork ore occurs approximately midway along the crest of the southern anticline, immediately above the massive ore body. Here the stockwork veins tend to show a preferred orientation in the plans of the regional slaty cleavage, S_1 .

In summary, it appears that there are two conflicting manifestations of the deformation of the volcanics in the stockwork ore zone: (1) the deformation of bedding involves the development of small scale, first generation folds, (2) the stockwork veins, although structurally complex, do not exhibit recognisable small scale folds. From these observations it is concluded that the stockwork veins were emplaced after the regional first phase folding.

Second generation folds are confined to the less competent rock types, and show their best development in the pelitic rocks of unit 7. These folds deform both bedding and the slaty

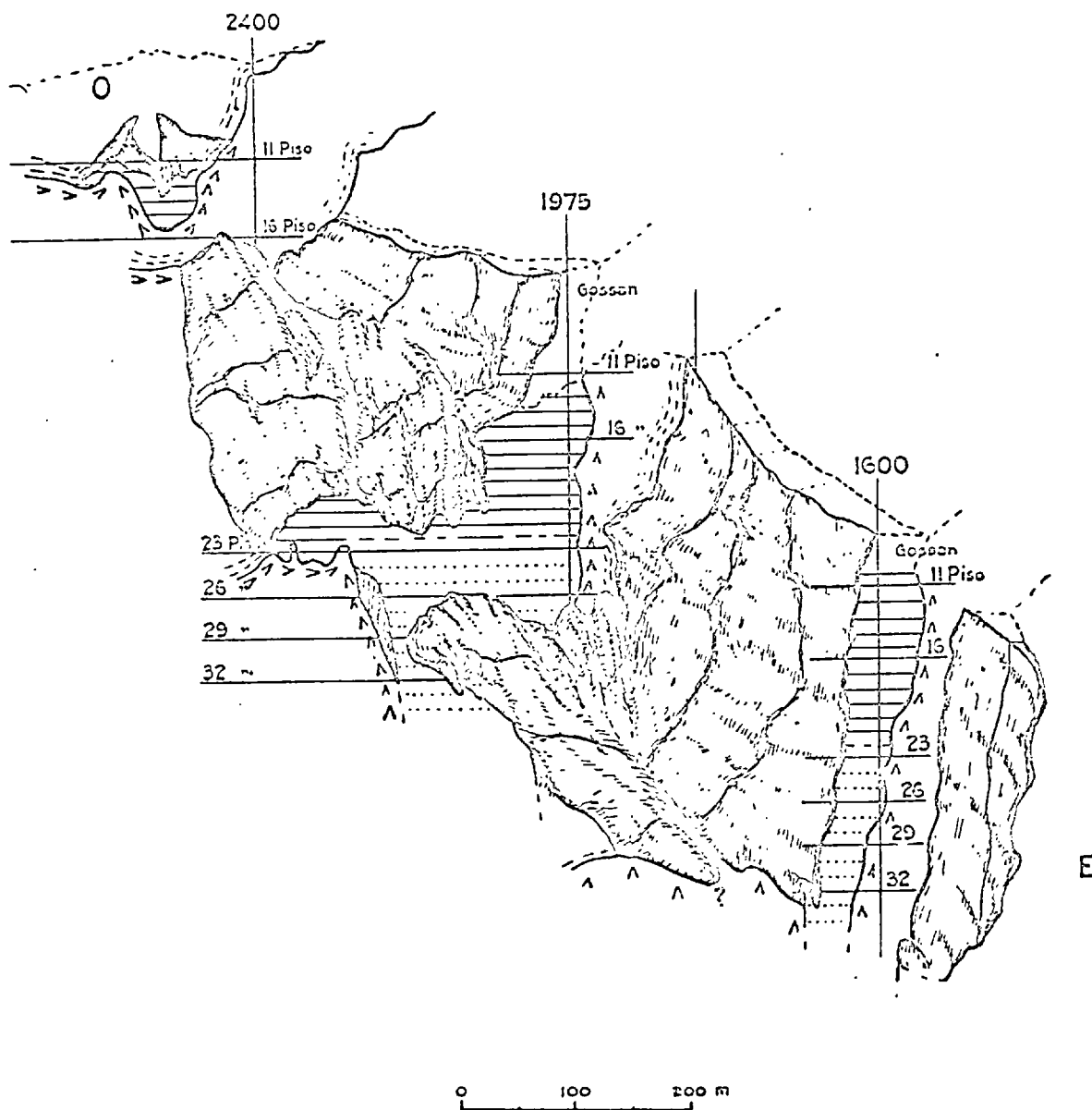


Figure 2.8 Three-dimensional form of the San Dionisio ore body (compiled by Rambaud Perez, 1963).

cleavage, S_1 . In contrast to first phase folds, the second generation structures have a notably less penetrative (Fracture cleavage) axial plane surface (denoted by S_2). Second phase folds are developed only on a small scale. There is no evidence, either from direct observations or, indirectly, through orientation patterns showing regular changes in the attitude of S_1 , that folds belonging to this system are responsible for minor or major features of the outcrop pattern. Wave-lengths are typically in the order of millimetres or centimetres, though in the competent volcanics, second generation folds are developed only on a microscopic scale. In addition to the axial plane cleavage, the profiles of second phase folds (Plate 2.2) are characteristic and generally show obvious differences when compared with those of first generation structures (compare Plates 2.1 and 2.2).

The axial plane cleavage (S_2) shows a high degree of preferred orientation, striking east-west and dipping 60° south (fig. 2.6). The measured, constant orientation of second phase fold axes (fig. 2.7), which lie at the intersection of S_1 and S_2 , reflects the uniform orientation of S_1 and S_2 . Unlike first phase folds, those of the second generation plunge consistently at low angles to the east and show no major plunge reversal over the investigated area.

On S_1 cleavage surfaces, where the lineations defining the orientation of second phase fold axes are measured, there are often two sets of crenulations intersecting at an oblique angle (usually not exceeding 20°). The intersection of a well defined strain-slip cleavage (the measured S_2) on S_1 corresponds to one set of crenulations (the measured second phase fold axes), whereas, for the other set, a corresponding form surface is either absent or very difficult to discern. Therefore, although the second generation fold system refers collectively to all structures responsible for the deformation of S_1 , it is geometrically rather complex and not fully represented by the orientation diagrams of figs. 2.6 and 2.7. The two coexisting

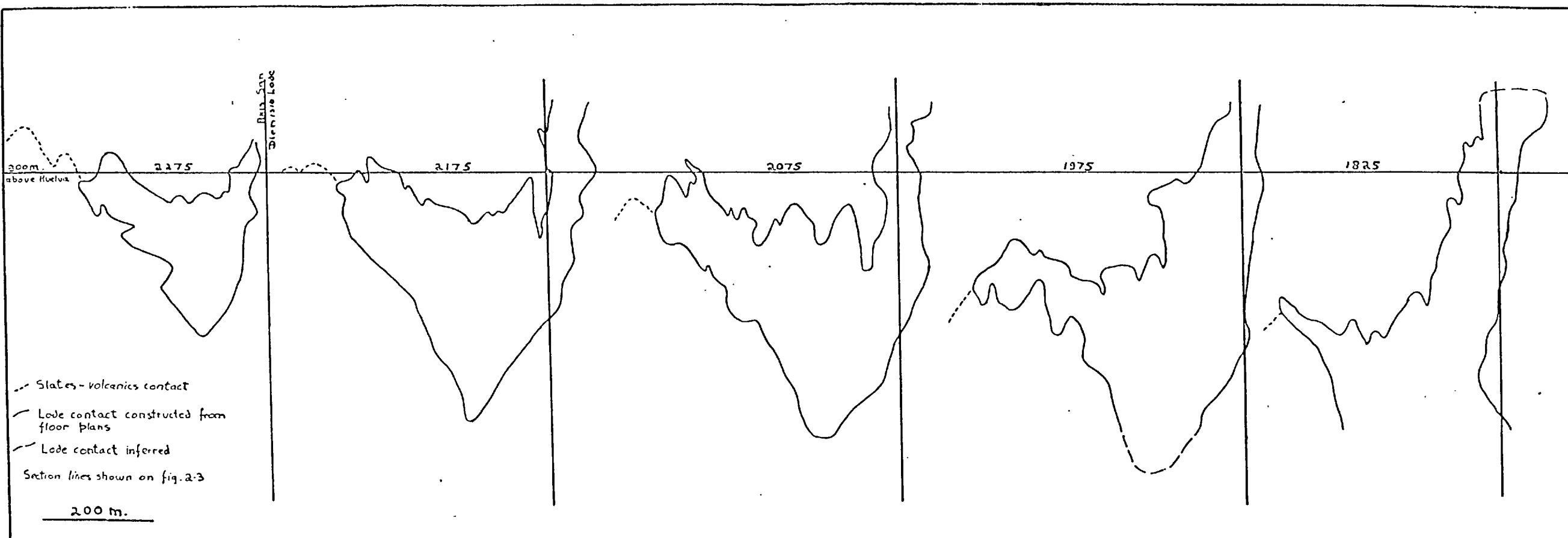


Figure 2.9 Five representative sections showing the detailed configuration of the San Dionisio ore body. The sections trend north south and are sub-normal to the plunge of the lode.

sets of crenulations may constitute a conjugate fold system involving contemporaneous deformation.

Faulting is not common in the vicinity of the San Dionisio lode. At the eastern extremity of the ore body, and separating it from the next ore body to the east (South Lode), the largest fault in the mine area outcrops over a distance of several kilometres, trending approximately north-south and having a major horizontal displacement of some 200 m. (D. Williams, 1934, p. 609 and Plate 26). D. Williams' map (1934) shows several less prominent faults which are readily visible in the north face of the opencast mine. These structures, however, can probably better be regarded simply as fractures since, judging by the continuity of mappable stratigraphic units in the area of the faults (see fig. 2.3, and D. Williams, 1934, Plate 26), there is no evidence of associated displacements.

2.7 Configuration of the San Dionisio Ore Body

The three dimensional shape of the ore body has been reconstructed in a simplified form from the Mines plans by Rambaud Perez (1963, fig. on p. 92), and is reproduced in fig. 2.8. The five profiles shown in fig. 2.9 are representative of the detailed sectional configuration of the lode. It is evident from these figures that the ore body occupies a synclinal and part of a contiguous anticlinal structure. Superimposed on these major structures, especially in the axial region of the main syncline, are a number of minor crenulations, the profiles of which conform broadly with, though are more irregular than, those of the major structures.

The east-west trend and the steep orientation of the axial plane to the major anticlinal and synclinal structures defined by the ore body indicate that these structures belong to the **first** generation fold system of the region. The plunges of the axes of these structures have been determined graphically (see the full lines in fig. 2.10) from profiles constructed through the ore body, and in the eastern two-thirds of the

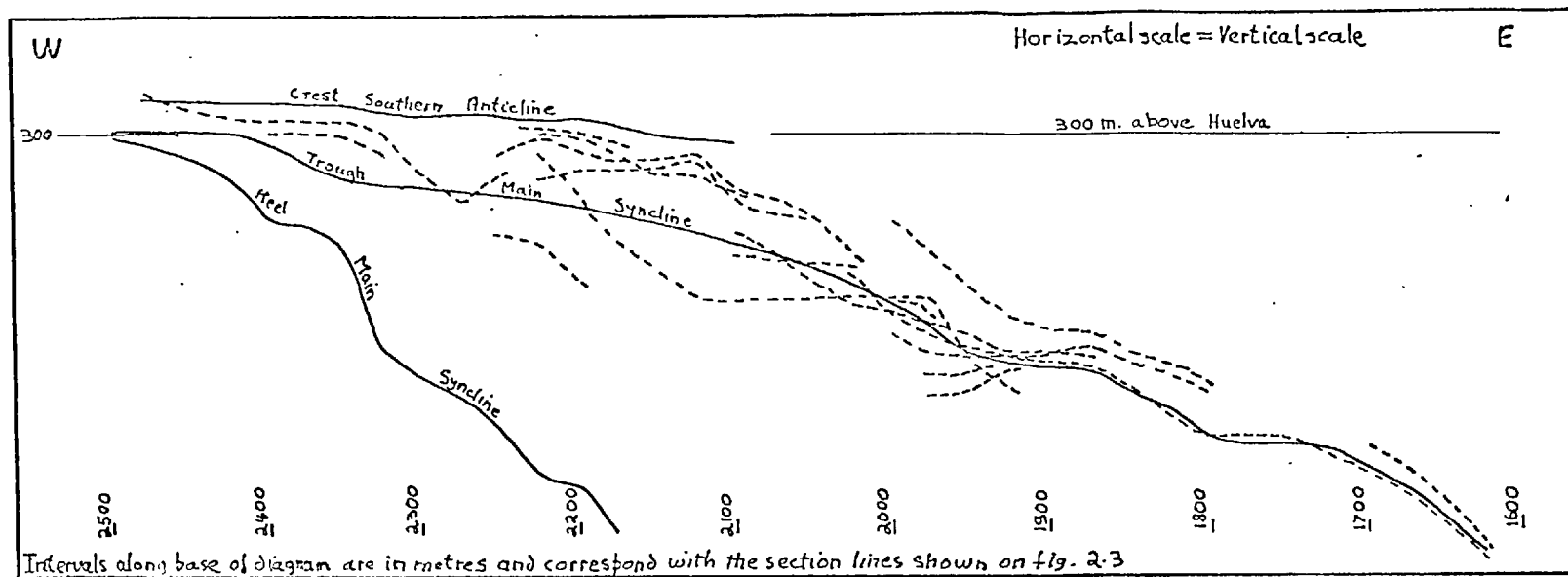


Figure 2.10 Graphical reconstruction of the orientation of axes of major folds (full lines) and crenulations (broken lines) of the contacts of the San Dionisio lode.

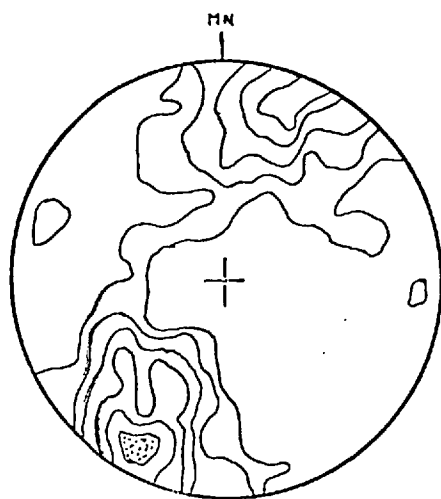


Figure 2.11 Equal area, lower hemisphere, stereographic projection. Orientation of 395 poles to the contacts of the San Dionisio lode (data from the Mines Plans compiled by Williams). Contours 0.5, 1, 2, 3, 5, 7 p.c. per one p.c. area.

latter are statistically parallel to first generation fold axes in the overlying metasediments (fig. 2.5 (b)). In the western one-third of the ore body, the axes of major structures plunge to the east (fig. 2.10) whereas first generation fold axes in the immediately overlying metasediments plunge to the west (fig. 2.5(a)).

The prominent crenulations along the upper contact of the ore body (see fig. 2.9) locally show anomolous profiles and it is not immediately apparent that they represent first generation folds. Since it is possible that these structures may, in part, represent primary depositional features, it is instructive to consider their form in further detail.

Apart from their locally anomolous shapes, which may be due to migration or to the needs of accommodation during deformation, the profiles of most of these structures are fairly regular and correspond well with those of the major folds of the ore body. In several instances, where profiles of fairly constant shape appear repeatedly over considerable distances (50 - 100 m.) along their strike, it appears reasonable to conclude that single, continuous structures are involved. For such structures, the orientation of their crestal lines has been determined graphically (see the broken lines in fig. 2.10), and it is evident that they plunge in directions broadly comparable with the orientation of the major folds of the ore body (compare the full and broken lines in fig. 2.10). The geometry of these crenulations is therefore essentially consistent with that of the first generation folds.

The statistical orientation pattern for the lode contacts provides additional confirmation of the validity of assigning the various fold structures of the contacts to the first phase fold system. Approximately 400 measurements of the orientation of the lode contacts at different localities were recorded on the original mines plans compiled by D. Williams. These have been assembled in fig. 2.11, whence it is evident that the

strong girdle distribution defines a fold axis whose orientation coincides with: (1) the average orientation of the same fold axis reconstructed graphically (fig. 2.10), and (2) the orientation of first generation fold axes in the sediments overlying the eastern two-thirds of the ore body (fig. 2.5 (b)).

2.8 Summary of Structural Relations Near the Ore Body Contacts

The conformity relationship between the ore body contact and bedding in the country rocks, as determined by surface mapping, could not be corroborated in detail by the correlation of structural data. It had been hoped to do this for small areas, either by comparing the orientation of the ore body contact with any regular banding in the ore body and with bedding in the sediments, or by comparing the orientation of fold axes (of the same generation) of all three of these surfaces. The degree of correlation obtained would then have provided some measure of the conformity of the surfaces involved. Comparisons of the first type represent the most direct approach, whereas those of the second type yield a measure of the conformity in two dimensions only.

The absence of bedding in the immediately underlying volcanic sequence makes structural correlations along the lower contact of the ore body impossible. The stratigraphic status of this contact cannot, therefore, be clarified further than has already been done by surface mapping. Even in the most favourable circumstances (i.e. had it been possible to observe manifestations of bedding in the volcanics), the task would have been a difficult one, simply because of the difficulty of assigning a position of constant significance to a frequently gradational boundary. Despite these problems it is noteworthy that in the next ore body to the east (South Lode) the conformity relationship is more easily established; slate

bands occur in the footwall volcanics and are parallel to the lower contact of the lode (D. Williams, pers. comm.).

Between the upper contact of the San Dionisio lode and the upper contact of unit 6 (the only other zone where useful correlations might be attempted), little evidence is available to improve upon the picture of the conformity relationship as already established by surface mapping. Because of the prevalence of small scale tight folds in the pelitic sediments overlying the ore body, it is evident that meaningful correlations between the orientation of bedding and the ore body contact cannot be made on the basis of widely spaced data, since significant correlations can only be made within the dimensions of single folds. Orientation data could not be collected (i.e. were not observable) at sufficiently close intervals to meet this condition. Hence, although several instances were noted where widely spaced orientation data indicate a parallelism between the upper ore body contact and the bedding in unit 6, these observations have little real significance.

For similar reasons, there is little to be achieved by attempting to correlate the orientations of fold axes of the ore body contact and of bedding in unit 6. Fold axes in unit 6 are known to show large and rapid changes in plunge. The orientation of fold axes of the ore body contact can only be determined graphically, from profiles constructed at regular intervals through the ore body. The orientations thus obtained are limited in their accuracy by the distance between the floor plans from which the profiles are constructed (usually 12.5 m.), and they represent only the average attitude of a fold axis at a particular locality. Any changes in orientation from one floor to the next could not be detected, thereby preventing any comparisons with the rapid variations of fold axis

orientation in unit 6 (contacts are shown on the floor plans of intermediate cuts between the main levels in some parts of the mine, but these cuts are of little use because of their limited extent and the low plunge angle of the fold axes).



3.1

2 cm



3.2

2 cm



3.3

2 cm



3.4

2 cm

Plate 3.1 Megascopically banded ore near the lower contact of the lode.

Plate 3.2 Stockwork vein (high-reflecting) and disseminated mineralisation in the volcanics underlying the ore body. The disseminated mineralisation is concentrated in the darker coloured layers in the volcanics.

Plate 3.3 First generation folds in the banded ore. Along the upper margin of the specimen the axial plane cleavage is defined by alternating laminae of pyrite, sphalerite and gangue minerals. Other bands are defined principally by compositional changes, and textural variations of pyrite and gangue minerals.

Plate 3.4 First generation similar-fold in banded ore composed of pyrite and gangue minerals.

CHAPTER 3

INTERNAL STRUCTURE OF THE SAN DIONISIO ORE BODY

The stratiform lode, as distinct from the adjacent stockwork zone, can be subdivided into two main parts, which are readily distinguishable in the field. More than ninety per cent of the lode consists of compact, fine grained pyrite, generally known as massive ore, the remainder consisting of megascopically banded ore. Although the occurrence of banded sulphides is strictly localised there is no sharp boundary between the two types of ore. However, their megascopic features are quite different, and it is convenient in this chapter to describe the banded and massive ores under separate headings.

3.1 Banded Ore

Small-scale mineralogical and textural banding occurs at a few localities along or near to the upper and lower contacts of the ore body. Banded ore has also been reported (D. Williams 1934, p. 625; Finlayson, 1910, p. 413) from the immediate vicinity of the "horses" in the old mine workings, and especially from the small contiguous ore body, the Eduardo Mass.

Along the lower contact banding (Plate 3.1) occurs only where the lode contact is gradational, and even then it is but rarely observed. In the nearby stockwork zone the disseminated mineralisation tends to be more concentrated in certain lithologically distinct layers in the volcanic host rocks (Plate 3.2). All the banding observed along the lower contact of the lode is planar and approximately parallel to the trend of the northern bounday of the lode, definition of the banding being due to the variation of the gangue content and to grain size variation of the pyrite.

Where banding occurs along the upper contact of the lode

1 cm

3.5

2 cm

3.6

5 cm

3.7

2 cm

3.8



Plates 3.5 and 3.6 Pyrite (high-reflecting)-gangue (low-reflecting) intercalations in the banded ore. In both specimens the coarse pyrite grains tend to define a lamination oblique to the banding; in the upper right of Plate 3.6 the oblique lamination is exceptionally penetrative.

Plate 3.7 Euhedral pyrite porphyroblasts in the sediments of unit 6. These grains are frequently elongate, and their long axes tend to be aligned parallel to the strain slip cleavage/slaty cleavage intersection.

Plate 3.8 Pyrite laminae (high-reflecting) parallel to bedding (trending horizontally) and the strain slip cleavage (trending diagonally) in the slates of unit 7.

it is sharply defined and readily visible in the field. Its orientation is generally parallel to the upper contact of the lode and, statistically at least, to the local orientation of bedding in the overlying metasediments. Where the banding is not parallel to the lode contact and bedding, it is parallel to the local slaty cleavage, or fracture cleavage. At one locality bands were observed in the form of fold structures (Plates 3.3, 3.4) whose orientation corresponds with that of the regional first generation folds. The axial plane surface to some of these folds is defined by sulphide layering (Plate 3.3).

Most occurrences of banded ore along the upper contact are manifested by alternating layers of pyrite and gangue minerals (Plates 3.5, 3.6). Banding is also conspicuous where pyrite and gangue layers alternate with bands of chalcopyrite, sphalerite and galena (Plate 3.3). Compositional layering is usually accentuated by grain size and other textural variations, the grain size changes being especially prominent in pyrite layers. The larger grains of pyrite are frequently concentrated along the boundary of individual layers (Plate 3.5), and in many cases they tend to define a lineation oblique to the banding (Plate 3.6).

At some localities above the lode sparse disseminated mineralisation persists up to at least ten metres from the contact. Isolated pyrite porphyroblasts (Plate 3.7), which constitute part of this disseminated mineralisation, are entirely restricted to the most homogeneous host sediments (i.e. unit 6). In the overlying slates, discrete laminae of pyrite are confined to the bedding planes between pelitic and quartzitic layers, and to bands parallel to the fracture cleavage. (Plate 3.8).

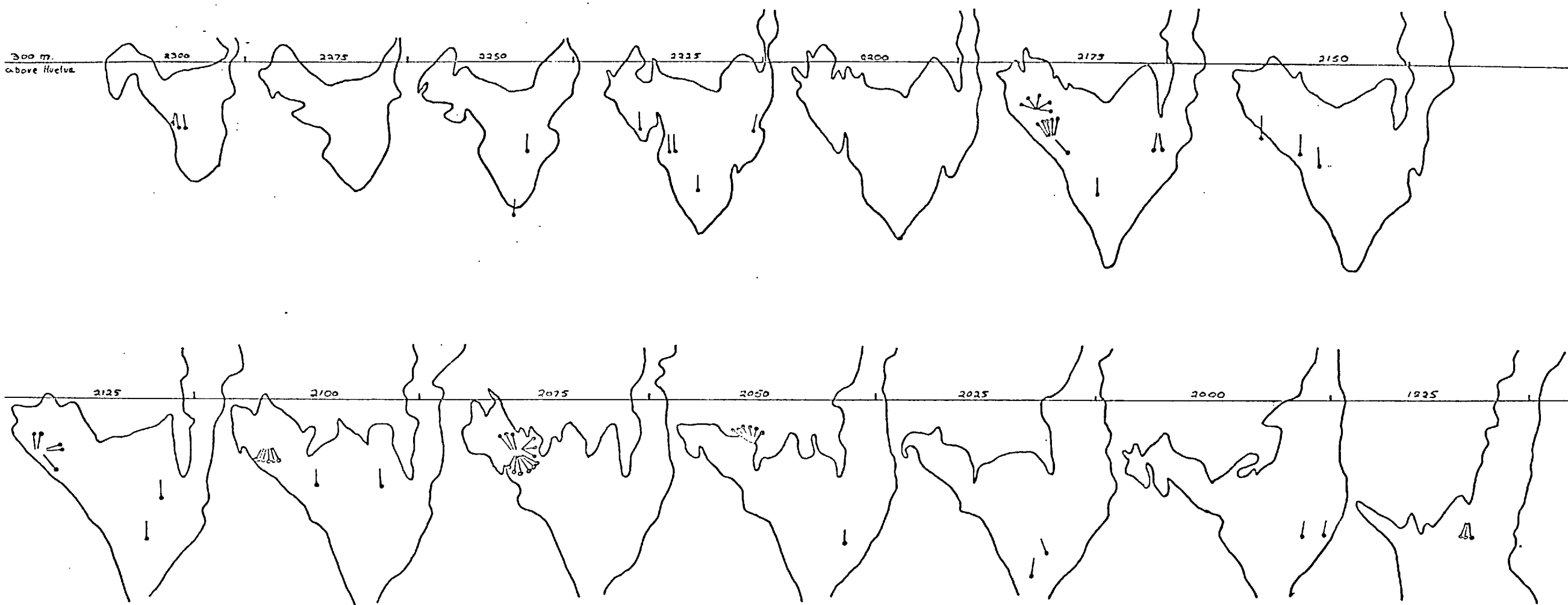


Figure 3.1 Sample localities. Full circles denote samples for which flat-ground surfaces and polished surfaces were prepared. Open circles denote samples for which flat-ground surfaces were prepared. The extreme eastern and western section lines are shown on fig. 2.3. Sections 2300 to 2000 are spaced at 25 m. intervals along the axis of the San Dionisio lode.

3.2 Massive Ore

3.2.1 Field Characteristics

Fresh and weathered exposures of the massive ore are characterised by their remarkable homogeneity. Apart from joints and slickensides (sects. 3.2.3 and 3.2.4), the sulphide aggregate is essentially dense, free of gangue, and isotropic.

Over most of the lode the megascopic appearance of the massive ore at different localities is identical. However, there are recognisable variations, well appreciated by the miners who distinguish three types of ore according to their strength or stability in mining operations.

In some parts of the lode the miners can point out vague zones of very hard ore, where much of the ore is certainly more compact than elsewhere. However, since the very hard ore is not restricted to these zones, the latter are better described as areas where the amount of very hard ore is considerably greater than usual. It would be virtually impossible, however, to map the distribution of the hard and less hard types of ore.

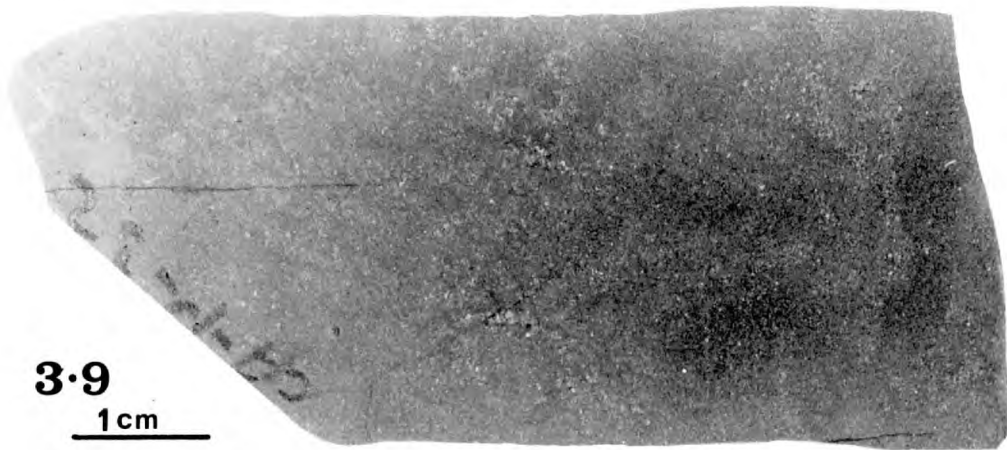
Variations of coherency which occur over a few square metres may also occur over a few square centimetres, and there is no significant way to establish a scale at which to delimit equivalent boundaries. Changes of physical character are essentially continuous and may be extremely subtle, so that distinguishing between the two types of ore can be a real problem. The vague limits of the ore types indicated by the miners are a fair description of their distribution; the hard ore is said to occupy a smaller volume than the less hard ore, and occurs in more or less equidimensional zones ranging up to several tens of metres across.

The third and most distinctive type of ore recognised

by the miners is an abnormally friable aggregate. This material occurs in isolated patches called "husillos", whose location, as shown on the mine plans, is largely confined to a zone which coincides with the axial region of the main synclinal structure. The most friable aggregates which crumble under a light hammer blow, grade outwards into normal coherent ore. Typical developments of this material are highly porous and sometimes contain quartz veins.

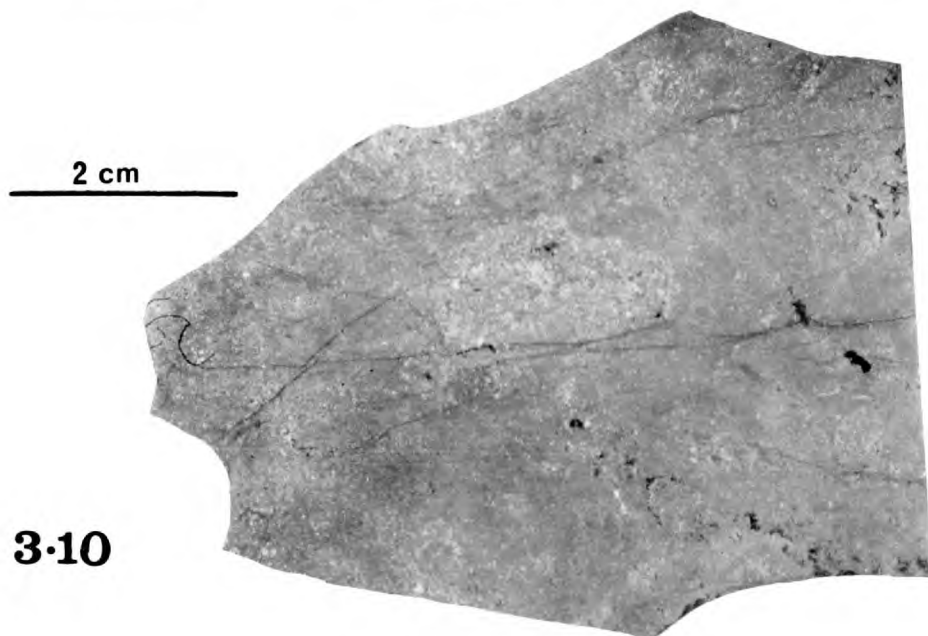
Apart from the foregoing subdivision of the massive ore, no other manifestations of an internal structure of the lode as a whole can be discerned. For example, no major stratification or other laminar features similar to those in the country rocks can be recognised. Exposures resulting from mining operations are almost entirely composed of joint or pre-existing fracture surfaces. These surfaces show artificial markings (including horizontal and vertical laminar markings) due to weathering, and their appearance is virtually identical throughout the lode.

The character and apparent uniformity of natural exposures presents a major problem in any attempt to study the composition of the lode. Actually the massive ore is not homogeneous, for it exhibits several important structures which are not visible in the field but are readily apparent on flat-ground surfaces, and sometimes on fresh fracture surfaces. It is possible to study these structures in small specimens, but their continuity and inter-relationship is largely unknown since there is no means of making direct observations of the real composition of the ore over continuous exposures in the



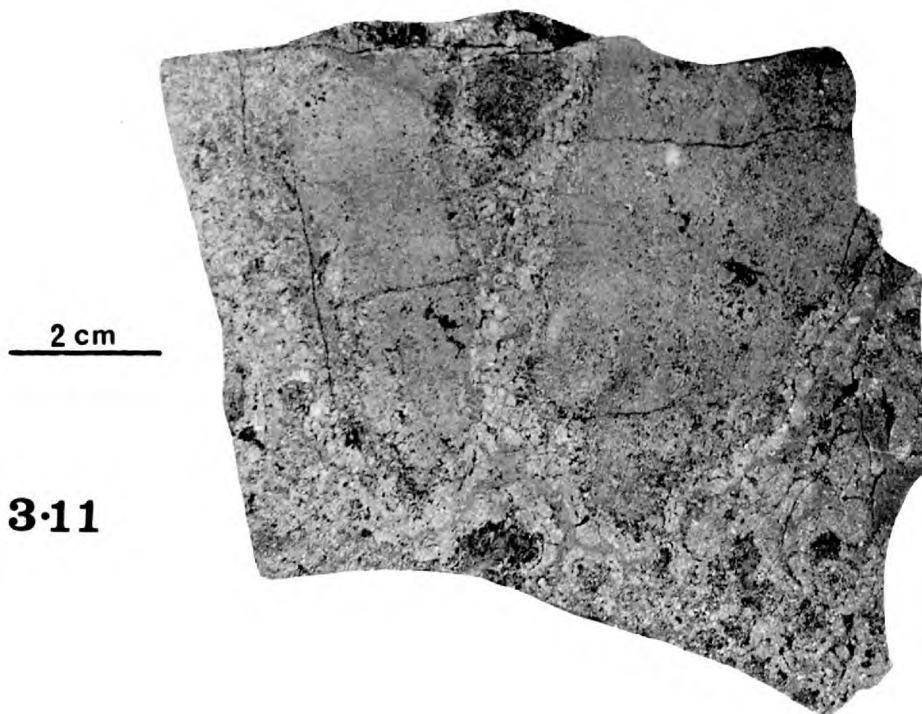
3.9

1 cm



3.10

2 cm



3.11

2 cm

Plate 3.9 The typical internal structure of samples of compact massive ore which appear isotropic on freshly fractured surfaces.

Plates 3.10 and 3.11 Structures defined by strong grain size differentiation in the massive ore.
Megascopic pore spaces appear black.

field.

3.2.2. Megascopic Structure

The descriptions presented here are a summary of observations made on approximately 700 hand specimens collected from different parts of the lode (see fig. 3.1 for localities). These specimens were sawn in half, and one of the faces ground flat. Fifteen of the samples were oriented, and for these the ground face was cut at right angles to the plunge of the lode. Some samples were serially sectioned, and on a few others three faces were sawn at right angles. Two large specimens (approximately cubic, with one foot sides) were collected to test the continuity of structures observed in hand specimens. These were oriented and four serial sections were cut from each, at right angles to the plunge of the lode.

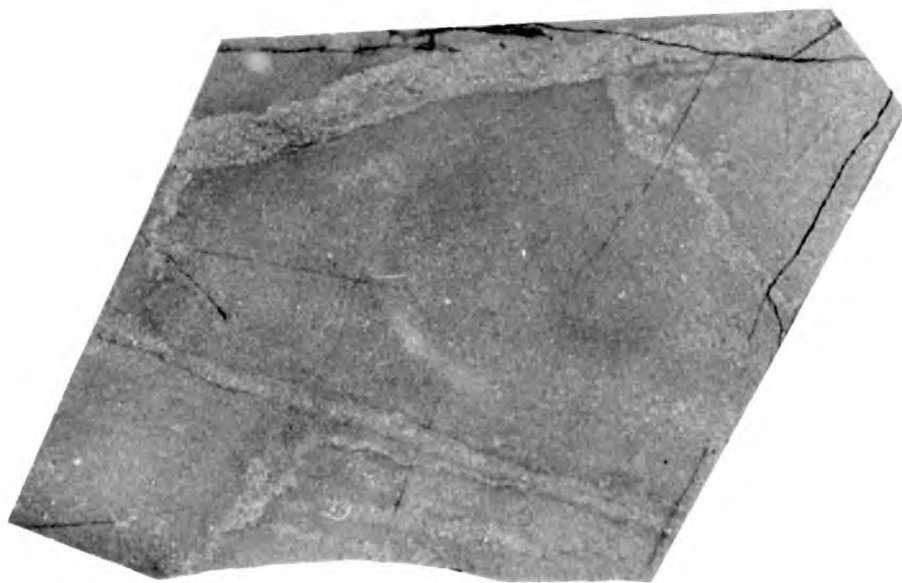
The heterogeneity of the ore is principally determined by the grain size of the pyrite and by porosity variations. On ground surfaces, low-reflecting areas represent a finer grain size than higher-reflecting areas. Pore space (non-reflecting) is virtually ubiquitous and is present in the normal compact ore as well as in the friable zones in the axial region of the main syncline. The existence of pores, rather than the presence of chalcopyrite, sphalerite and galena, is undoubtedly the main factor in determining the average density of the ore (given as 4.5 - 4.8 by Finlayson, 1910, p. 413, and 4.7 by D. Williams, 1934, p. 625), which is below the theoretical density (5.1) of pyrite.

Samples taken from the most homogeneous parts of the massive ore are almost fully dense and split with a conchoidal fracture. Freshly fractured specimens appear to be quite isotropic, but this is invariably misleading



3-12

2 cm



3-13

2 cm

Plate 3.12 Structures defined by grain size differentiation in an almost fully dense sample of the massive ore.

Plate 3.13 Intersecting coarse grained bands (high-reflecting) defining vein-like structures which are also evident on freshly fractured surfaces. The fine grained host aggregate (low-reflecting) represents the maximum homogeneity of the massive ore as observed on flat-ground surfaces.

and ground surfaces nearly always reveal distinct heterogeneities. Aggregates which are effectively isotropic (for example, the fine grained component of the specimen shown in Plate 3.13) never persist over areas of more than a few square centimetres, which suggests that there are no continuous, large volumes of ore which are truly homogeneous.

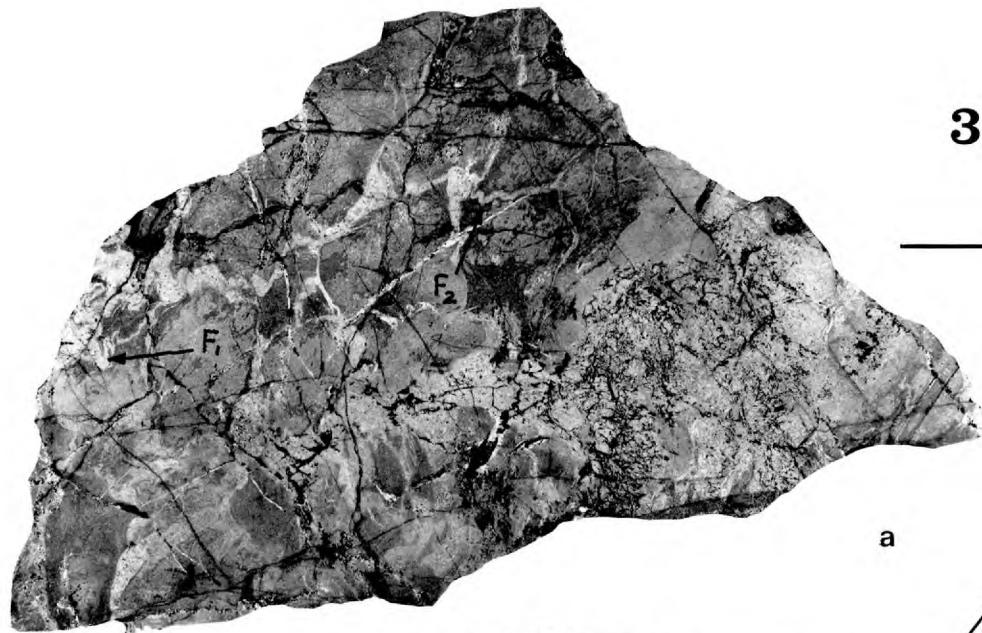
Typical samples of massive ore are predominantly fine grained and contain irregular and semi-continuous patches of coarse grained pyrite (Plate 3.9). The size of the coarse grained areas varies from a few to several hundreds of grains, and their boundary with the fine grained matrix may be gradational or abrupt. There is no regular arrangement of the different grain size components, and the overall structure of the aggregates is vague and difficult to characterise.

In most of the massive ore the different grain size components of an aggregate are strongly differentiated. Different grain sizes occur in well defined continuous areas, and the resulting structures are comparatively simple and regular. For example, predominantly fine grained aggregates sometimes contain isolated, sub-equant patches of coarse grained pyrite (Plate 3.10). In many samples the areas containing different grain size components are not isolated and the full extension of the structures they define are unknown (Plates 3.11, 3.12). The boundaries between different grain size areas are usually sharp and fairly smooth, but interfingering boundaries are sometimes observed (Plate 3.12), and these tend to be gradational. Large pore spaces are preferentially associated with the coarse grained areas (Plate 3.10).

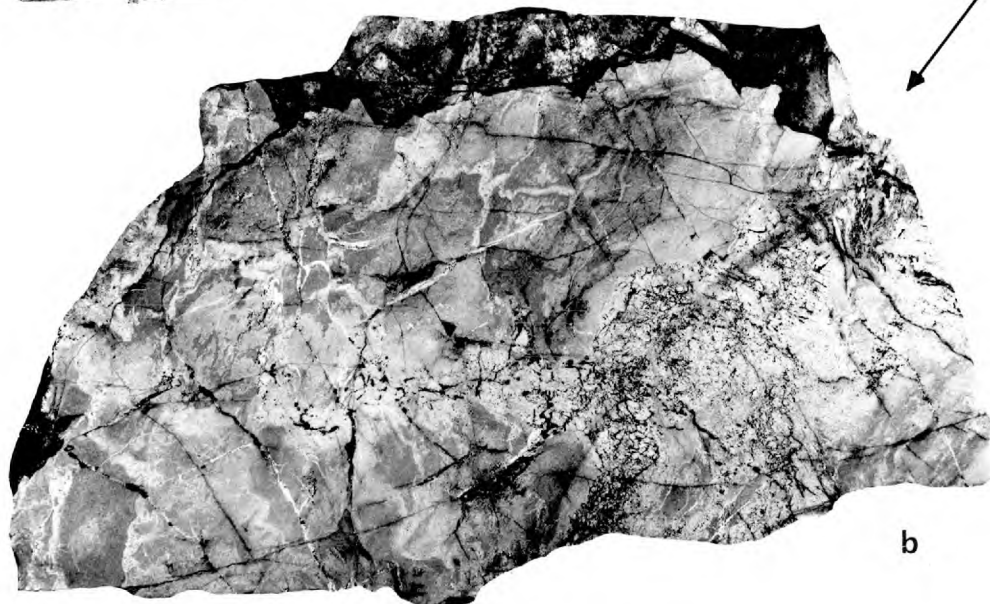
Plane and contorted laminar structures are a common feature of the massive ore, and their megascopic appearance is duplicated in the microstructure. Some of the most

3:14

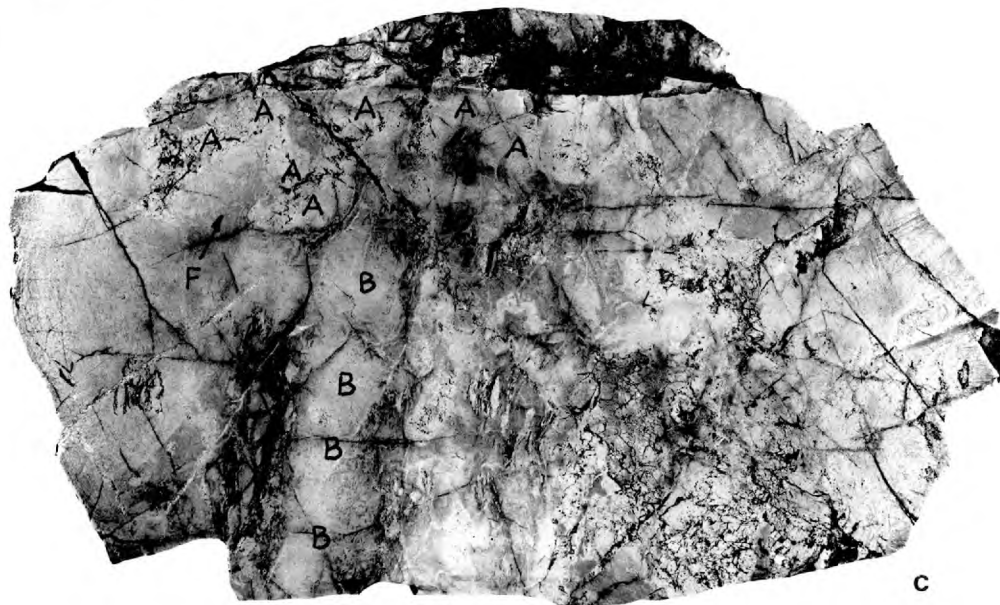
10 cm



a



b



c

Plate 3.14

Serial sections at right angles to the plunge of the lode, and oriented such that the double headed arrow is parallel to, and indicates the down-dip direction of the regional slaty cleavage. Sections (a) and (b) are approximately 1 cm. apart; section (c) is spaced approximately 15 cm. from section (b).

The sections illustrate that most structures persist for only short distances parallel to their **strike** - i.e. from section (a) to section (b), but not to section (c). The most persistent feature is the extensive fragment zone which occurs at the bottom right of each section.

In all three sections there is an overall laminar structure which trends parallel to the regional slaty cleavage.

In section (c) two extensive, though diffuse, coarse grained bands are denoted by arrays of the symbols A and B. To the immediate left of the band denoted B is a third layer containing several lenticular aggregates of coarse grained pyrite.

Narrow, high-reflecting and transgressive veins are composed of chalcopyrite.

A number of fold structures is indicated by the arrows marked F. The microstructure of the folds at F₂ is illustrated in Plate 3.20.

sharply defined coarse grained laminar structures resemble veins (Plate 3.13). However, the most prominent veins are composed of chalcopyrite and these may extend over distances of several centimetres, transecting all structural features of the host pyrite aggregate (Plate 3.14).

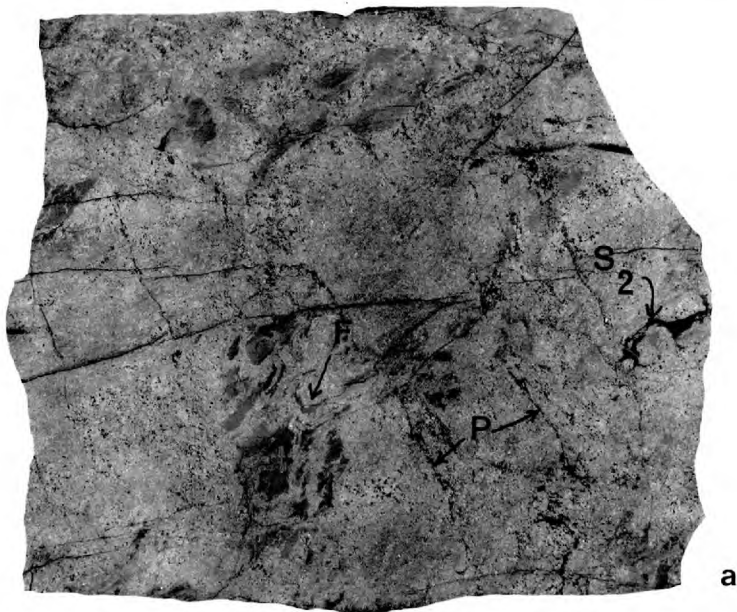
Layered assemblages of conformable bands are developed on all scales. Wherever oriented samples were collected, the attitude of the layering could be established by cutting two sections at right angles. In all oriented samples where a laminar structure is developed (6 of those collected) the strike of the layering is approximately east-west, and its dip ranges from sub-horizontal to approximately vertical. These orientations correspond to the attitudes of bedding and the cleavages in the country rocks.

Variations in the amount of chalcopyrite and sphalerite usually define only vague laminations. Abnormally high concentrations of galena define the most prominent polyminerale bands. Elongate pore spaces and zones of pore space sometimes define penetrative laminar structures which are usually transgressive to other types of banding (Plate 3.15). Simple types of banding in monomineralic pyrite aggregates are defined by variations of grain size, grain shape or pore space density. Most layering structures are defined by simultaneous variations of all these factors. Generally this amounts to a complete change in the fabric (see Chapter 4) of the aggregate, and the resulting differences can be readily discerned on ground surfaces.

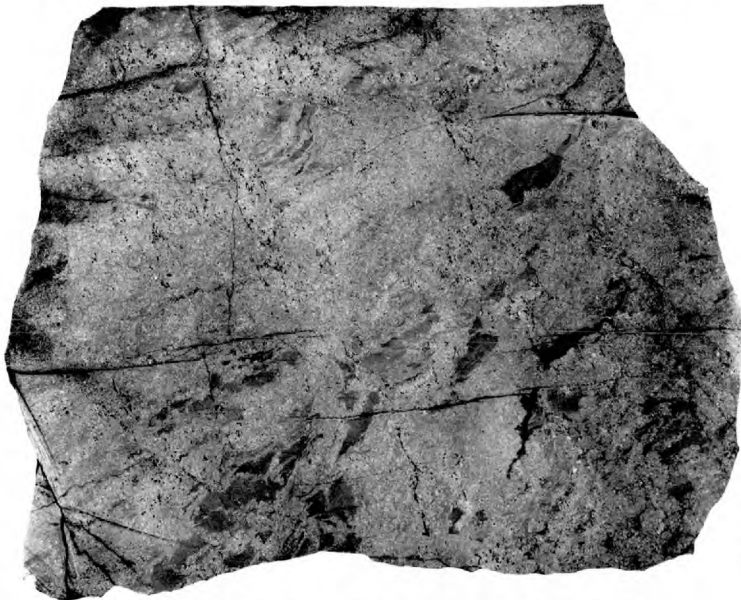
From bands and lenses one or two grains wide and a few grains long, there is a complete gradation to megascopic structures which, themselves, are frequently complex and composed of conformable sub-zones reflecting minor variations of the fabric. Single continuous bands

3·15

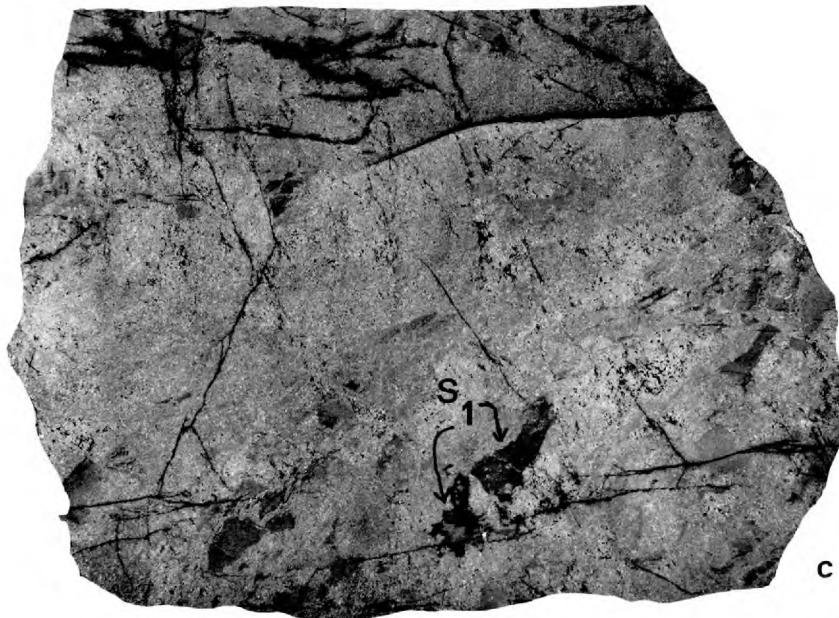
10 cm



a



b



c

Plate 3.15

Serial sections at right angles to the plunge of the lode, and oriented such that the double-headed arrow is parallel to, and indicates the down-dip direction of the regional slaty cleavage. Sections (a) and (b) are approximately 1 cm. apart; section (c) is spaced approximately 10 cm. from section (b).

A gross layering structure dips at approximately 45° north and is defined by a preferred orientation of discrete fine grained aggregates which occur with complex and variable forms. The gross banding persists parallel to its strike, but in the same direction the detailed structure changes rapidly.

The lowest-reflecting aggregates (S) are composed of pyrite spheres and ellipses.

Pore space is represented by the non-reflecting centres and is partly confined to narrow laminar zones (see for example the areas indicated P) which are oriented parallel to the regional fracture cleavage.

In section (a) part of a fold structure appears to be evident in the area indicated F.

which constitute part of a layered assemblage are generally not extensive. In one of the large specimens that were serially sectioned more or less continuous bands extend over several centimetres, but are vaguely defined and do not persist parallel to their strike (see for example the bands denoted by the symbols A and B in Plate 3.14 (c)). In the other large specimens fine grained aggregates occupy lenticular, irregular and sub-angular bands which are broadly conformable and define a gross layering structure (Plate 3.15). Groups of coarse grained lenses occupy a broad laminar zone to the left of the band marked B in Plate 3.14 (c). Small groups of fine grained lenses are frequently seen in hand specimens.

Several other non-laminar structures are evident in the section illustrated in Plate 3.14. Much of the coarse grained material is irregularly distributed, part of it occupying comparatively extensive and vaguely defined areas interconnected by narrow intersecting bands. Locally there are broad laminar zones of coarse grained pyrite, but their shape rapidly degenerates by thickening and thinning and by interconnection with other bands. Some boundaries against the finer grained material are sharp and gently curved, others are diffuse, and some are defined by the development of a network structure. Despite the vague and transgressive nature of many of these features, there is a fairly penetrative layering parallel to the regional slaty cleavage (orientation shown by the double headed arrow).

In samples which exhibit a lamination the layering is frequently distorted and defines a wide variety of fold structures. Several fold profiles can be observed in Plate 3.14 (a). On the left of the section narrow coarse grained bands exhibit ptygmatic-fold profiles (F_1), and at the upper centre concentric-folds (indicated F_2 ,

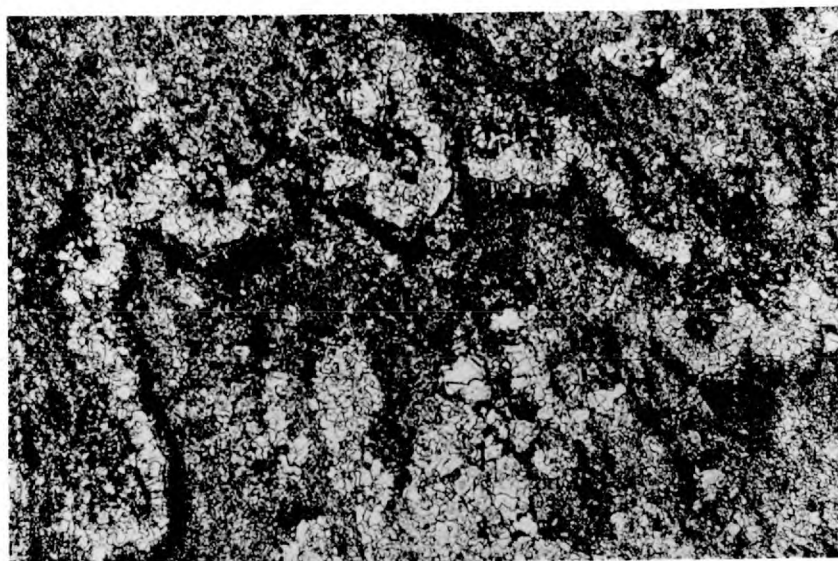
3-16

250 μ



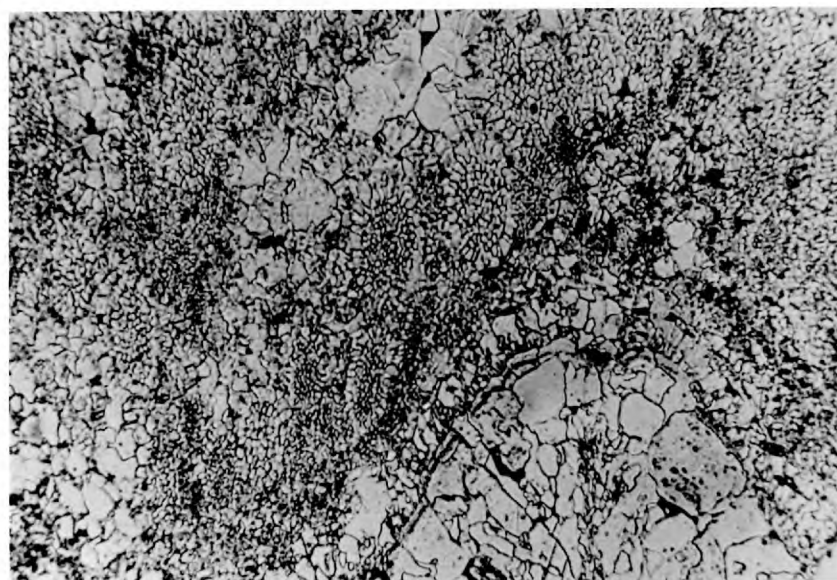
3-17

250 μ



3-18

50 μ



Plates 3.16 and 3.17 Concentric folds defined by coarse grained bands of pyrite which are evident only in the microstructure. The folded band in Plate 3.16 is connected to an extensive, non-banded and similarly coarse grained aggregate. In Plate 3.17 the folded bands terminate abruptly, and were perhaps previously connected.

Plate 3.18 Detailed microstructure of the folds shown in Plates 3.16 and 3.17. The coarse grained bands are largely composed of elongate grains which are radially arranged with their long axes approximately at right angles to the boundary of the band. The adjoining aggregate consists mainly of discrete elliptically shaped structures composed of fine grained pyrite (see Chapter 5). The long axes of the ellipses are parallel to the axial plane of the folds, but tend to become parallel to the limbs of the folds near the coarse grained bands.

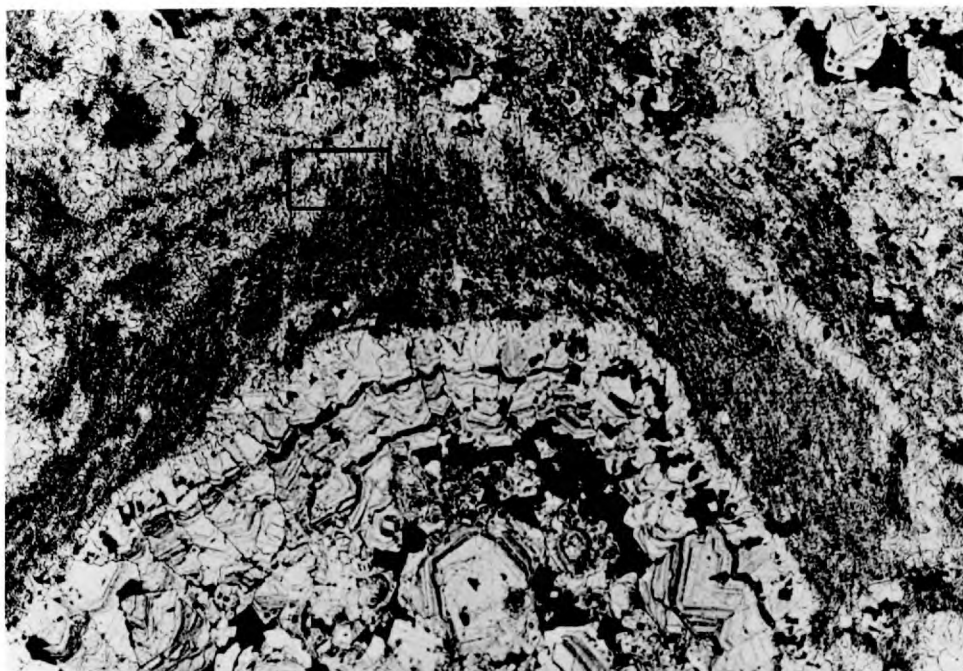
and also illustrated in Plate 3.20) are developed in a similar band. Plates 3.16 and 3.17 illustrate concentric folds in another sample, and Plate 3.19 (a) depicts part of a similar-fold profile in a third specimen. Part of a fold structure (F) appears to be evident in the centre of Plate 3.15 (a). In the section shown in Plate 3.14 (c) the coarse grained band marked A exhibits a folded shape. Below this band (in the area indicated F) are numerous fine laminations which are either highly contorted and wrap around the main profile, or have a more uniform trend parallel to the axial plane orientation; less well defined folds are also evident in the centre of this specimen. Folded bands do not extend for distances of more than a few centimetres, and are typically intersected by other contorted or laminar bands (Plate 3.14 (a)), or are connected to extensive massive aggregates (Plate 3.16).

The axial plane surface of most fold structures is defined by some type of laminar feature which is evident either megascopically (see the folds indicated F_2 in Plate 3.14 (a)), or at least in the microstructure. Definition of the axial plane in the microstructure is due to a preferred orientation of one of the following features:

(1) the major axes of discrete elliptically shaped structures composed of fine grained pyrite (see Chapter 5) (Plates 3.18, 3.19 (b)), (2) the long axes of elongate grains of pyrite (see sect. 4.2) (Plate 4.61), or (3) the long axes of inequant interstices which may be voidal or filled by chalcopyrite or sphalerite (Plate 3.20). Away from the individual bands that define the fold structures, the lamination produced by these features is strictly parallel to the axial plane (see Plate 3.18 and the lower centre of Plate 3.20). Near the boundaries of some of the folded bands, the laminar structure deviates

3-19

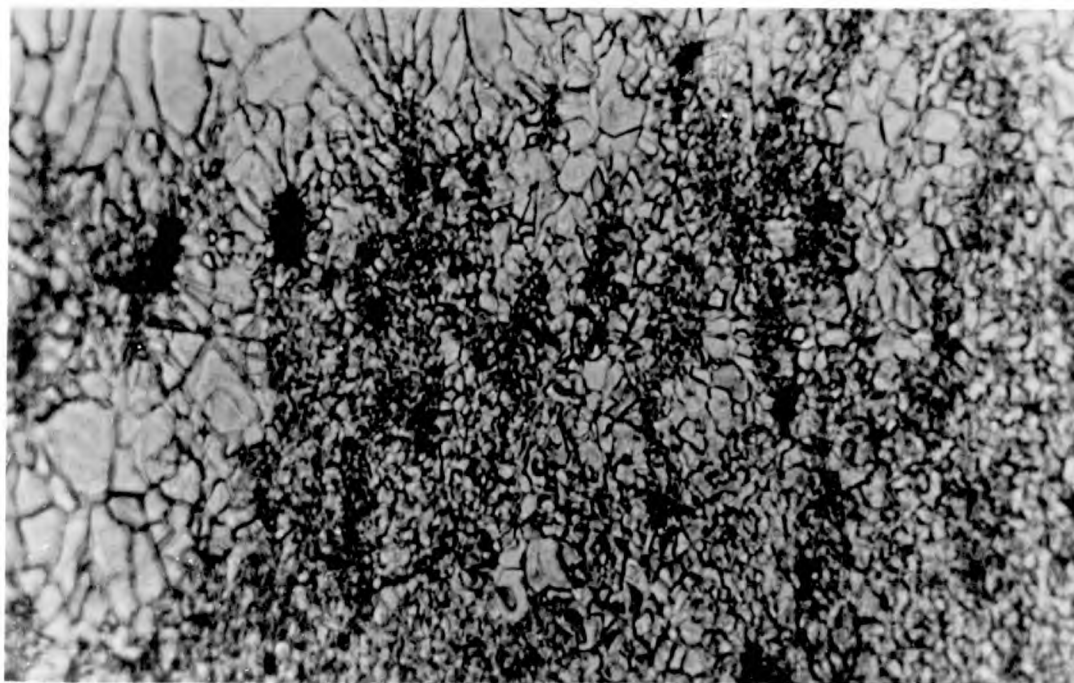
A



250 μ

3-19

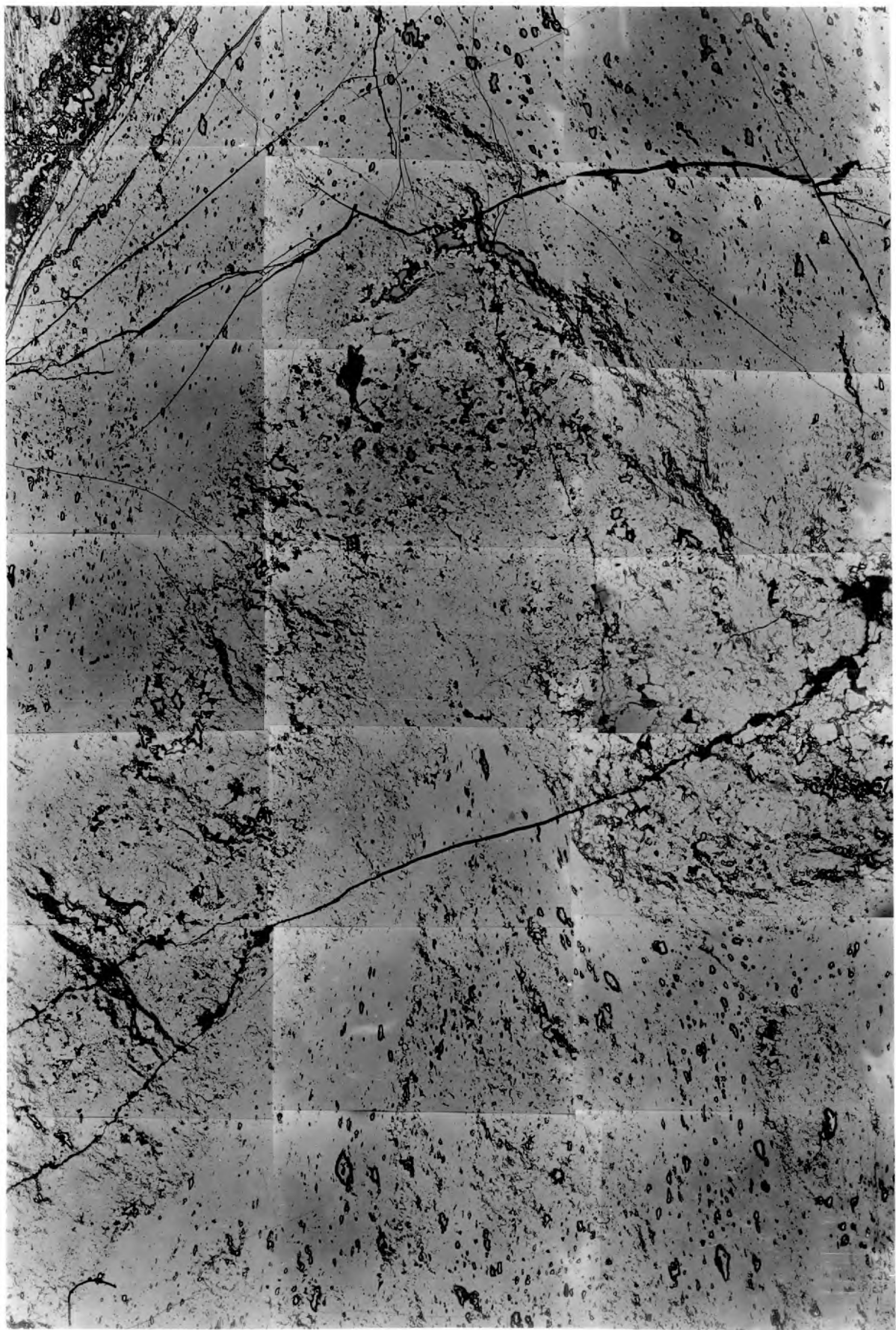
B



25 μ

Plate 3.19A Part of a similar-fold structure defined by alternating coarse and fine grained bands which are evident only in the microstructure. The coarse grained layers are composed of radially arranged grains. In the lower band the intra-granular zone structures indicate that all grains have grown from one side of the band; similar patterns of zoning are contiguous across the grain boundaries. The central fine grained band is composed of discrete elliptical structures which are illustrated in detail in Plate 3.19 B; the long axes of the ellipses are parallel to the axial plane of the fold in the crestal region, but tend to become parallel to the coarse grained band in the limb region.

Plate 3.19B illustrates the microstructure in the area enclosed by the rectangular frame near the apex of the fold shown in Plate 3.19 A.



3-20

1 mm

Plate 3.20

Unetched microstructure of the folds indicated at F_2 in Plate 3.14 (a). Several bands define the fold structures and are mainly distinguished by variations in the density of the pyrite aggregate.

The axial plane of the central anticline and the syncline at the right trends vertically (parallel to the regional slaty cleavage), and in the lower part of the illustration is defined by elongate interstices occupied by chalcopyrite and sphalerite. In some bands similar interstices are oriented parallel to the limbs of the folds, and tend to deviate towards the axial plane orientation in the crestal regions.

A second lamination (parallel to the regional fracture cleavage) trends from the upper left to the lower right of the illustration, and is well developed in the central bands where the definition is due to a preferred orientation of elongate, voidal and occupied interstices.

from the axial plane orientation and tends to assume a symmetrically fanned arrangement. In the relatively high-reflecting layers defining the folds shown in Plate 3.20 a lamination is developed parallel to the limbs of the folds, and shows a gradual transition to the axial plane orientation in the crestral regions.

Fold profiles were observed in three of the oriented samples. Apart from ptygmatic-folds, which have variable orientations, all these structures trend east-west, and their axial plane surfaces dip vertically or steeply to the north. These orientations correspond to the attitude of the first generation fold system in the country rocks. In two other oriented specimens elongate grains define a layering structure which is identical to the axial plane lamination associated with folds; in one other sample fine grained elliptical structures define a semi-penetrative lamination; in all three of these specimens the orientation of the layering is approximately parallel to the regional slaty cleavage - i.e. the axial plane cleavage of first generation folds. In the folds shown in Plate 3.20, a second laminar structure (trending from the upper left to the lower right of the illustration) transects the axial plane surface, and its orientation corresponds to that of the fracture cleavage in the country rocks (i.e. the axial plane cleavage of the second generation fold system). In the sections illustrated in Plate 3.15, elongate voids and laminar zones of pore space have a preferred orientation which corresponds to the regional fracture cleavage orientation.

3.2.3 Jointing

Joints are a characteristic feature of the massive ore where they are far more prominent than in the surrounding metasediments. There are two dominant systems; one trends north-south and dips steeply to vertically, and

the other is sub-horizontal. Joint planes belonging to the north-south trending system are normally spaced at distances in the order of a few centimetres or less. The sub-horizontal system is considerably less penetrative, and shows spacings in the order of a metre between prominent joints.

Joints in the massive ore ~~are~~ notably planar, and may be either filled (with sphalerite, chalcopyrite or quartz) or unfilled. Displacements at right angles to the joint faces range from a few microns to approximately half a millimetre. The overall planarity of the joint planes gives way in detail to a fine surface relief which can be correlated with the underlying grain structure. Counterparts of single grains or groups of grains can always be accurately matched across the joint faces. The normal displacements across opposing joint surfaces and the absence of lateral displacements suggest that most joints are tensional structures.

Progressive readjustments of the stress conditions in the lode due to mining excavations cannot account for the development of the large **majority** of the joints. In both the opencast and underground workings where residual stresses within the ore body are, respectively, largely and only partly relieved, the orientation and incidence of joints remains the same.

For three main reasons it is unlikely that the joints are consolidation phenomena developed in initially flat lying deposits which were subsequently folded: (1) the idea of consolidation as applied to clastic sediments in general has little application to crystalline deposits such as those represented by the sulphide ore bodies. From the first stage of their history following the close of mineralisation, the sulphide deposits have been coherent and can be regarded as rigid, elastic bodies. (2) consolidation joints involving essentially dilational

strain are unlikely to survive a later compressional folding phase, and (3) the joints do not exhibit folded configurations.

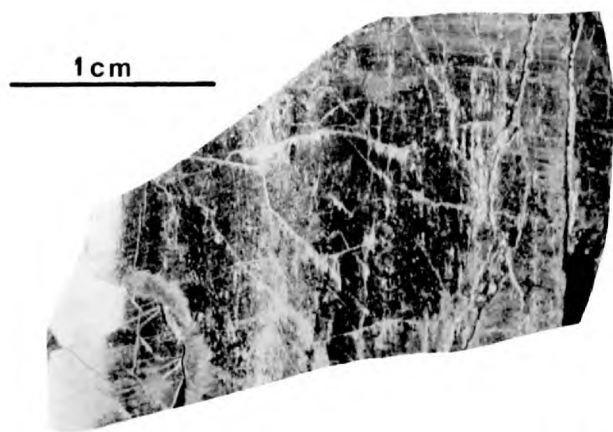
The development of jointing in both the lode and the country rocks can be related to the overall tectonic history of the region. At the stratigraphic level of the ore deposit folding must have taken place under a considerable depth of cover (i.e. that represented by some 3000 - 4000 metres of overlying sediment). Since the development of jointing postdates the regional fold system, it is reasonable to suppose that the joint systems now exposed in rocks at the Earth's surface developed in response to alterations in internal stress conditions consequent upon uplift and denudation of the folded stratigraphic pile. This interpretation is also consistent with the symmetry relationship between the joint systems and the regional first phase fold axes.

The presence of a joint system in the ore body does not clarify the time relationship between the deposition of the lode and the development of the regional first phase fold system. The probable development of the jointing during regional uplift bears no implication as to the time at which the lode was formed. In order to account for the observation that jointing postdates the regional fold system, it can be assumed that, prior to uplift, the ore body was either: (1) initially present as part of a flat-lying stratigraphic succession and subsequently folded, or (2) introduced in its present configuration into an already folded structure.

3.2.4 Slickensides

Occurrence, Structural Relationships and Evolution

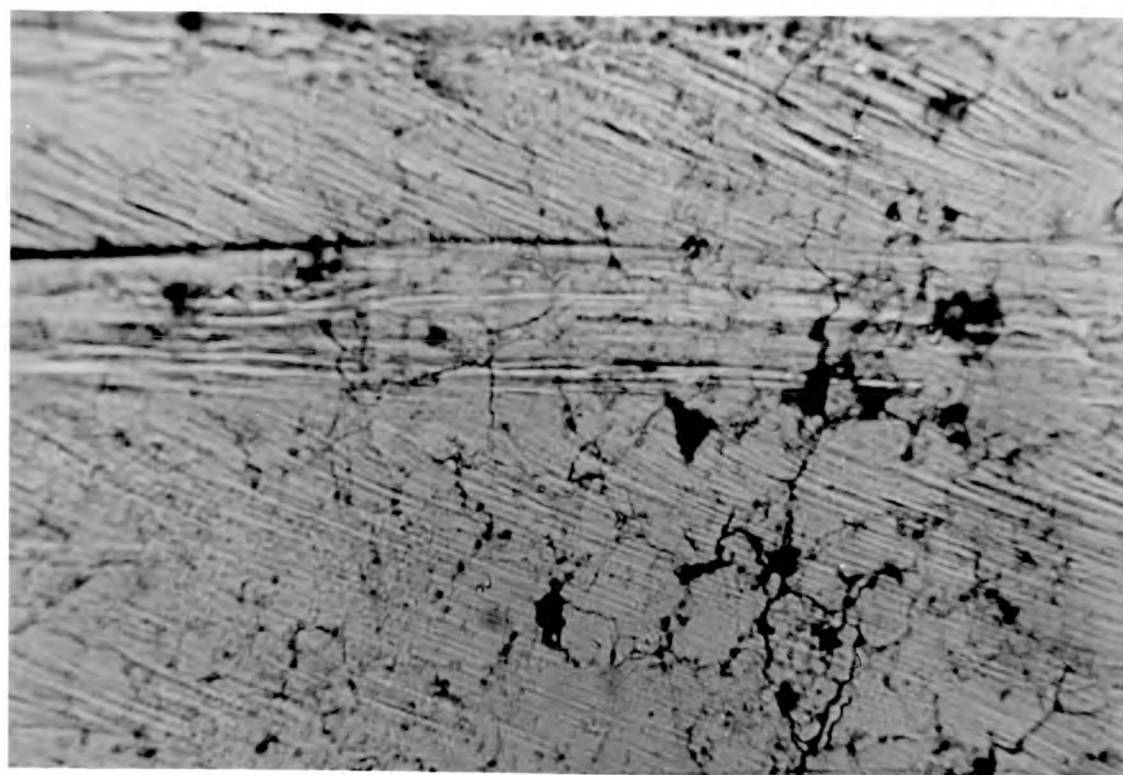
Partially to highly polished slickenside planes are conspicuous features of the massive ore. In the axial



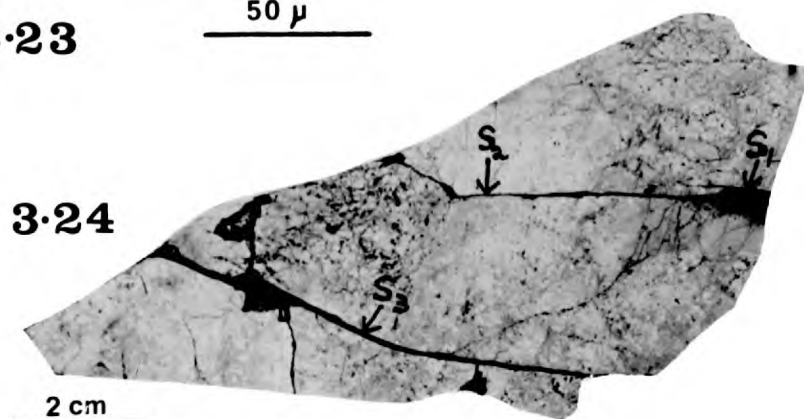
3-21



3-22



3-23



3-24

Plate 3.21 Part of a highly polished and weakly striated slickenside plane. Gentle undulations of the surface trend parallel to the striation direction (vertical) and are manifested by the alternating high- and low-reflecting areas. Narrow transverse fractures are approximately normal to the striation direction.

Plate 3.22 Part of a highly polished slickenside plane showing complex curvature and deep striations. Near the lower margin of the specimen the slickenside plane becomes locally discontinuous. At the upper margin the slickenside terminates abruptly and does not extend into the surrounding aggregate from which this specimen was taken.

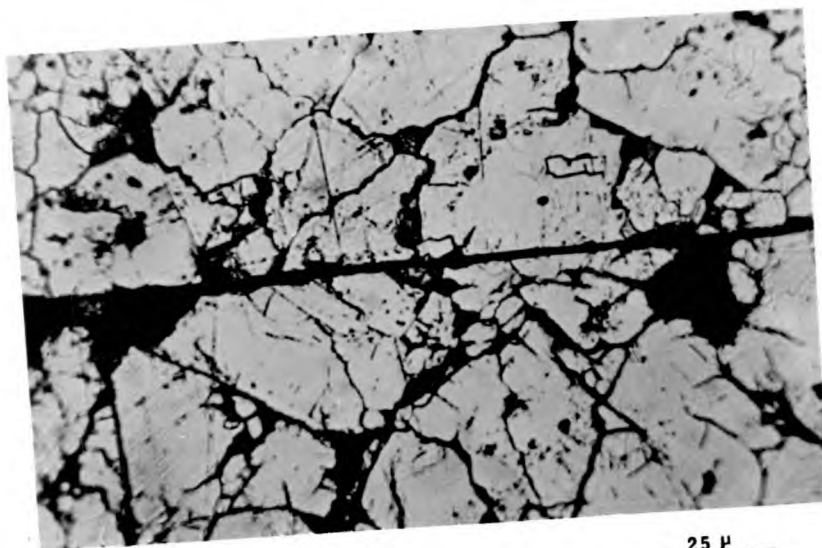
Plate 3.23 Microstructure of a heavily striated slickenside surface. The major striation direction trends horizontally. Subsidiary striations are oblique and are truncated at the edges of the major striation zones.

Plate 3.24 Flat-ground surface oriented at right angles to three slickenside planes (S_1 , S_2 and S_3) and parallel to their striation directions. The plane S_1 terminates at its left-hand extremity in the massive aggregate. The planes S_2 and S_3 show matching surface configurations; small scale structures (manifested by reflectivity variations) in the massive aggregate can be correlated across these planes.

region of the main synclinal structure, the slickensides are abundant and are often spaced as closely as a few millimetres apart. Single planes have continuous areal extensions ranging from several square metres, down to a square millimetre or less. The slickensides are strictly discontinuous features, and ~~terminate~~ within the ore body. The most extensive structures (Plate 3.21) tend to be planar, weakly striated and spaced at intervals of a metre or more. The less extensive planes (Plate 3.22) tend to be strongly curved, heavily striated and more closely spaced. Some slickensides occur in the form of fracture planes whose surfaces exhibit numerous disconnected slickenside patches. On a given plane there is generally only one, sometimes two, and rarely more, sets of striations; each set has a constant orientation within a few degrees, and one of the sets is always much more conspicuous than the others (Plate 3.23). The slickenside planes, and their associated striations, show highly variable orientations on all scales.

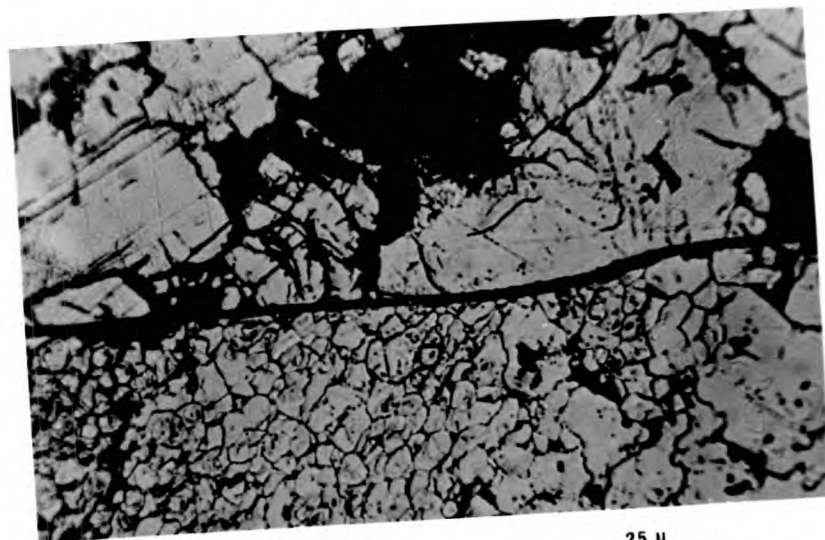
Opposing slickenside planes are either in almost perfect contact or separated by distances of up to approximately 50 microns. The intervening space may be either voidal or wholly or partly occupied by quartz or a compact and extremely fine grained, dull black deposit. The undeformed crystal faces of infilling quartz indicate a late stage of deposition.

A remarkable feature of the slickensides is the total absence of displacements in the plane of the slickenside. This is most conclusively demonstrated by their frequently abrupt termination within massive undeformed aggregates (Plates 3.22, 3.24). Further evidence is provided by the matching shape of opposing slickenside planes. Plate 3.24 illustrates the typical configuration of slickenside planes in sections normal to the plane and parallel to the predominant striation



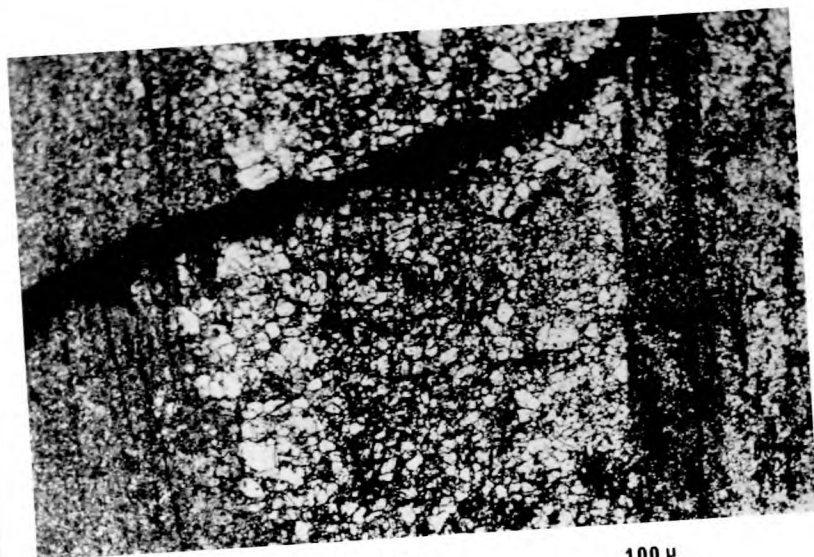
3-25

25 μ



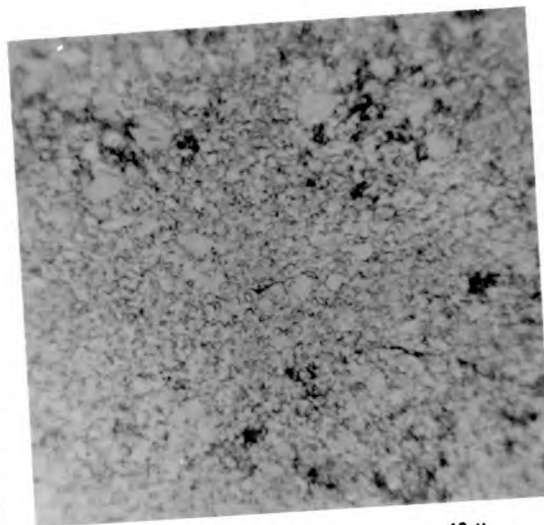
3-26

25 μ



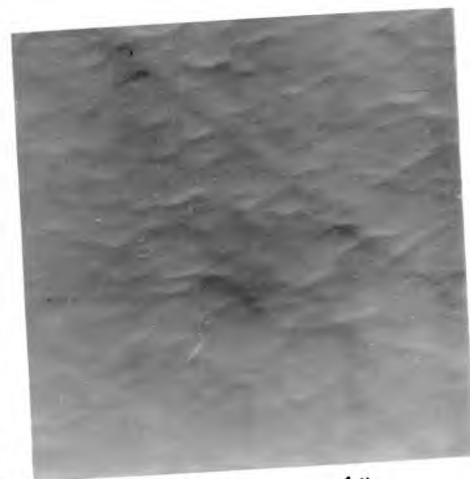
3-27

100 μ



3-28

10 μ



3-29

1 μ

Plates 3.25 and 3.26 Each plate illustrates the microstructure at two different localities, approximately 100 microns apart, along the same slickenside plane. In Plate 3.25 the main features of the grain structure can be correlated across opposite sides of the slickenside. In Plate 3.26 the microstructure is truncated at the slickenside.

Plate 3.27 Etched microstructure of a naturally polished slickenside surface. The major striation direction trends vertically.

The coarse grained bands (high-reflecting) exhibit microstructures corresponding to the primary fabrics of the massive ore. The fine grained bands (low-reflecting) are recrystallised equivalents of the primary aggregates and their detailed microstructure is illustrated in Plates 3.28 to 3.33.

Plates 3.28 and 3.29 Etched microstructure of the ultra fine grained zones on naturally polished slickenside surfaces. In the optical photomicrograph Plate 3.28 the small grains are not properly resolved; several large grains are disseminated through the fine grained matrix. The microstructure of the ultra fine grained aggregate is shown in the electron photomicrograph Plate 3.29.

direction. Areas of relatively sharp curvature separate adjacent regions which are either planar or gently curved. At all points the opposing faces match accurately. Since it can be shown that the surrounding sulphide aggregate, which is part of the normal massive ore, is undeformed (see Chapter 8), there can be no major offsets along the slickenside plane. Differential movements between rigid blocks along complexly shaped planes of this type necessitate, in general, that there are considerable areas over which no contact is maintained from the outset of the movement. Such areas could not acquire a polish. Observations, however, show that (except for local gaps unrelated to changes in the orientation of the slickenside surface). the entire area of slickenside planes is polished. Hence, contact must have been maintained at all points, and ~~no~~ bulk displacements can have taken place at any stage during the polishing process.

Attempts to correlate the grain structure across the slickenside planes lead to contradictory results. Across some planes matching grains or groups of grains are ubiquitous (Plate 3.24), thus substantiating the foregoing conclusion that bulk displacements are absent. Across other planes (Plates 3.25, 3.26) the granular structure ~~can~~ can be correlated at most points along the surface (Plate 3.25), though there are notable exceptions where certain parts of the microstructure are truncated and do not appear on both sides of the slickenside (Plate 3.26).

It is obvious that the slickensides are neither pseudomorphic nor tensional features, and that they must represent shear planes. The absence of bulk lateral displacements is not without precedent, and is indeed a characteristic feature of shear joints. Nevertheless, the polished character of the surfaces must be ascribed to differential movements. By assuming a non-uniform

stress environment close to the upper limit of the elastic region for the sulphide aggregate it is possible to account for these movements, for the absence of displacements, and for the discontinuity of the shear planes.

In regions where the stress difference was sufficiently high shear failure would occur and the fracture planes thus formed would propagate until they encountered lower differential stresses in some part of the surrounding region. Due to lack of cohesion across the shear planes, displacements would ensue. These displacements would always be small since they could only be taken up by elastic strain in the surrounding coherent aggregate. Moreover, if the elastic strain is subsequently recovered, there will be no direct evidence for the earlier displacements. In spite of the usual implications concerning movements along slickenside planes in most deformed rocks, there seems to be no reason why the polish observed on these sulphide surfaces could not have been produced by extremely small displacements. Evidence suggesting that the movements were cyclic (see below) lends additional support to this view.

At the smallest scale of observations, in sections parallel to the striation direction, the planarity, and in the case of curved planes, the local planarity, of slickenside faces is retained (Plates 3.25, 3.26). In view of the microstructure of the sulphide aggregates, it might be expected that the orientation of the initial shear plane would show local departures from regularity (e.g. deviations along grain boundaries intersecting the shear plane at low angles). The discrepancy between the observed and predicted configuration of the shear plane suggests that the slickenside surfaces do not coincide precisely with the earliest configuration of the shear planes.

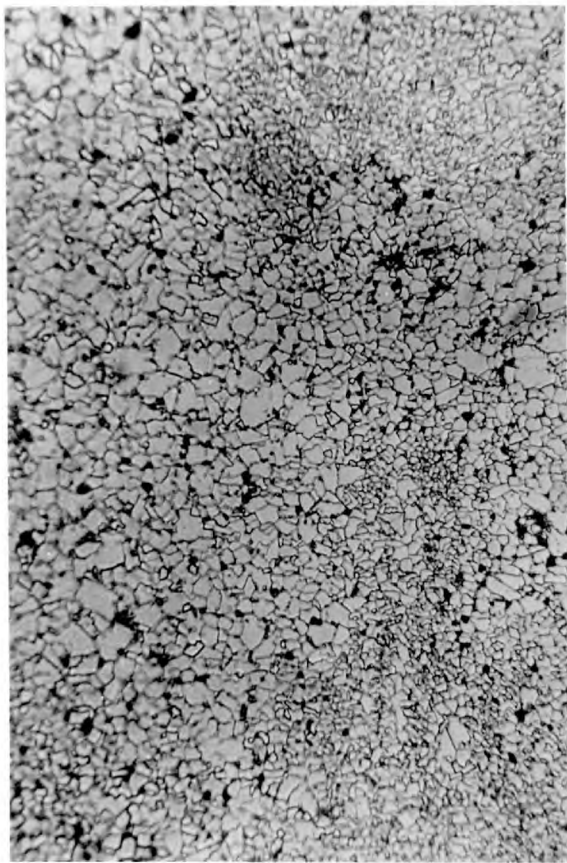
The development of planar surfaces from initially

irregular shear planes could be accomplished by granulation and the removal of material from "high spots" during the movement episode. It seems probable that for such a process to be effective the movements would need to be cyclic, and this can be readily envisaged in terms of minor stress fluctuations. Under these conditions the granulated material could be reduced to such an extremely fine grain size as to function as an effective polishing agent. The fine grained black deposit frequently present between adjacent slickenside faces constitutes the most direct evidence of granulated material removed from the initial shear planes. The normal displacements between opposing slickenside planes might partly be due to the effects of the granular material in maintaining separation between the planes. Truncation of the microstructure at certain points along many slickensides provides further confirmation of the removal of material.

Microstructure of Slickenside Surfaces

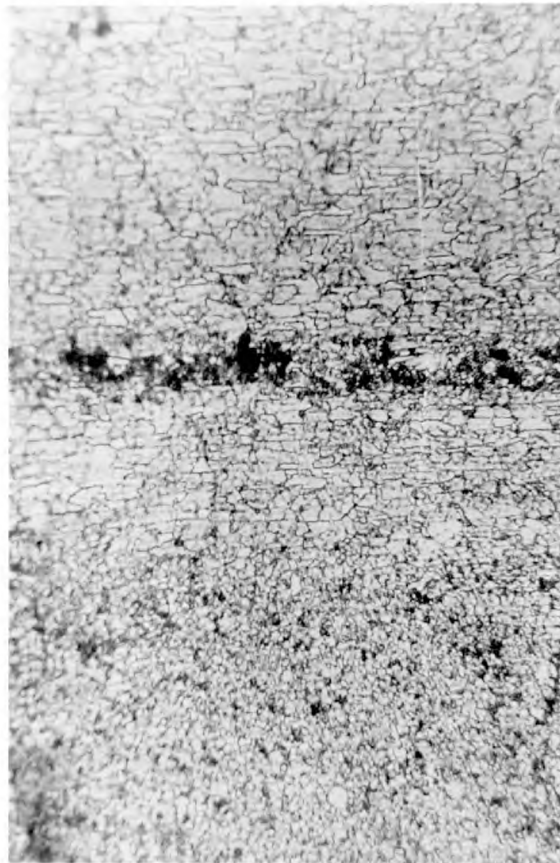
Polished slickenside surfaces are frequently as highly reflecting as artificially polished surfaces, and can be directly observed under the microscope. On etched surfaces two types of microstructure can be seen to occupy separate, laminar or broadly lenticular zones trending parallel to the major striation direction (Plate 3.27). The two types of microstructure are most readily distinguished by their large grain size difference. Some zones (the high-reflecting areas in Plate 3.27) exhibit a relatively coarse grained fabric which is identical to the microstructure observed in sections polished at right angles to the slickenside plane, and corresponds to one or other of the primary fabrics of the massive ore (Chapter 4).

The second type of microstructure occurs in fine



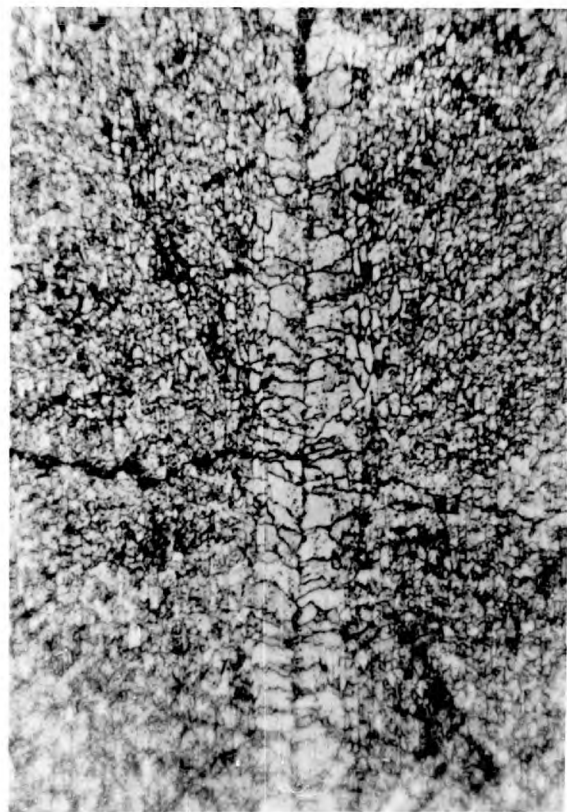
3.30

50 μ



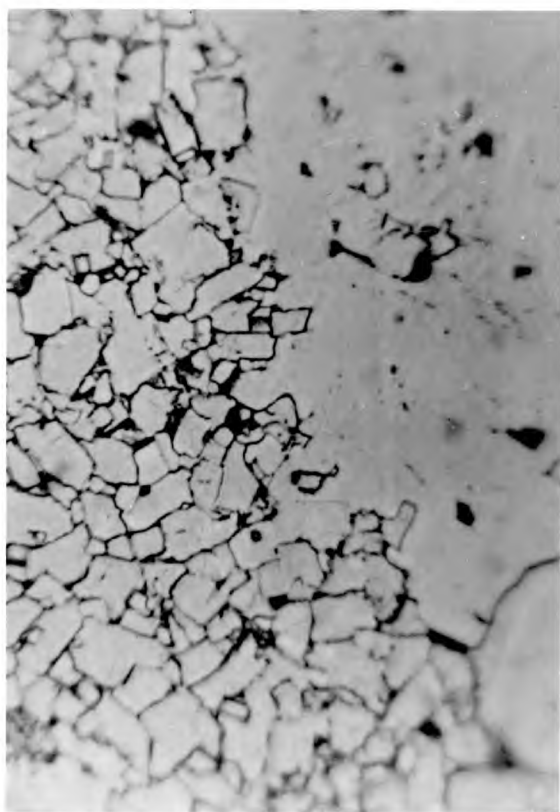
3.31

50 μ



3.32

50 μ



3.33

10 μ

Plates 3.30, 3.31 and 3.32 Etched microstructures of the fine grained zones on naturally polished slickenside surfaces.

The grain size in aggregates such as those shown in Plates 3.28 and 3.29 increases continuously, and where the microstructure can be resolved optically (Plate 3.30) the fine grained zones consist of compact aggregates of polygonal, unzoned grains. Equant grain aggregates grade into fabrics composed of unzoned, elongate grains whose long axes are parallel to the striation direction (Plate 3.31); some of these aggregates contain discontinuous rows of symmetrically oriented grains whose long axes are oblique to the striation direction (Plate 3.32).

Plate 3.33 Etched microstructure of the contact between fine and coarse grained zones on naturally polished slickenside surfaces. The microstructure of the fine grained aggregate determines the detailed configuration of the contact. The marginal grains tend to exhibit euhedral terminations.

grain size bands and although distinctive, it exhibits several variations.

Some zones are extremely fine grained and uniform; their microstructure cannot be effectively resolved by optical microscopy (Plate 3.28), but in one specimen observed using a scanning electron microscope, the grain structure was well defined (Plate 3.29). Some parts of these aggregates appear to be remarkably homogeneous, but other areas contain disseminated larger grains (Plate 3.28) which may even reach sizes sufficiently large to suggest that they belong to a coarse grained fabric zone.

Other fine grained fabric zones on the slickenside planes consist of alternating bands, lenses and broadly elongate patches of unzoned equant (Plate 3.30) and elongate (Plate 3.31) grains. Equant grains average about 5 microns in diameter, but range in size from the sub-microscopic aggregates described in the preceding paragraph to approximately 10 microns. The size range for elongate grains is approximately the same as that for equant grains, and their axial ratio ranges up to a maximum of about 5:1. The elongate grains have a strong preferred orientation parallel to the striation direction, though occasional narrow bands consist of two symmetrical layers of obliquely oriented grains (Plate 3.32).

The transition between the fine and coarse grained zones of the slickenside planes is usually abrupt. The gross form of boundary between the two zones is sometimes remarkably linear (Plate 3.27), but in detail is defined by the microstructure of the fine grained fabric (Plate 3.33).

Sections polished at right angles to the slickenside plane show that the fine grained zones are restricted to an extremely thin surface layer (estimated maximum thickness, approximately 2 - 3 microns).

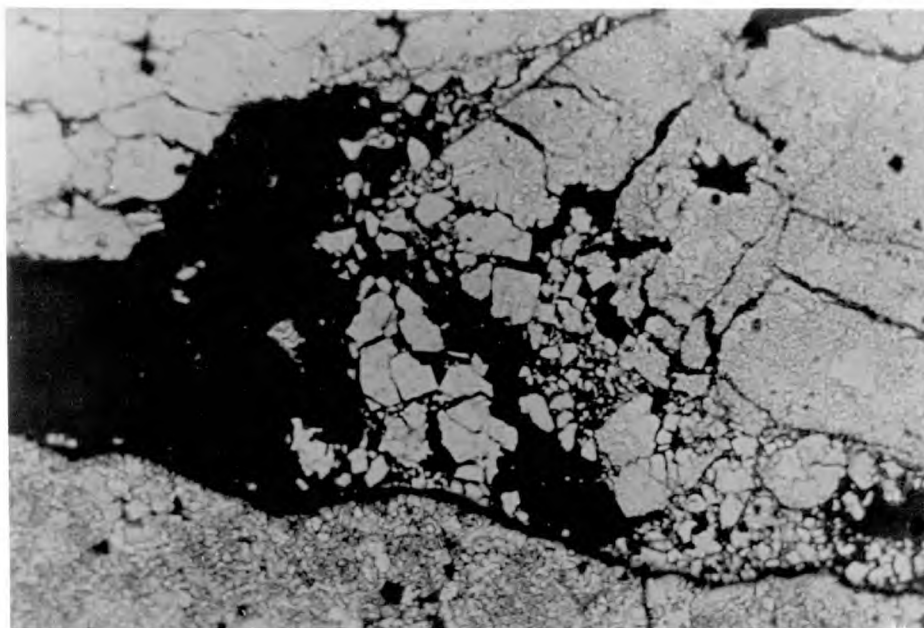
The microstructure of the fine grained fabric zones

on the slickenside planes has virtually unique properties, and has not been observed elsewhere in the banded or massive ore. The confinement of fine grained zones to a narrow surface layer, and their elongation and internal banding parallel to the striation direction, strongly suggest the origin of these fabrics is directly connected with the evolution of the slickenside planes themselves. Moreover, their association with linear zones of a recognisable primary fabric suggests that the fine grained zones were derived from a pre-existing primary fabric. It seems reasonable to conclude that the fine grained fabrics were produced by recrystallisation, and that this process was activated by the heat generated during the slickenside movements, and possibly facilitated by the development of plastic strain in a narrow surface layer.

3.2.5 Leaching Zones

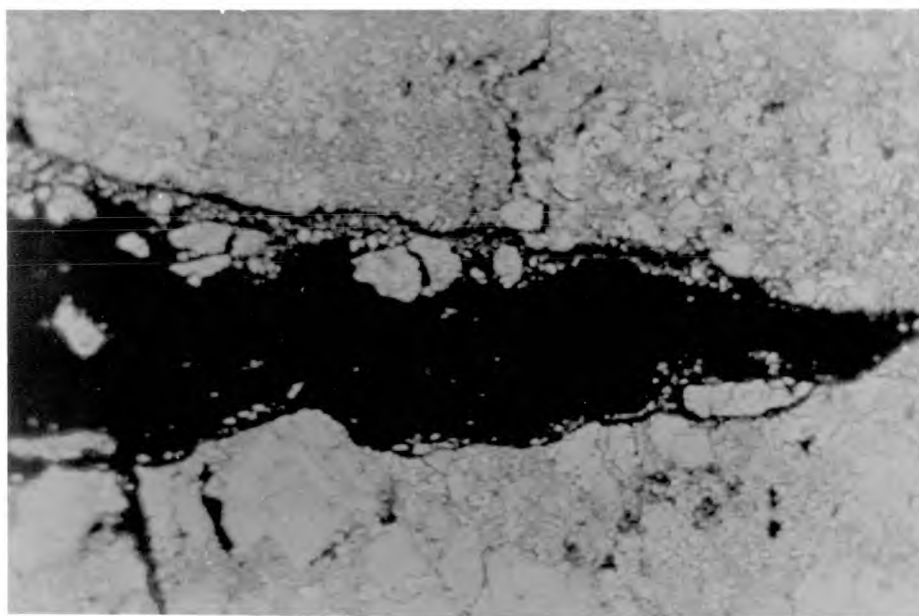
In many parts of the massive ore body there are local zones characterised by an abnormally high concentration of pore space. The voids are generally not lined by euhedral crystals, and are therefore dissimilar to the more widely occurring euhedral interstices (sect. 4.6.1), which are primary growth features. Although many of the pores are either partly or completely occupied by quartz, their infilling is not significant in the present context and the analogous terms pore space and void will be used throughout.

The porous zones considered here occur in several different forms. Many of them are found in the normal compact ore which is coherent and stable under normal mining conditions. However, their major development is in the friable zones, or "husillos", which occur in the axial region of the main synclinal structure. In these zones the bulk pore space density of the ore is abnormally high; the porous zones are interconnected, and the



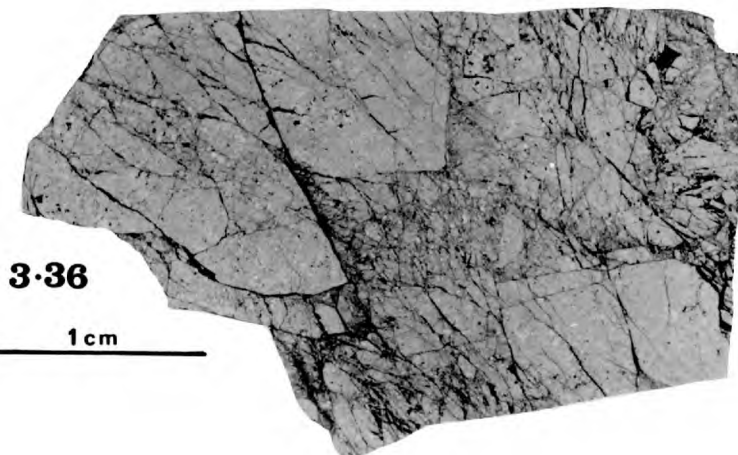
3-34

250 μ



3-35

250 μ



3-36

1 cm

Plate 3.34

Microstructure of part of a large pore space infilled by quartz. Various shaped fragments occupy part of the void, and locally show matching boundary relations, both between neighbouring fragments and with the walls of the void.

Plate 3.35

A large pore space infilled by quartz and containing numerous fragments which are confined to a narrow marginal zone.

Plate 3.36

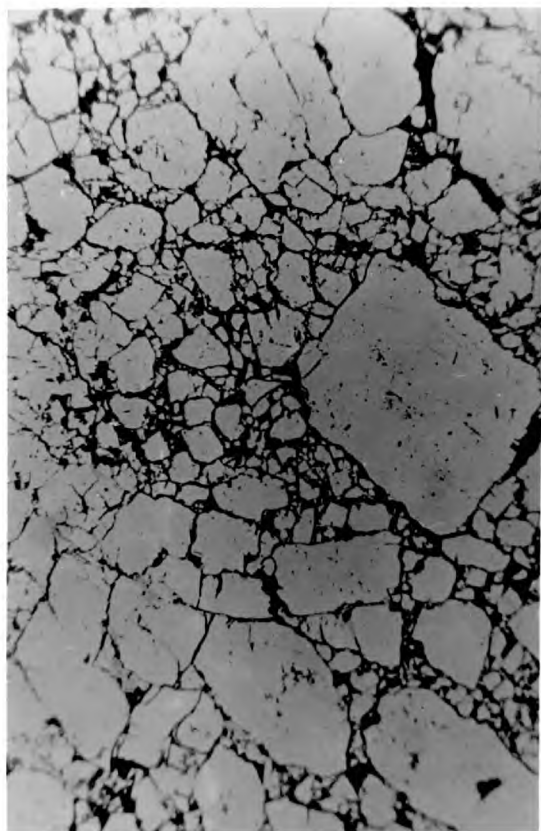
Flat-ground surface showing the fragmental structure of the massive sulphide in friable zones ("huisillos") of the ore body. The high-reflecting areas, which correspond to the normal massive ore, are almost fully compact, but are traversed by highly elongate pores (Plate 3.39) which show a preferred orientation. Several large voids (non-reflecting) occur in the upper right of the section.

In the central and lower left parts of the section a low-reflecting, interstitial matrix surrounds discrete massive fragments which are locally connected to the enclosing compact aggregate. The microstructure of the matrix zones is illustrated in Plates 3.37 and 3.38.

resulting mechanical stability of the ore is considerably less than elsewhere.

Megascopic pore zones consist of isolated and interconnected voids with dimensions ranging from a few microns to several millimetres. The distribution of the voids may be confined to narrow undulose zones or spread over wide, sharply or vaguely defined areas. Several examples are illustrated in Plate 3.15. In this specimen most of the voids occur in the coarse grained areas, and are entirely absent from the finest grain size bands, a relationship which is frequently observed. Linear zones of pores are strongly developed and have approximately the same orientation, transgressive to the main layering structure. Narrow pore zones pass into more extensive areas of voids, which are either irregular in shape or partly conformable with the layering. Several of the smaller non-laminar areas are effectively isolated. Some contain a remarkably high pore space volume, whilst in others the voids are more sparsely disseminated. Sharply delimited and extensive areas containing a high pore space volume are also evident in the bottom right of the sections illustrated in Plate 3.14.

Discrete pore spaces almost invariably contain numerous isolated fragments whose internal microstructure is identical to that of the surrounding compact aggregate. In large pore spaces, which are readily visible to the naked eye, the fragments tend to be confined to the margin of the void (Plate 3.34), and unless observed microscopically, they can easily be confused with the surrounding compact aggregate. Neighbouring voids, which appear to the naked eye to be isolated are frequently intimately connected through continuous interstitial pore space associated with clusters of fragments. In some voids, especially those which are elongate, the confinement of



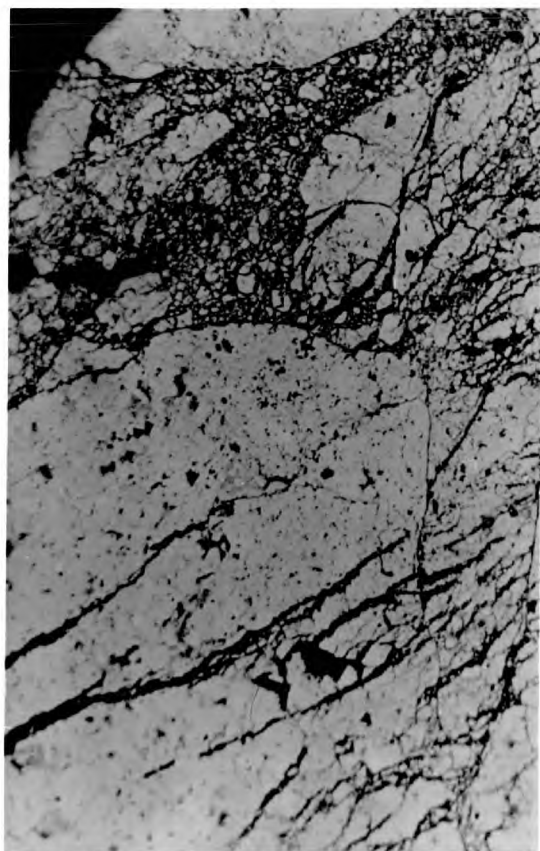
3-37

50 μ



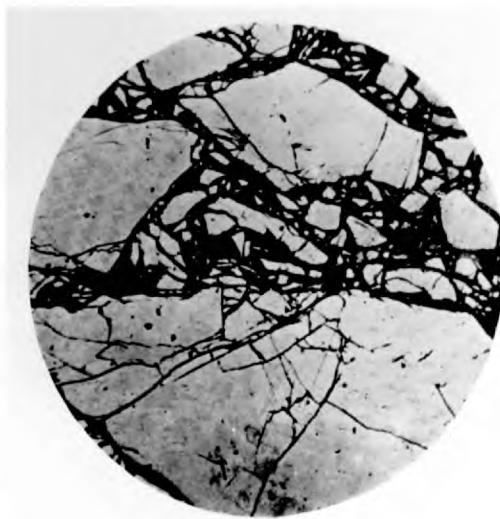
3-38

50 μ



3-39

250 μ



3-40

1mm

Plates 3.37 and 3.38 Typical developments of the fragmental structures occurring in the interstitial matrix zones shown in the central and lower left parts of the section illustrated in Plate 3.36.

In Plate 3.37 the fragments are characterised by delicate shapes, extensive interconnections and matching boundaries.

In Plate 3.38 the surrounding massive aggregate terminates abruptly at the fragment zone. At the upper left of the illustration several fragments show matching boundaries against the margin of the massive aggregate. Within the fragment zone matching fragments occur only locally, in small groups; most fragments are completely isolated, but some appear to represent an intermediate state of sub-division. Many fragments exhibit delicately shaped boundaries.

Plate 3.39 Microstructure of highly elongate pores associated with the fragment zones shown in Plate 3.36.

The boundaries of these voids are approximately parallel sided but their detailed configuration is characterised by delicate irregularities. Several of the elongate voids ~~themselves~~ contain small fragment zones.

Plate 3.40 Cataclastic structure of a pyrite aggregate illustrated by Edwards (1947, fig. 38).

fragments to a narrow marginal zone is extremely well marked (Plate 3.35).

In the friable ore zones, or "husillos", the extreme development of pore space frequently results in extensive aggregates which exhibit distinctive fragmental structures. A typical example is illustrated in Plate 3.36; the high reflecting areas are composed of almost fully compact pyrite aggregates and are traversed by highly elongate pores (Plate 3.39) which show a strong preferred orientation. Megascopic, sub-angular voids are also conspicuous. The central and lower left parts of the specimen illustrated in Plate 3.36 consist of small massive fragments surrounded by a lower-reflecting, interstitial matrix which contains a high pore volume and is itself composed of microscopic fragments isolated in a virtually continuous void. Typical fragmental structures of the interstitial matrix are illustrated in Plates 3.37 and 3.38.

The fragmental character of many porous regions bears a marked resemblance to breccia structures, and it is instructive to consider their origin from this viewpoint. In fact there are several structural features which are inconsistent with this interpretation, and which indicate that leaching is the major factor responsible for the development and configuration of the pore spaces.

It seems probable that many previous references to cataclastic structures in pyrite aggregates are directly concerned with structures occurring in the associations described above. Claims have been made for the occurrence of cataclastic phenomena in the Rio Tinto deposits (see e.g. Kinkel, 1962, p. 1077), but no illustrations or detailed descriptions are available to judge whether these so-called cataclastic phenomena are really equivalent to

the structures described here. Cataclastic structures illustrated by Edwards (1947, fig. 38), however, can probably be regarded as analogous to the cataclastic phenomena previously ascribed to certain parts of the Rio Tinto deposits. The structures illustrated by Edwards (reproduced in Plate 3.40) bear considerable resemblance to the fragmental structures described above. Judging from other illustrations in the literature (e.g. Vokes, 1963, fig. 14; Hutchinson, 1965, fig. 14 - 17; Ramdohr, 1953, fig. 173), and from observations made in several other massive pyritic ore bodies from the Huelva Province, Norway and Canada, it seems likely that many of the points of interpretation discussed below may have widespread application.

Wherever fragmental structures occur it can always be shown that the surrounding compact aggregate has not been deformed. This conclusion is most obvious where the fragmental zones are isolated (Plate 3.15). If movements occurred in these zones, there could have been no continuity of the displacements into the surrounding compact aggregate. All porous zones are in fact isolated within the massive ore body, either at the scale of the micro-structure, or over greater areas, where it may be necessary to study larger specimens or outcrops in order to establish the extension of particular zones. Where the fragmental zones are penetrative and widely distributed their isolation is not apparent in hand specimens. However, even in these instances there is sufficient continuity and accurate packing in the overall structure to indicate that there have been no megascopic displacements (Plate 3.36).

Several features indicate that there were no displacements in the fragmental zones themselves:

- 1) Where the total pore space volume is comparatively low (Plate 3.37), the incidence of matching fragment boundaries is extremely high. Even where the pore volume is at a maximum, many fragments can be fitted together in small groups (Plate 3.38). On the basis of their matching boundaries, adjacent fragments can often be linked together in continuous traverses extending over the entirety of a fragment zone. At several points the marginal fragments show matching relations with the boundary wall (Plate 3.38). The internal microstructure of neighbouring fragments can be correlated to the same extent that fragments can be matched by their boundary conformity. If later displacements had occurred in the fragmental zones, the observed incidence and precision of matching fragment structures could not be expected to persist.
- 2) Many fragments exhibit delicate shapes which include smoothly curved, re-entrant and projecting forms (Plates 3.34, 3.37, 3.38). These features could not be expected either to originate or to persist during a movement episode which involved brittle fracturing and attrition.
- 3) Where the pore space volume is low (Plate 3.37) many fragments are not entirely isolated, but are connected to neighbouring fragments by narrow bridges. In fact a large number of fragments are better described as connected to, rather than disconnected from, their neighbours. Several fragments are intersected by narrow, parallel sided pores and appear to represent an early stage of sub-division. Where the pore space volume is high (Plate 3.38), most fragments appear to be isolated, though even here some are bridged and others seem to be in an intermediate stage of sub-division. These features cannot be explained

in terms of brecciation since they effectively invalidate the existence of discrete fragments which could behave independently.

- 4) The boundary between fragmental zones and the surrounding compact aggregate is characteristically sharp. This suggests that a possible fragmentation mechanism might involve exfoliation of successive fragments from the wall of a large pre-existing pore space. The non-uniform stress concentration surrounding a cavity might produce the requisite stress conditions to initiate such a process, comparable on a small scale to the rock bursting phenomena encountered in mining practice.

Using the brittle strength data for pyrite given by Robertson (1955, fig. 20), and assuming elliptical pores with an axial ratio of 2:1, it was calculated from the equations given by Ford (1963, p. 305) that exfoliation would occur at a depth of burial of about 15,000 feet. Although this mechanism appears to be feasible in principle, it is extremely difficult to evaluate since the assumption of an initial large pore space cannot be independently confirmed. Moreover, the magnitude of the stress at the cavity can only be determined within vague limits. The principal factor controlling the stress concentration is the actual configuration of the pore space, and this is unknown.

In the microstructure of the fragmental zones there is considerable evidence to suggest that an exfoliation mechanism was not operative. Fragments detached from the pore wall would be likely to fracture along one or two approximately plane surfaces (i.e. shear planes), and neighbouring fragments would have equivalent boundary morphologies corresponding to the shape of the fracture plane. Hence,

the presence of non-matching, re-entrant and delicately shaped fragment boundaries is inconsistent with exfoliation. Bridged fragments cannot be accounted for by this mechanism since they imply that parallel fragment boundaries terminating at a bridge do not represent fracture surfaces at all. Fragment boundaries terminating at a bridge do not generally define wedge shaped structures, which implies that the fragments have not been rotated about a fulcrum at the bridge.

In all occurrences of the fragmental zones, the shape of many parts of the walls of the zones is characterised by protrusions, embayments and other irregular forms (Plates 3.34, 3.37, 3.38). These features are typical manifestations of leaching, and are well known in the supergene environment of many types of ore deposits. Their occurrence in the fragmental zones suggests that the development of the pore space is due to active dissolution in a pre-existing compact aggregate. Several other features in the microstructure support this interpretation, and cannot be accounted for in terms of mechanical disturbance.

In the early stages of leaching, when only small amounts of material have been removed, the dissolution channels will be relatively narrow and disconnected. With continued leaching the channels become enlarged and interconnected. During the early stages of leaching, when the dissolution channels are narrow, the effects due to any differences in the dissolution rates on opposite sides of a given channelway will be small in comparison to the accumulated effects at advanced stages. In terms of the resulting microstructure, these trends mean that:

- 1) at early stages of leaching:

- a) the total pore volume is low;
 - b) the aggregate is sub-divided by narrow, semi-continuous channelways into a number of bridged or extensively connected fragments;
 - c) the channelways tend to be parallel sided, and neighbouring fragments have matching boundaries.
- 2) at advanced stages of leaching:
- a) the total pore volume is high;
 - b) the aggregate is sub-divided by wide, continuous channelways into a number of isolated fragments;
 - c) opposite sides of the channelways acquire different shapes by dissolving at different rates, and neighbouring fragments have non-matching boundaries.

The predictions listed under (1) and (2) above show a close correspondence with the microstructure of the fragmental zones illustrated in Plates 3.37 and 3.38, respectively. The agreement between the observed and predicted microstructures holds, not only for each zone as a whole, but also for local areas in Plate 3.37 where the pore space volume is abnormally high, and for local areas in Plate 3.38 where the pore space volume is abnormally low. In view of these correlations and the characteristic shapes of many fragments, it is concluded that the fragmental aggregates represent zones of leaching.

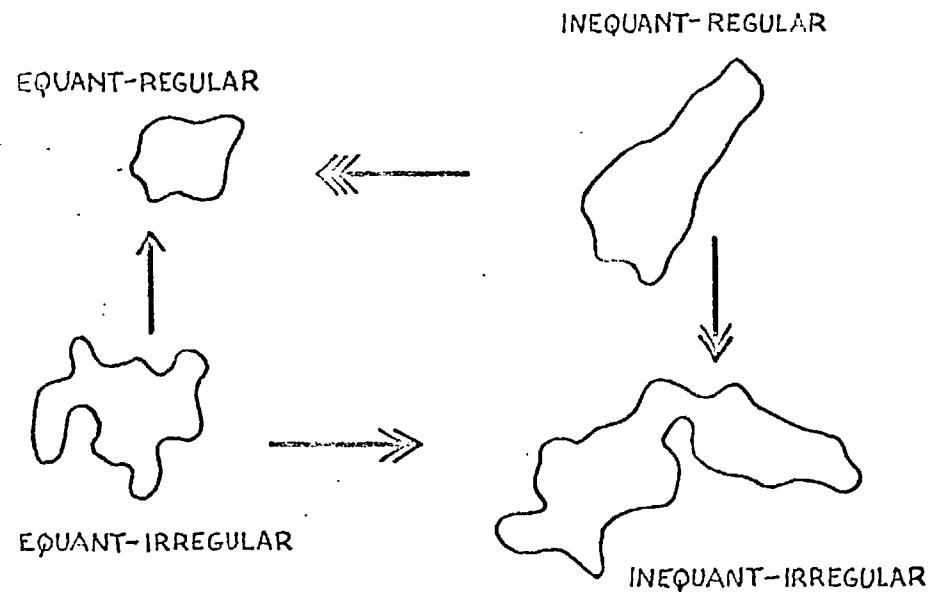


Figure 4.1 Diagrammatic classification of the grain shapes in the massive fabrics. The arrows indicate approximately the relative preferences for the development of each of the four end member types.

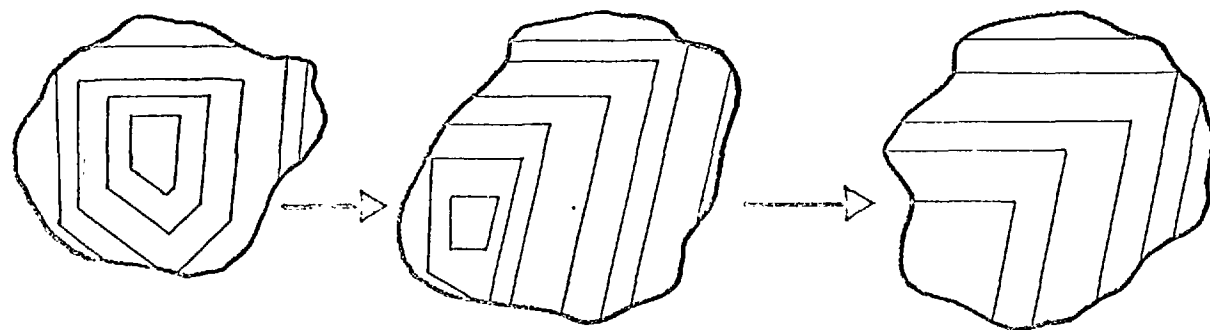


Figure 4.3 Diagrammatic representation of the progressive transition from closed to open, euhedral zone structures. The observed incidence of open and closed structures in the massive fabrics increases in the direction of the arrows, so that grains in which open zones are predominant are the most common.

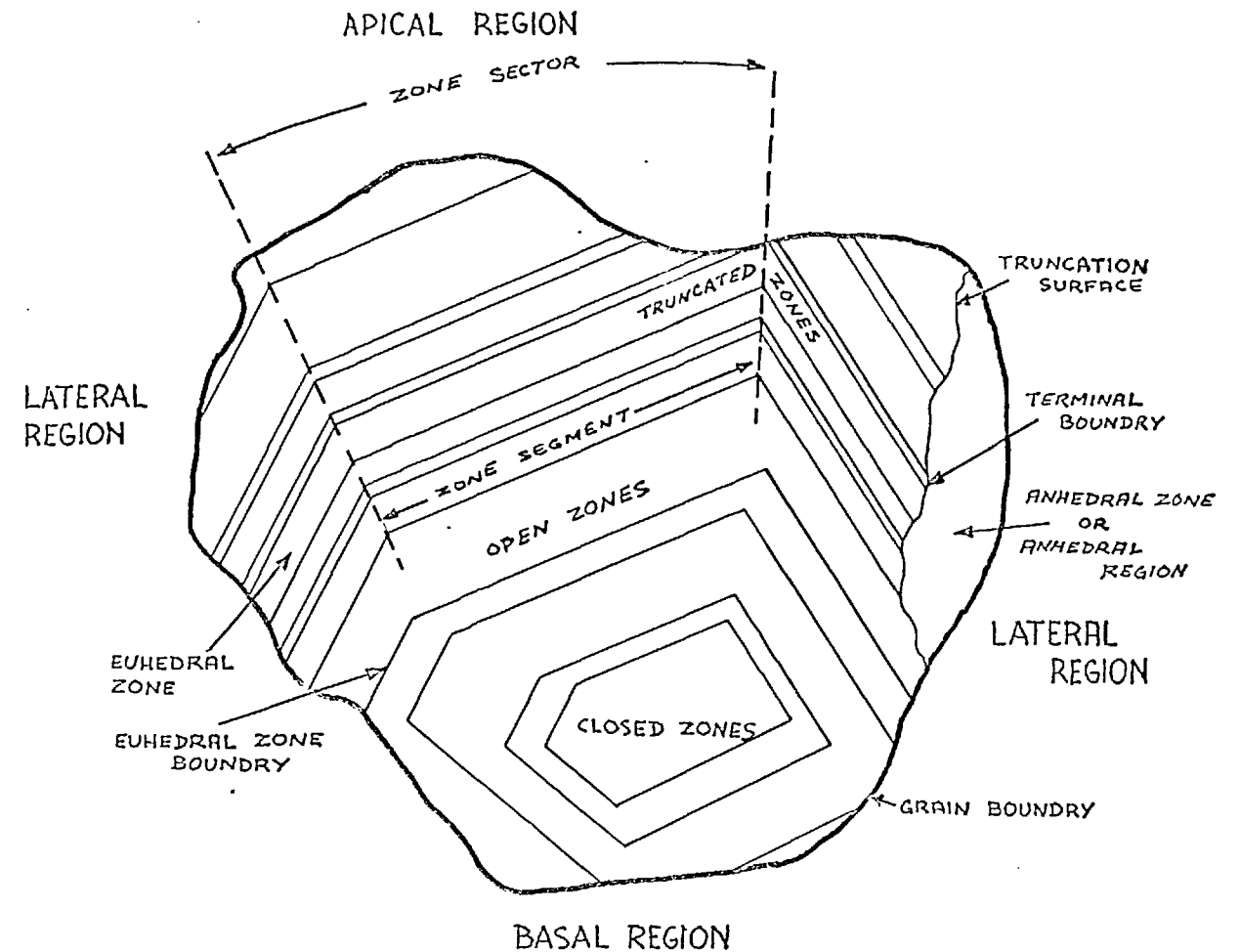


Figure 4.2 Diagrammatic illustration of the terminology used for the description of intragranular zone structures.

CHAPTER 4

MICROSTRUCTURE OF THE MASSIVE PYRITE ORE

On ground surfaces of the massive ore, megascopic structures (sect. 3.2.2) (e.g. banding) are defined by sharp and subtle colour differences and by variations of indefinite textural patterns. To a large extent many of these changes reflect variations of the average grain size. However, this is a gross simplification of the actual variations involved, as it is usually impossible to describe and distinguish different aggregates in terms of their grain size alone. The microstructure of polycrystalline aggregates is determined by many factors, among which the following are the most important: (1) grain size, (2) grain size distribution, (3) areal distribution of the grain size range, (4) grain shape, (5) grain arrangement, (6) internal grain structure, (7) distribution of pores and interstitial sites. In reality, all these factors show wide and variously combined variations, and the resulting microstructures cover an enormous range of different types.

No previous attempts have been made to describe the grain structure of the massive ore, and there are no comprehensive descriptions of other similar types of pyritic deposits. As a record of the genesis of the ore there are many significant features in the microstructure, and in connection with deformation and recrystallisation, the microstructure of the ore is extremely important. Consequently an attempt has been made during the present study to describe and systematise the microstructural features of the massive ore.

The results of this attempt have led to the development of a classification scheme, in which several different types of microstructure are distinguished. Some of the sub-divisions in this scheme are well defined (sects. 4.2, 4.3, 4.4), but some types of microstructure are closely inter-related (sect. 4.1)

and their separate classification must be largely an arbitrary decision. Almost certainly, parts of this scheme will need to be revised when sampling is extended to other parts of the ore body. However, the essential similarity of the microstructure in many samples already collected from widely different parts of the lode suggests that the ~~general form of the~~ classification is fairly well established.

Descriptions of the microstructures are presented in the following sections of this chapter. They summarise observations on approximately 70 polished sections, the locations of which are shown in fig. 3.1. Except where it is explicitly stated to the contrary, these descriptions refer only to pyrite aggregates which, however, may contain up to a maximum of about 10% of other sulphide minerals or gangue.

4.1 Massive Fabrics

Throughout the lode there is an extensive range of fine and coarse grained aggregates which exhibit a common tendency to be isotropic over volumes of a few cubic centimetres or more. These aggregates display fabrics which are described by the term massive. Among the massive fabrics it is convenient to distinguish three main groups, namely, massive-discrete, massive-homogeneous, and massive-composite. The basis for this sub-division rests largely on criteria relating to grain size. This type of distinction depends greatly on scale. At large scales, massive fabrics tend to be composite. At small scales they become homogeneous, and at intermediate scales, the classification can be continuously altered by arbitrary selection of particular volumes. Over large volumes the microstructure is extremely variable, and cannot be properly treated in any generalised way. It is obviously necessary to attempt some kind of system-

atisation, and the distinctions which are employed here have been devised for that purpose.

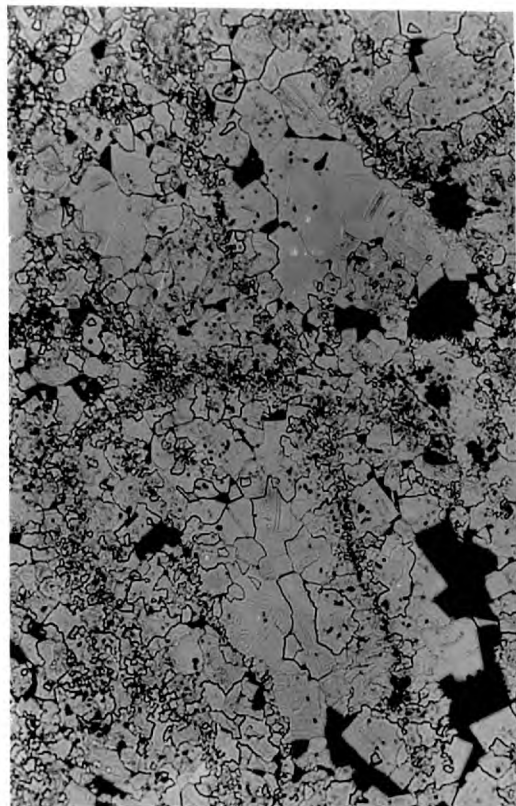
It should be stressed that there is in fact no sharp distinction between most specific microstructures. The massive-discrete fabrics are an exception to this and can usually be readily distinguished. There is an extremely close connection between the massive-homogeneous and massive-composite fabrics, and it must be emphasised that the proposed dividing line between them is necessarily flexible; dependence on scale is of prime importance, but even when the scale is carefully chosen it is difficult to classify many aggregates. In the following descriptions the main emphasis is laid on typical developments of the three groups of massive fabrics.

There are many aggregates whose fabrics are completely defined when the scale is a fairly constant factor, the scale being then determined as a continuous area containing in the order of hundreds of grains. The absolute dimensions of this area are highly variable and depend on the average grain size. The more isotropic fabrics can be defined over areas containing much less than hundreds of grains. When groups of only a few grains are considered, all aggregates belonging to the massive fabrics are essentially homogeneous, though at this scale it is scarcely meaningful to retain the concept of a fabric since single grains have then become the dominant entity.

Taken together, the three groups of massive fabrics constitute the largest volume contribution to the total sulphide ore. Judging from the samples collected for this study, it is estimated that the massive fabrics comprise somewhere in the region of 75% - 90% of the lode. Of this, the massive-homogeneous and massive-composite fabrics comprise more than two-thirds.

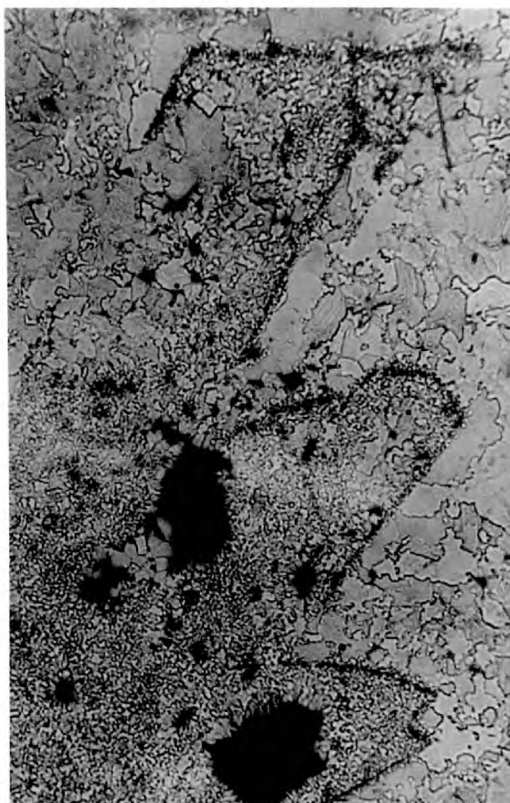
4.1.1 Massive-Discrete Fabrics

The total grain size variation in the massive-discrete



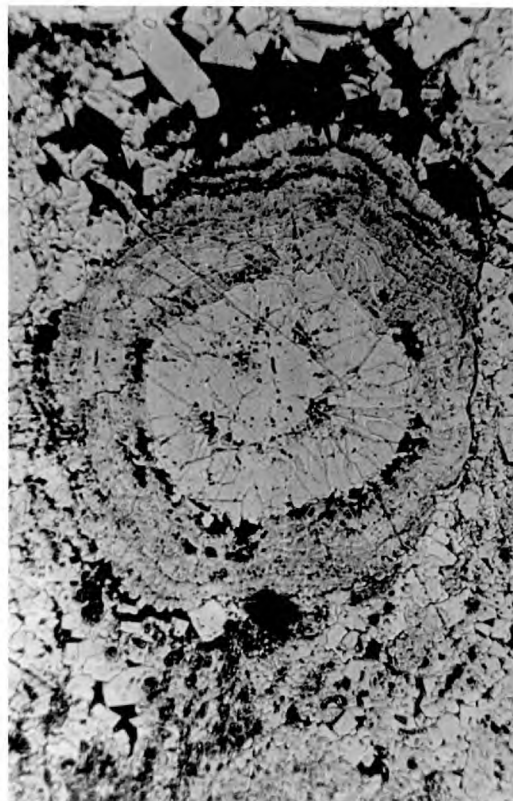
4.1

100 μ



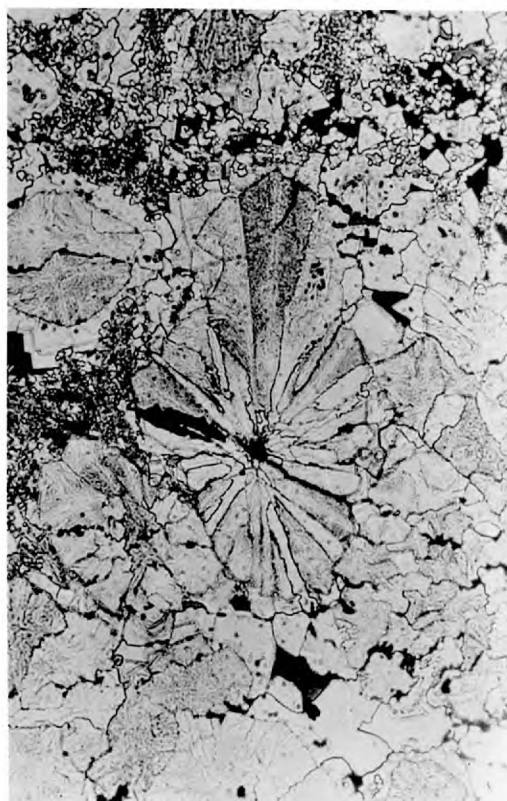
4.2

250 μ



4.3

100 μ



4.4

100 μ

Massive-Discrete Fabrics

- Plate 4.1 General aspect of the planar network structure showing the distribution of fine grained bands in a coarse grained host aggregate.
- Plate 4.2 The fine grained area represents part of an angular zoned structure, showing the typical plane boundaries and sharp definition against the surrounding coarse grained matrix.
- Plate 4.3 Isolated spherical grain aggregates showing concentric layering and a radial grain arrangement.
- Plate 4.4 Isolated elliptical aggregate showing the characteristic radial grain arrangement and symmetrical grain size variation.

fabrics ranges from approximately 1 to 100 microns. Although the grain size distribution is usually complex, it is clear that the maximum and minimum grain sizes occur with the lowest frequency. If the whole range of these fabrics is taken together, the most common grain diameters range between approximately 10 and 50 microns.

The manner in which different types of grains (characterised by size, shape and internal structure) are arranged constitutes the distinguishing feature of the massive-discrete fabrics. There are several different types of grain arrangement, and these define specific structures which serve as the most suitable basis for a systematic description.

- 4.1.1 (1) Planar Network Structures (Plate 4.1) are defined by intersecting arrays of comparatively narrow, fine grained bands contained in a predominant coarse grained matrix. The fine grained bands exhibit a random orientation, and a planar or smoothly curved configuration. Individual bands are usually only one or two grains wide and have a maximum separation in the order of a few tens of grain diameters. Their microstructure is characterised by the following features:
- (i) The terminal boundaries of the grains facing the matrix tend to be euhedral.
 - (ii) The grain shapes are frequently elongate at right angles to the trend of the band.
 - (iii) Internal growth zone structures exhibit a preferred orientation indicating that the dominant growth direction was normal to the trend of the band, and on both sides of its centre, towards the neighbouring matrix.
 - (iv) The central region is frequently defined by an abnormally high inclusion density, or by a semi-

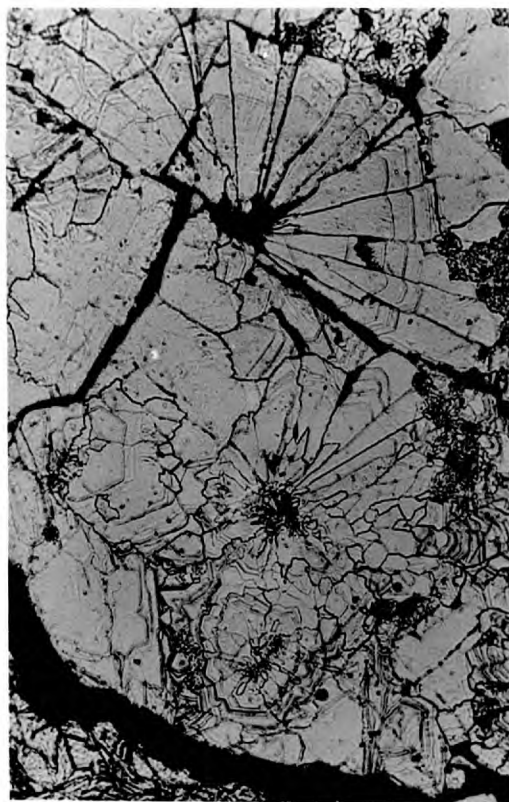
continuous pore space showing morphological features characteristic of leaching.

- 4.1.1 (2) Angular Zoned Structures (Plate 4.2) are characterised by numerous combinations of special types of grain arrangement which occur together, and are confined to strictly independent regions sharply distinguished from the host aggregate. These isolated regions are angular and have overall shapes which can generally be described as equant or tabular. The dimensions of single structures is in the order of 1 or 2 mm.

The internal zonal patterns of the angular structures is complex and variable. A semi-continuous banding parallel to the outline of the structure frequently tends to develop close to the margin. The resulting overall concentric structure degenerates towards the central region, but may be vaguely evident in the gross arrangement of other internal structures. Multiple concentric zones sometimes occur at a number of centres, and are either irregular in shape, or distinctly spherical or elliptical. In some structures the zoning takes the form of a more or less penetrative layering with a constant trend parallel to one of the major boundaries of the structure.

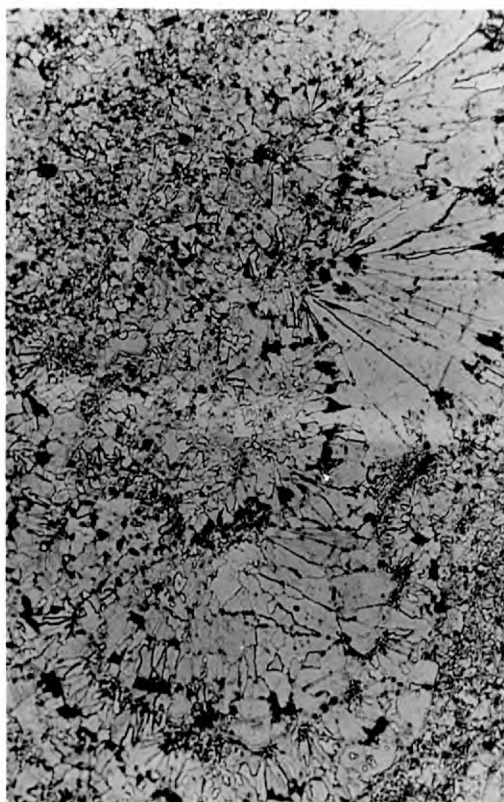
Definition of the zonal pattern is due to varying microstructural assemblages. Internal layering is sometimes defined by a preferred orientation of elongate grains, and the microstructure of the boundary region is essentially the same as that of the fine grained bands which characterise the planar network structures described above.

- 4.1.1 (3) Spherical, Sub-Spherical and Elliptical Structures are defined by polycrystalline aggregates, and are



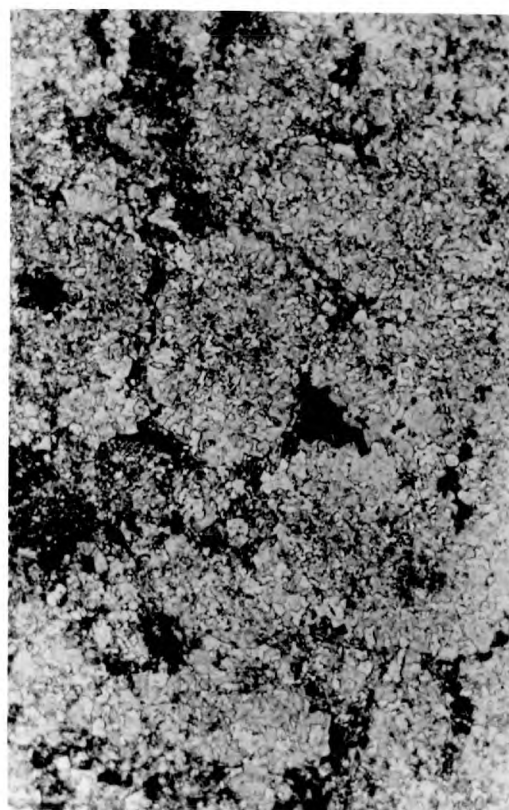
4.5

100 μ



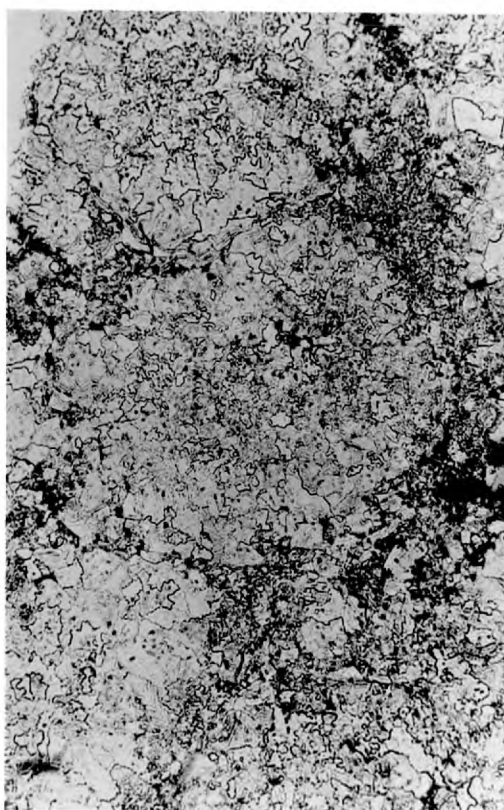
4.6

100 μ



4.7

250 μ



4.8

100 μ

Massive-Discrete Fabrics

Plates 4.5 and 4.6 Two examples of incompletely developed spherical structures which are partly continuous with the surrounding matrix.

Plate 4.7 Close-packed spherical and sub-spherical structures, representing part of a continuous aggregate containing at least a few tens of discrete structures. Interstitial black areas are voids; intermediate-reflecting areas represent a fine grained matrix.

Plate 4.8 Detailed microstructure of close-packed, spherical and sub-spherical grain aggregates. The grain shapes are irregular, but tend to be grossly elongate near the margin of the structures. Continuity of the growth zone patterns between adjacent marginal grains is faintly evident along the border of the sub-spherical structure in the lower left corner.

either (i) disseminated or (ii) close-packed. The diameters of these structures range between approximately 0.1 and 0.5 mm.

- (i) Disseminated Structures usually exhibit a marked sphericity (Plate 4.3), but regular elliptical forms are also developed (Plate 4.4). The spherical form of some structures is incompletely developed, the grain aggregate being partly continuous with the matrix and partly delimited by a curved border across which the transition to the matrix is discontinuous (Plates 4.5, 4.6); these structures are frequently joined together in groups of two or three. Incomplete spherical and elliptical aggregates are often complexly and intimately connected with the host and their identity is not always immediately obvious.

The component grains of disseminated sub-spherical structures are generally elongate and radially arranged. The orientation of intra-granular zones indicates a predominant growth direction away from the central region. In elliptical aggregates the grain size and arrangement tends to vary symmetrically about the major and minor axes of the ellipse (Plate 4.4).

- (ii) Close-packed structures (Plates 4.7, 4.8) have shapes which are often modified by a tendency to occupy the interstitial space between neighbouring structures. Especially where considerable size differences exist, asymmetrical elliptical forms are developed, but these have no preferred orientation except in a few localised groups consisting of up to a maximum of four or five

individual structures. The boundaries between neighbouring structures may be indistinct, leaving only the internal grain structure to define a number of discrete, equidimensional units.

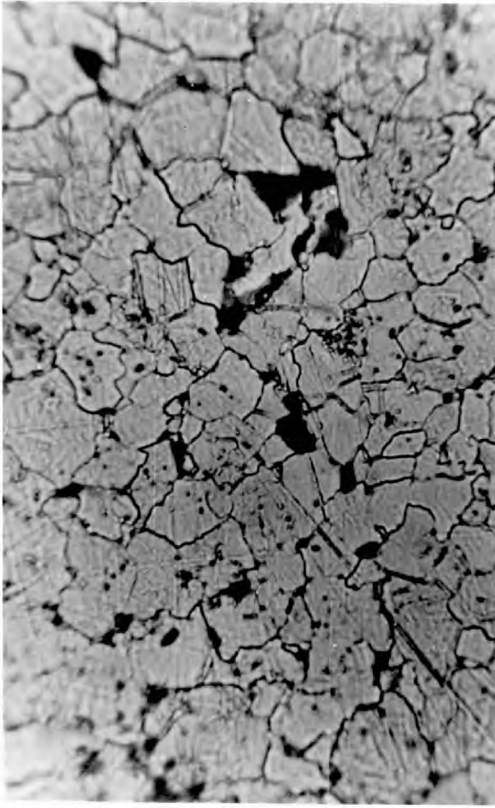
The arrangement of the component grains is essentially radial, though the central region tends to be isotropic, and elongate, radially arranged grains are characteristic of only the outer zone. Even in the outer region, however, the elongation of grains and their radial arrangement is not always clearly defined, and may be complicated by the development of irregular grain shapes (Plate 4.8). Intragranular zoning indicates a predominant growth direction away from the centre of individual structures and the marginal region is characterised by continuity of equivalent growth zones between adjacent grains.

4.1.2 Massive-Homogeneous Fabrics

The grain size characteristics for the massive-homogeneous and massive-composite fabrics are inextricable because the latter fabrics are essentially composite assemblages of massive-homogeneous fabrics. The data presented below refer to both fabric types.

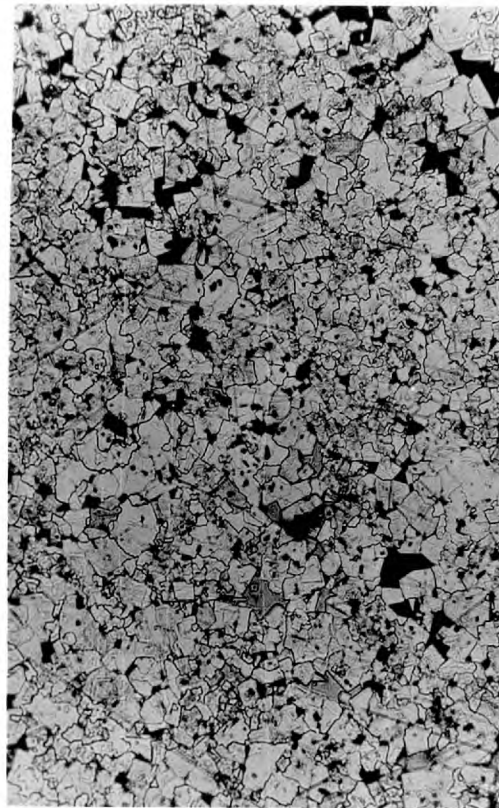
The commonest grain sizes are in the range 10 - 50microns, and the maximum or near maximum sizes approximately (1 - 2mm) occur with the lowest frequency. Grains with diameters close to the lower limit (approximately 1 - 2microns) make an important contribution in some aggregates.

The grain size distribution tends to be either uni-modal or bi-modal. In some instances, although usually only locally, these patterns are strongly developed. Both uni-modal and bi-modal aggregates cover the whole range of



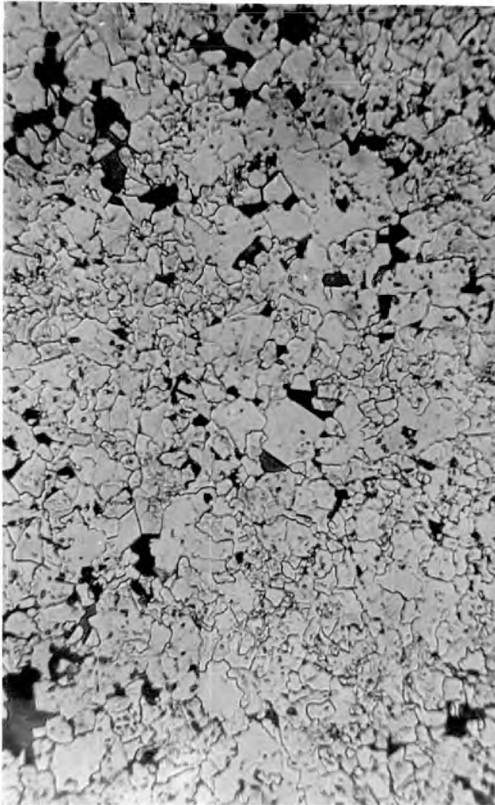
4.9

10 μ



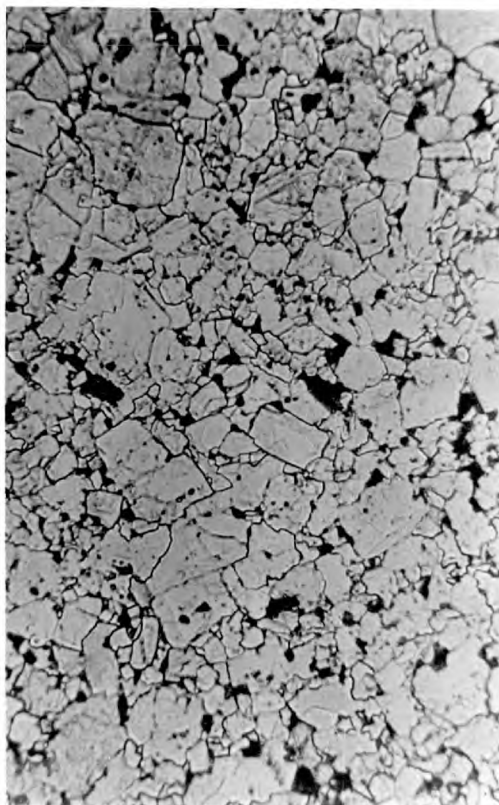
4.10

100 μ



4.11

50 μ



4.12

50 μ

Massive-Homogeneous Fabrics

Plate 4.9 Aggregate showing maximum uniformity of grain size and microstructure.

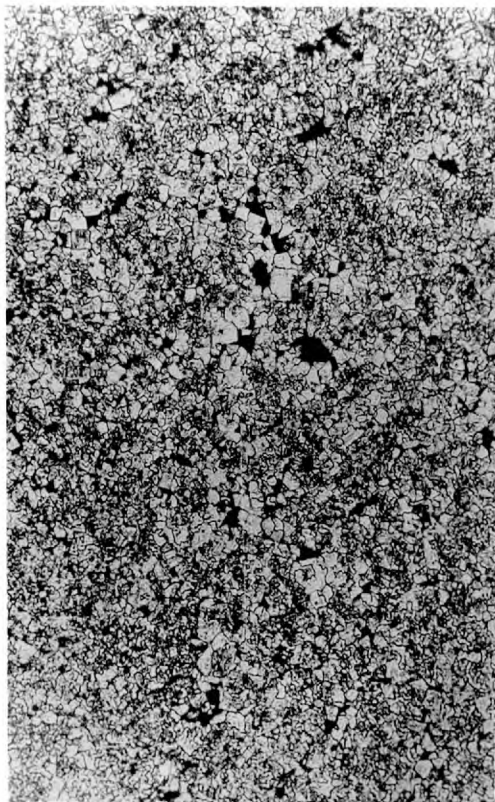
Plate 4.10 Aggregate showing typical development of maximum grain size and structural uniformity over comparatively large areas.

Plates 4.11 and 4.12 Aggregates showing extensive grain size variations, and representing the common transitional fabrics intermediate between the end-member types characterised by single and dual component grain size ranges.

grain sizes. In different bi-modal aggregates, overlapping of the main grain size components is a common feature. Typically, the coarse grain size component of one aggregate may be equivalent to the fine grain size component of another. In bi-modal aggregates the average diameter of the fine grain size component is usually about a half to one tenth the diameter of the coarse grained component. This ratio is particularly applicable when the coarse component falls in the intermediate part of the total grain size range.

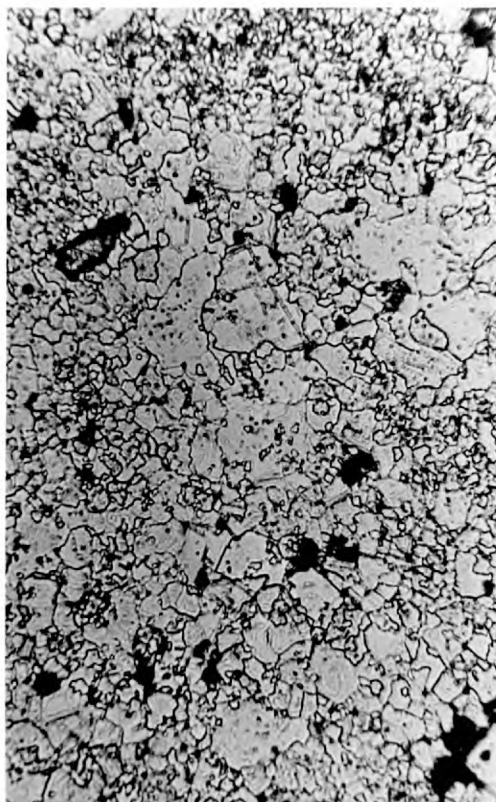
The grain size characteristics discussed above do not necessarily account for the presence of the large euhedral or embayed grains which have widespread occurrence, especially in the intermediate and finer grain size aggregates. These grains (Plates 4.25 to 4.29) have dimensions which fall within the total grain size range, but their occurrence produces a fabric in which the local grain size distribution is always at least bi-modal; the bulk fabric can be described as porphyritic. In some instances the large isolated grains belong to the disseminated marginal region of an adjacent coarse grained aggregate. On other occasions they belong to the vein structures described in sect. 4.3. However, many of these grains have a more obscure origin. Frequently they appear to have no connection with polygranular aggregates of a similar grain size, and this suggests that they may represent a separate growth event. Where there is a tendency towards euhedralism of grain shape the growth of these grains must precede that of the matrix. Even where the grain shapes are characterised by embayments, the size of the large grains almost certainly means that their growth predates that of the matrix.

Maximum uniformity of the massive-homogeneous fabrics occurs in aggregates where the grain size distribution



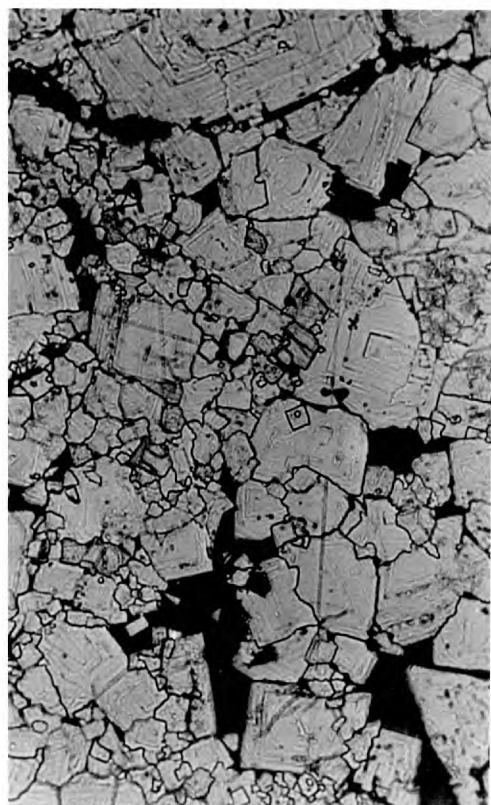
4-13

100 μ



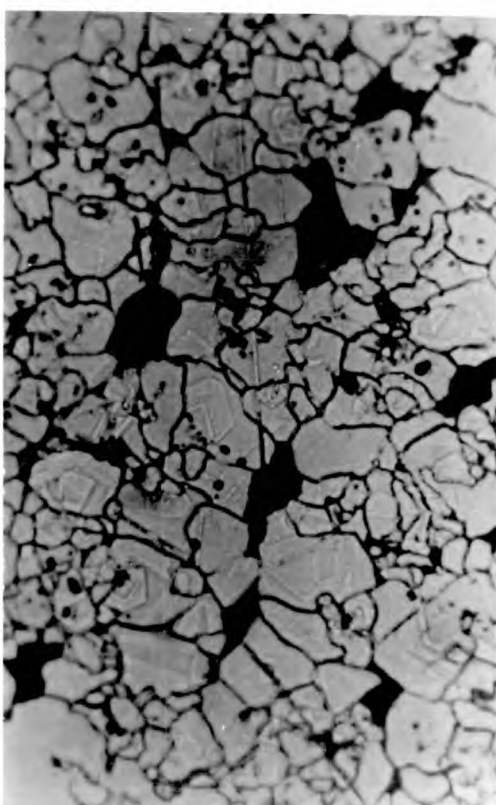
4-14

50 μ



4-15

100 μ



4-16

25 μ

Massive-Homogeneous Fabrics

Plates 4.13 and 4.14 Aggregates showing typical developments of the bi-modal grain size distribution. In Plate 4.13 the coarse grains preferentially enclose large interstitial sites (additional-growth interstices); the fine grains are scarcely resolved, but are concentrated at low-reflecting centres.

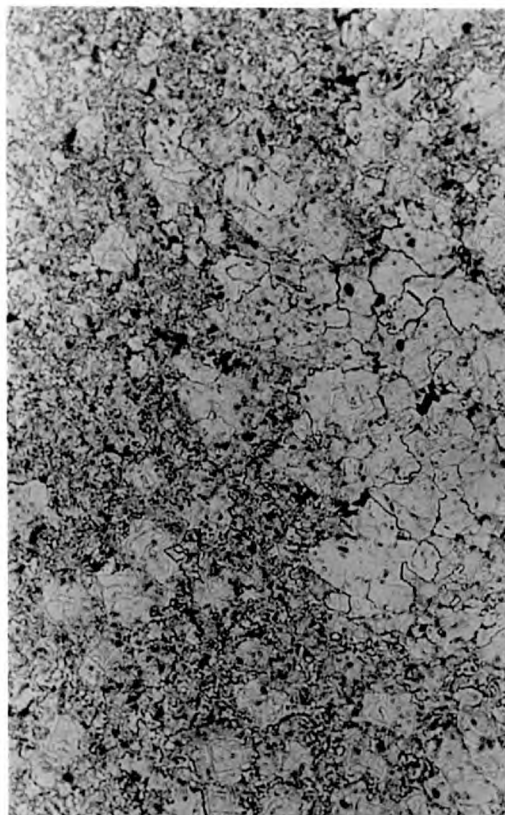
Plate 4.15 Detailed microstructure of a bi-modal aggregate showing marked grain size differentiation, and grouped occurrence of the fine and coarse grains.

Plate 4.16 Detailed microstructure of a bi-modal aggregate where the grain size range is less extensive than that illustrated in Plate 4.15, and where the fine grains tend to be correspondingly disseminated rather than concentrated in discrete clusters.

is uni-modal (Plates 4.9, 4.10). Over small areas the grain size of these aggregates can be extremely uniform and their structure virtually isotropic (Plate 4.9). However, over larger areas there are invariably minor grain size variations, but even here the spatial distribution of the different grain sizes is uniform and the overall structure of the aggregate remains remarkably homogeneous (Plate 4.10). As the grain size range increases the maximum and minimum grain sizes become more strongly differentiated, and this trend eventually leads to the development of a bi-modal aggregate. In the transition from fabrics where the grain^{size} is uniform to fabrics where there is a well-defined dual component size range, the intermediate aggregates, such as those shown in Plates 4.11 and 4.12, probably represent the most common type of massive-homogeneous fabric.

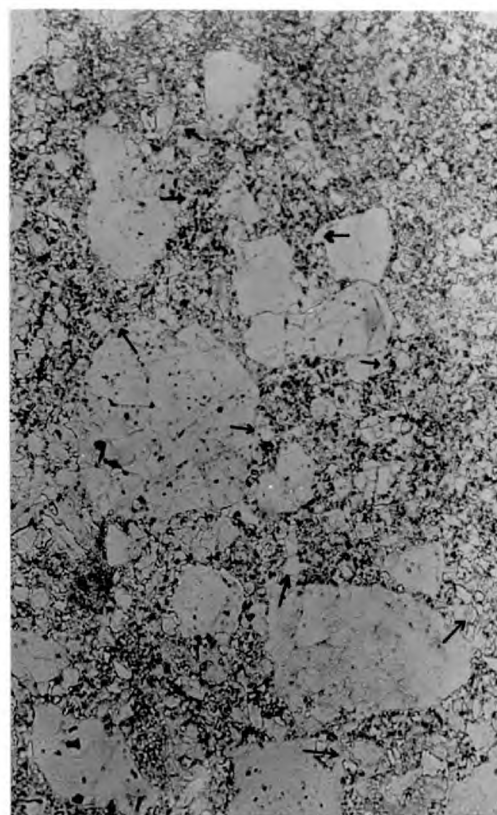
Bi-modal, massive-homogeneous fabrics are distinctly concentrated in the intermediate and lower grain size range. Their general homogeneity is apparent from the examples illustrated in Plates 4.13 and 4.14. There are certainly instances in which this type of uniformity persists over the complete area of a polished section.

Typical bi-modal aggregates are represented by relatively heterogeneous assemblages of grains in which there is no regular structure. When large areas are considered, the overall fabric is distinctly uniform (Plate 4.13), but over smaller areas the grain size differentiation becomes important and the details of the fabric are much more heterogeneous (Plates 4.15, 4.16). The coarse grained component tends to occur as single, isolated grains, or as small groups of grains which are frequently centred at interstitial sites. The finer grained component can be regarded as an interstitial, though discontinuous matrix. When the difference between the maximum and minimum grain sizes is large, the smaller



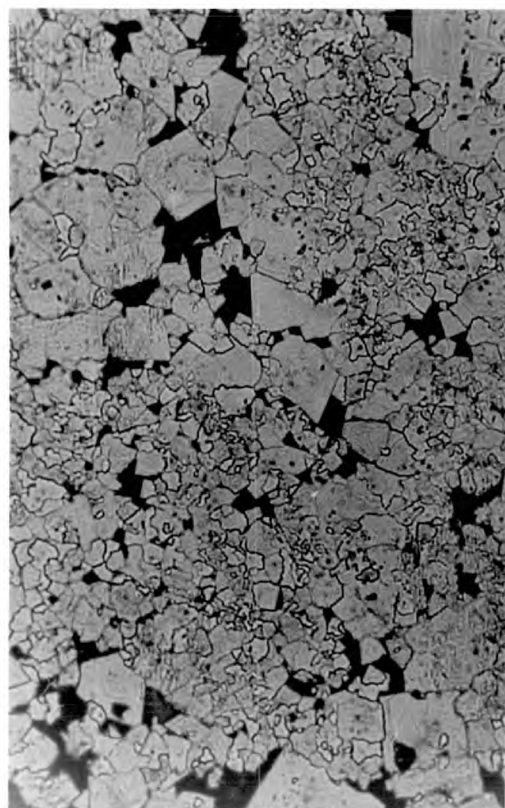
4.17

100 μ



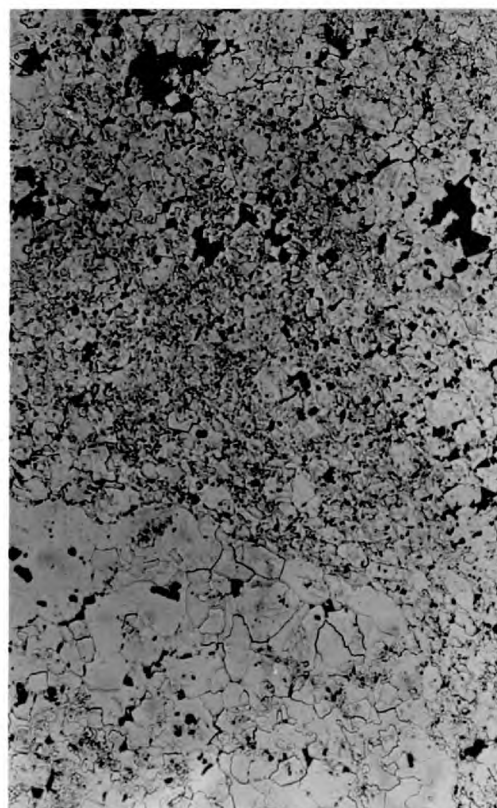
4.18

100 μ



4.19

100 μ



4.20

100 μ

Massive-Composite Fabrics

Plate 4.17 Aggregate showing the typically irregular shape of coarse grained clusters and their tendency to be surrounded by a continuous fine grained matrix. The boundary between the two grain size components is mainly determined by the microstructure of the coarse grained clusters.

Plate 4.18 Singly occurring and small clusters of coarse grains isolated in a continuous fine grained matrix. Arrows indicate projections extending from the coarse grains into the surrounding matrix.

Plate 4.19 Part of an aggregate in which the boundaries between the coarse grained and the matrix components are gradational.

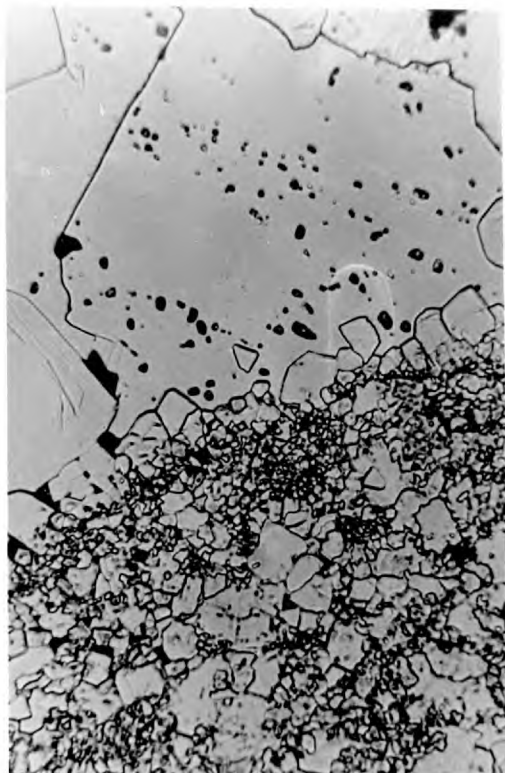
Plate 4.20 Part of a massive-composite fabric in which the boundaries of the coarse grained clusters tend to be smoothly curved and independent of the microstructure of both grain size components.

grains tend to be concentrated in discrete areas which are sharply distinguished from the coarse grained clusters (Plates 4.13, 4.14, 4.15). With decreasing disparity between the maximum and minimum grain sizes, the fabric becomes increasingly uniform even in small areas, and the smaller grains tend to be disseminated rather than concentrated in isolated groups (Plate 4.16).

4.1.3 Massive-Composite Fabrics

The principal feature of the massive-composite fabrics is the presence of two major grain size components. Grains belonging to each of the size ranges are grouped together and occupy separate areas which are more or less sharply defined. The overall fabric appears as clusters of grains belonging to one of the size ranges, surrounded by a matrix of grains belonging to the second size range (Plates 4.17 to 4.24). The gross structural appearance of the fabric reflects a simple bi-modal grain size distribution for the aggregate as a whole, and although this property is sometimes complicated by a tendency for the grain size variation to be continuous (Plate 4.19), the two structurally isolated grain size groups can be distinguished, and will be referred to by the terms fine, or matrix component, and coarse component.

The coarse grained component usually occupies a smaller volume than the fine grained component, and under these circumstances the coarse grained clusters are essentially isolated and surrounded by a continuous fine grained matrix (Plates 4.17, 4.18). However, even where the coarse grained component is predominant, the fine grains tend to be distributed over volumes which are essentially continuous, and are rarely confined to isolated clusters. The continuity of the fine grained matrix is best developed where there is a large grain size difference between the fine and coarse components (Plates 4.17,



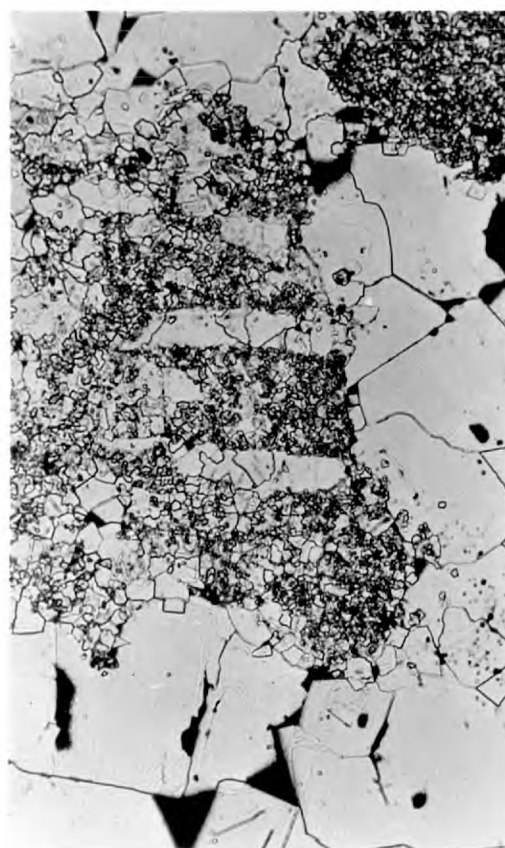
4.21

50μ



4.22

25μ



4.23

100μ



4.24

100μ

Massive-Composite Fabrics

Plate 4.21 Detailed microstructure of a smoothly curved boundary between a coarse grained cluster and a matrix component. Most of the matrix grains immediately adjacent to the coarse component display euhedral terminations. Internal zone structures are developed in some of the marginal grains, and indicate a preferred growth direction towards the coarse grained cluster.

Plate 4.22 A coarse grained cluster showing an approximately tabular shape. The growth zone structures are truncated along plane surfaces (trending vertically on the left and right of the cluster), on which overgrowths are superimposed. The tabular shape of the cluster is due to the parallelism between the two truncation surfaces.

Plates 4.23 and 4.24 Two examples of massive-composite fabrics in which the coarse grained clusters show angular shapes, and have boundary morphologies which are largely independent of the microstructure of both grain size components.

4.18). Although the matrix becomes less continuous as the grain size difference decreases (Plate 4.19), the tendency towards an extensive rather than a localised distribution of the fine grained component remains marked and is a characteristic feature.

The size of the coarse grained clusters is extremely variable, and it is difficult to specify their dimensions for the whole range of fabrics. Clusters comprising in the order of tens of grains are probably the most common. An upper limit cannot properly be defined; when the clusters contain in the order of thousands of grains, the structures they define are virtually macroscopic. The minimum size for the clusters is single grains, though this is rare, and the smaller groups generally contain at least two or three grains (Plate 4.18).

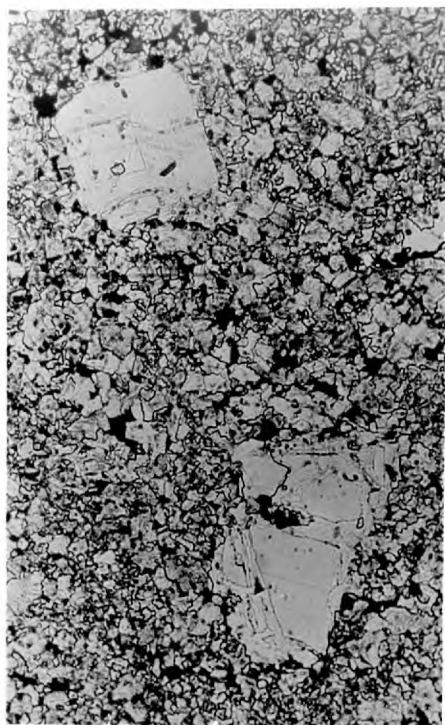
The shape of the coarse grained clusters is variable, and to some extent can be correlated with the nature of the transition zone between the coarse and the matrix components. There are local occurrences in which the transition zone is distinctly gradational (Plate 4.19), and in these instances the shape of the coarse grained clusters is irregular and difficult to characterise.

It is much more common for the coarse grained and the matrix components to be sharply distinguished by a sudden grain size change. Under these circumstances the coarse grained areas define a variety of structures, but again irregularly shaped clusters are by far the most common (Plates 4.17, 4.18). However, a number of special shapes are also characteristic of the coarse grained areas. For example, the boundaries of the clusters are frequently defined by surfaces which are remarkably regular and which may be either curved or planar (Plates 4.20 to 4.24). Such boundaries commonly extend over distances amounting to tens of grain diameters, and in many instances they enclose the entire perimeter of a cluster (Plates 4.23,

4.24). The resulting shape of the coarse grained aggregate may be angular or smoothly rounded. Elsewhere regular boundaries frequently comprise a part of the total perimeter, and produce local terminations which are either plane or smoothly curved (Plates 4.20, 4.21, 4.22).

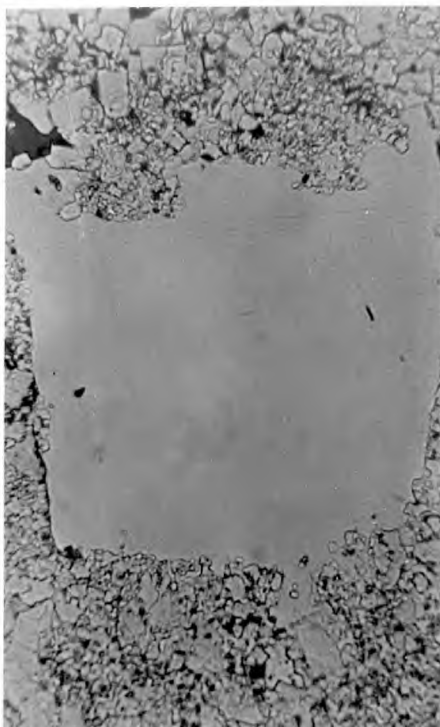
Where the transition between the coarse grained and the matrix components is sharply defined, the actual border zone is characterised by one of four types of microstructure:

- (i) In most massive-composite fabrics the margins of the coarse grained clusters are predominantly defined by the terminal boundaries of the coarse grains themselves (Plates 4.17, 4.18). The terminations are not euhedral and the overall boundary morphology is generally irregular (Plate 4.17). In some fabrics, although the gross shape of the coarse grained clusters is fairly regular and equant, the detailed morphology of their boundaries is defined by embayments and projections which transgress the microstructure of the matrix component (see the arrowed areas in Plate 4.18).
- (ii) Many coarse grained clusters which exhibit angular or smoothly rounded shapes are defined by boundaries which are virtually independent of the microstructure of both the coarse grained and the matrix components (Plates 4.20, 4.23, 4.24).
- (iii) Boundaries of the type shown in Plate 4.21 are mainly defined by the terminations of the matrix grains. In the zone occupied by the first one or two matrix grains at the border, the microstructure is essentially identical to that in one of ~~grains at~~ the symmetrical halves of the fine grained bands which characterise the planar network structure (sect. 4.1.1 (1)).
- (iv) Either the entirety or local parts of the marginal region of some coarse grained clusters is characterised by the microstructure shown in Plate 4.22. Here



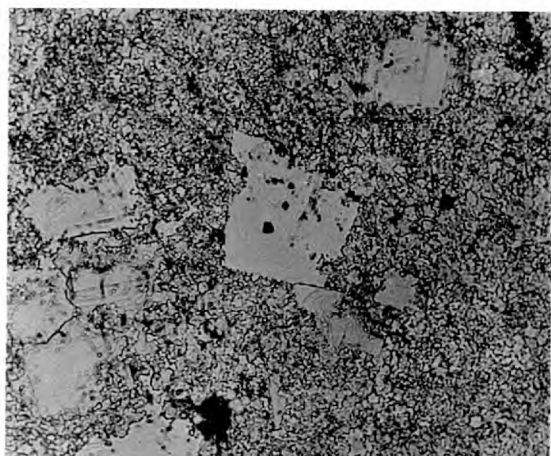
4.25

100 μ



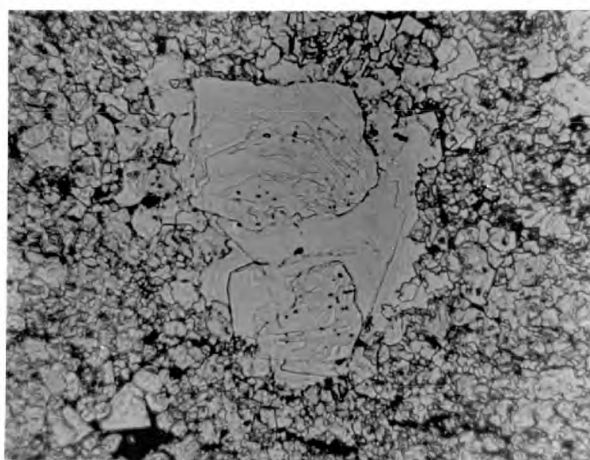
4.26

50 μ



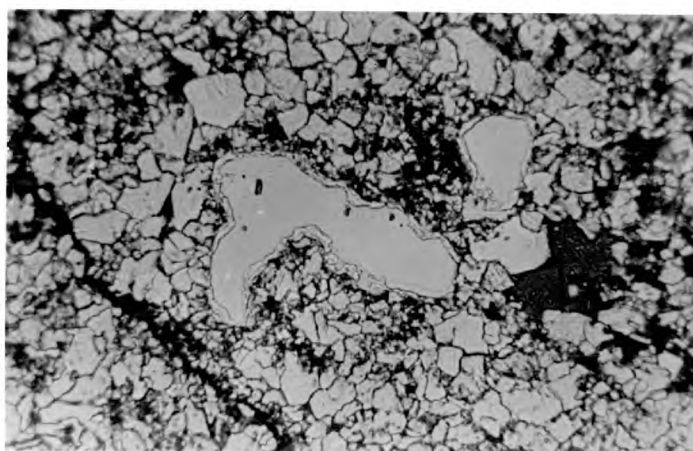
4.27

100 μ



4.28

50 μ



4.29

50 μ

Plates 4.25 to 4.29 Abnormally large grains surrounded by comparatively uniform, massive fabrics, and showing the range of typical shape developments.

The grain in the upper left of Plate 4.25 exhibits a high degree of euhedralism.

Plates 4.26 and 4.27 illustrate relict euhedral forms modified by marked embayments and protrusions.

In Plates 4.28 and 4.29 the grain shapes are distinctly anhedral.

Truncation of the internal growth zone structures can be observed in Plates 4.27, 4.28, 4.29 and in the grain in the lower right of Plate 4.25.

the marginal or near-marginal grains exhibit a preferred growth direction normal to the border and towards the centre of the cluster. Their internal growth zones are truncated along a remarkably planar surface which often persists with constant orientation over several grain diameters. This surface may also be marked by an abnormal inclusion density, and its orientation is often interrupted by local offsets or angular or irregular projections. The surface of truncation itself may represent the actual margin of the coarse grained component, or as in Plate 4.28, a narrow zone of overgrowth may separate the truncation interface from the matrix.

4.1.4 Structure of Single Grains in the Massive Fabrics

Three factors determine the microscopic structure of single grains, namely grain shape, grain boundary morphology, and internal structure.

4.1.4 (1) Grain Shape

The euhedralism of grains can be inferred from their gross angularity. In etched aggregates, this inference is thoroughly confirmed by the conformable orientation of internal growth zones. Complete euhedral grains are an extremely minor component of all types of fabrics. Euhedral terminations are characteristic of the border of interstitial regions (sect. 4.6).

The abnormally large grains referred to on page 57, which are frequently disseminated through the massive fabrics, exhibit a variety of shapes, some of which are characterised by rather special features and are usually less well, or less commonly, developed in the surrounding aggregate. In some instances, the abnormally large grains are substantially euhedral (see the grain in the upper left of Plate 4.25).

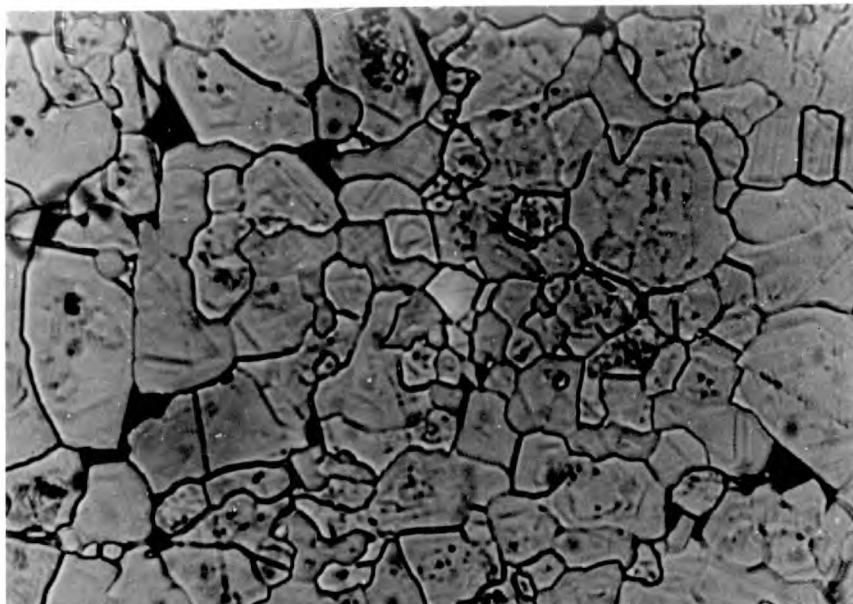
However, there is usually a marked tendency for either the whole or a part of the perimeter to degenerate by the development of protrusions or embayments. These features may be imposed on a gross euhedral form (Plates 4.26, 4.27), or they may determine the entire grain shape (Plates 4.28, 4.29). The embayments transect internal growth zones (Plates 4.27, 4.28, 4.29), and a second set of zones, conformable with the embayed surface, may occur at the grain margin (Plate 4.29). The morphological features of the subhedral and anhedral grains strongly suggests that their shape was derived by surface leaching. If this is so, then the fact that the matrix grains occupy the leached embayments must mean that both the growth and the surface dissolution of the large grains predates the deposition of the surrounding aggregate.

There are a few instances where simple elongate grains occur in the fine grain size components of massive-homogeneous and massive-composite fabrics. These grains are found only singly or in groups of up to a maximum of about five, and are essentially isolated by a matrix of equant grains. The elongate grains are characterised by having a preferred dimensional orientation.

In compact aggregates the predominant grain shapes can best be described by reference to four end-member types. The idealised classification, shown in fig. 4.1, utilises a division based on the gross dimensional ratio, and on the degree of regularity. The terms equant and inequant in fig. 4.1 are self-explanatory; the terms regular and irregular denote the relative complexity of grain shape, and are defined in terms of the number of discrete segments comprising a grain boundary. Considering a discrete segment as each part of the grain

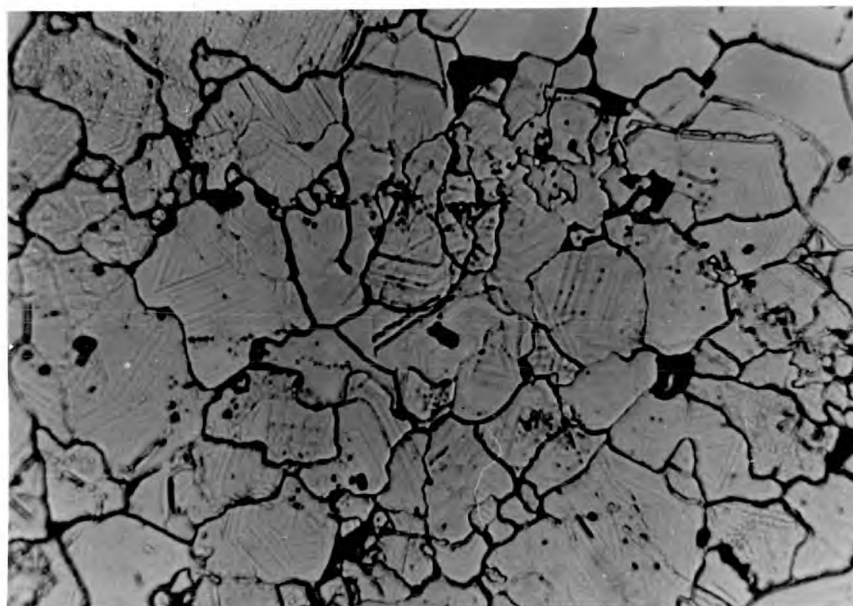
4.30

10 μ



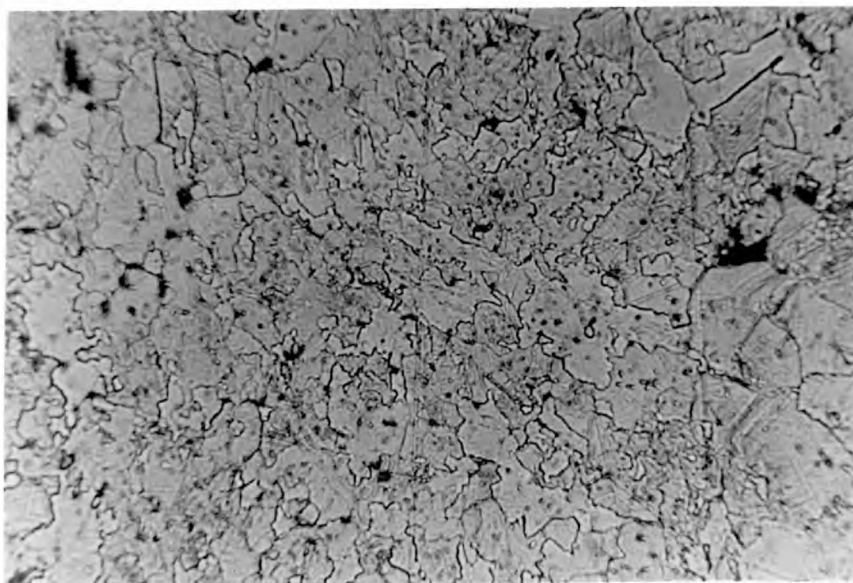
4.31

25 μ



4.32

50 μ



Plates 4.30, 4.31 and 4.32 Three aggregates showing the range of grain shapes developed in the massive fabrics.

Advanced stages in the development of equant-regular and inequant-irregular grain shapes are shown in Plates 4.30 and 4.32, respectively.

The most common grain shapes in the massive fabrics are intermediate between the end-member types, and are illustrated in Plate 4.31.

boundary which is distinguished by a fairly constant orientation, then the trend from regular to irregular shapes corresponds to an increasing number of segments. The complexity aspect of shape is of course intimately connected with the detailed grain boundary morphology, a property which is considered separately (sect. 4.1.4 (2)). Shape complexity is distinguished as a separate property when the grain boundary morphology is manifested at a scale such that it controls the gross shape of the grain.

The development of equant-regular shapes reaches an extreme in aggregates such as that illustrated in Plate 4.30. These occurrences are fairly common, but the trend towards irregularity is usually more manifest. In massive fabrics the most common grain shapes are of the type illustrated in Plate 4.31, and in the equant grain group it is unusual for the shape complexity to become very much greater than that shown in the latter illustration. In general there is a tendency for equant grains to exhibit regular shapes. This trend becomes increasingly marked as the grain size decreases from the intermediate range, and near the lower limit of the grain size the shape of the grains can nearly always be described as equant-regular. At intermediate and larger grain sizes, the effects due to the detailed grain boundary morphology are very often inseparable from the gross shape characteristics. Towards the upper limit of grain size range, the details of boundary morphology become subordinate in comparison to the gross shape, and the latter can usually be readily classified. Coarse grains in general tend to be equant-regular.

In fact, complications due to boundary morphology are even greater than implied above. Although there are distinctive, fine-scale types of boundary

structure (see (2) below), there are also structures of a similar type developed on a larger scale. If all these structures are considered independently of grain size, there is no sharp sub-division based on their scale of development.

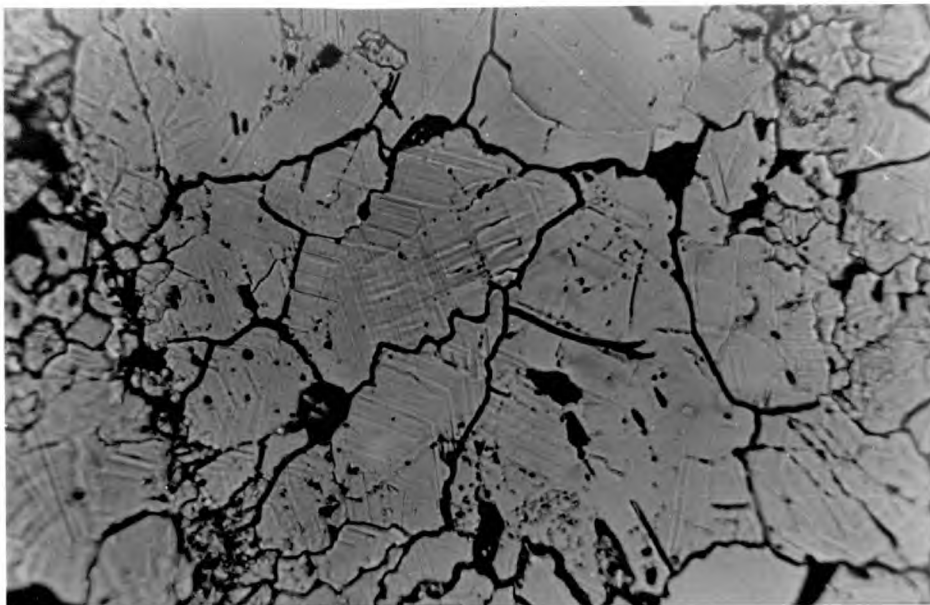
Despite the difficulties just mentioned, the recognition of an irregular grain group is both necessary and convenient. Once again, the grain shapes within this group are not uniformly distributed, and there is a distinct tendency for irregular grains to be inequant. A typical example of an advanced development of this trend is shown in Plate 4.32. These grains appear most commonly in the intermediate grain size range. Numerous planar segments compose the grain boundaries, and the arrangement of these grains frequently produces a vaguely recticular pattern in the bulk aggregate. Grains of this type comprise the close-packed spherical structures described in sect. 4.1.1 (3). They also occupy small, non-structured aggregates in other types of massive fabrics, but the shape development shown in Plate 4.32 does not persist over areas containing more than a few tens of grains.

The occurrence of markedly inequant, regular grains is insignificant. Shapes falling in this category are the elongate grains which occur in some of the massive-discrete fabrics.

In summary, it is worthwhile to point out that the grain shapes in the massive fabrics exhibit a fairly definite bias to be grouped in one of two categories, namely, equant-regular and inequant-irregular. This grouping accords with the three principal observations, namely: (1) inequant-regular shapes are rare, (2) equant grains tend to be fairly regular, and (3) distinctly irregular grains tend to be inequant.

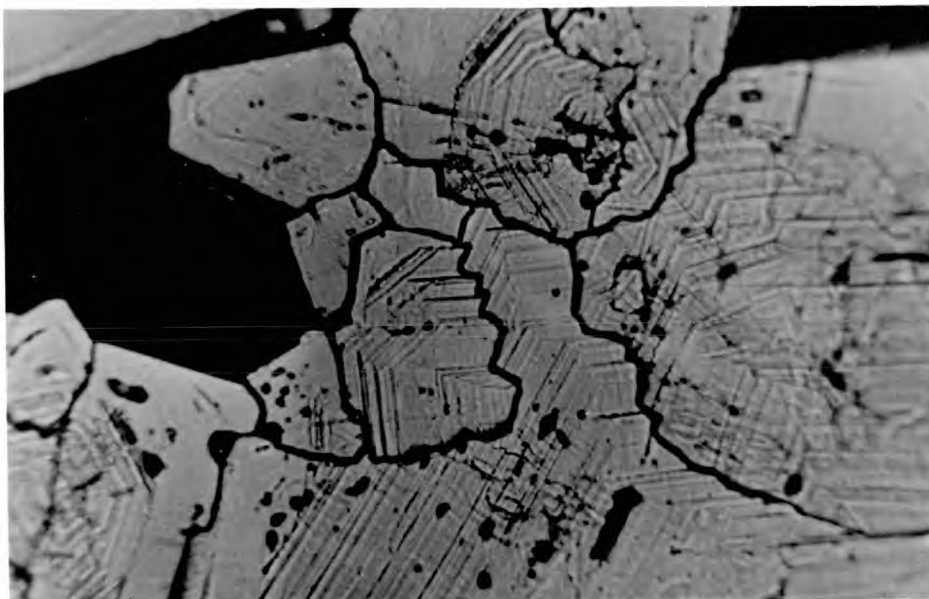
4.33

25 μ



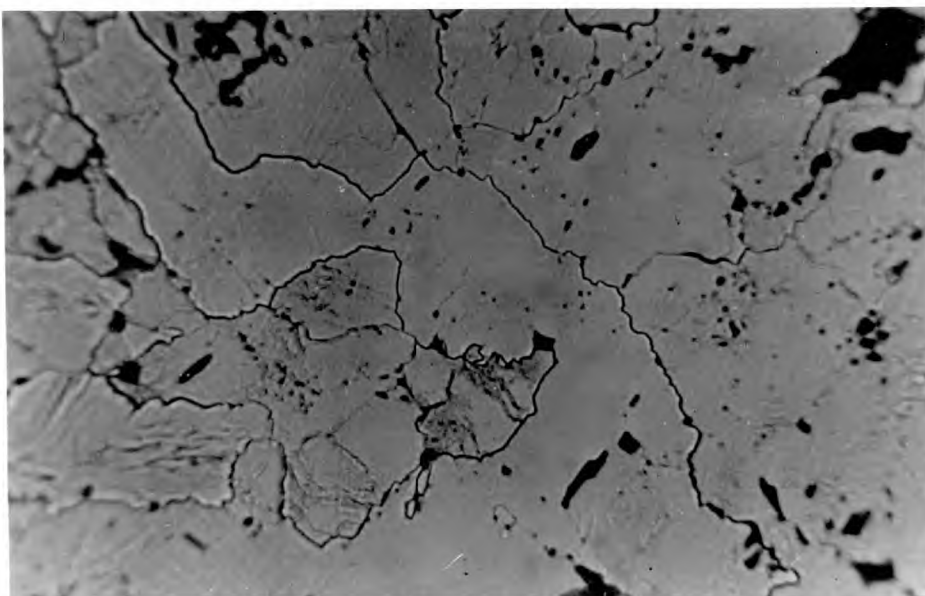
4.34

25 μ



4.35

25 μ



Plates 4.33 and 4.34 In both illustrations the boundaries of the central grains exhibit coarse-scale irregularities, but these features do not determine the gross shapes of the grains. Note that in both cases there is a marked correlation between grain boundary irregularities and the succession of euhedral zones.

Plate 4.35 Serrate grain boundaries. The morphological irregularities are developed at a much smaller scale than those illustrated in Plates 4.33 and 4.34. Apart from a few euhedral zones, the internal structure of the grains is almost homogeneous.

The bulk shape of a grain (i.e., whether equant or inequant) is determined by the overall growth anisotropy. If all growth surfaces have similar growth rates the resulting grains are equant. Inequant grains can develop when some surfaces have significantly higher growth rates than others; they may also develop when the accretion of material is confined to certain surfaces because of the structure of the growing aggregate or of the host matrix. The latter factors presumably control the development of inequant grain shapes in radially structured spherical aggregates, and in groups of grains growing simultaneously from a common surface of nucleation (see also the foliate fabrics; sects. 4.2 and 8.3.2 (3)). In view of the isometric symmetry of pyrite, the widespread occurrence of equant grains is only to be expected.

4.1.4 (2) Grain Boundary Morphology

Grain boundary morphology is defined as the relatively fine-scale surface structure which is independent of the gross features of grain shape. Three main types are recognised.

- (i) The simplest boundaries are either strictly planar or smoothly curved (Plate 4.30). Plane boundaries are largely restricted to subhedral and euhedral terminations. Smoothly curved boundaries are characteristic of the fine grain size range, but become rapidly less important as the grain size increases.
- (ii) A second type of boundary morphology is characterised by the presence of sporadic and rather blunt or gently curved irregularities (Plates 4.33, 4.34). The latter can frequently be distinguished as non-shape determining features

but as already pointed out, there are also many instances where this distinction is virtually impossible.

- (iii) In addition to becoming increasingly gross features, boundary irregularities may also follow a second trend. This involves an increase in their density (i.e. decreased spacing), and a tendency to develop sharper or even angular shapes. The resulting boundary morphology can be described as serrate (Plate 4.35). Typical serrate grain boundaries are not widespread, and their distribution is sporadic even in small aggregates containing a few tens of grains.

The total external morphology of a grain, as given by its gross shape and its grain boundary morphology, can be developed under one of two conditions. If the growth of a grain ceases before the aggregate becomes fully dense, then the shape of the grain is independently determined and partly controls the shape of the contiguous grains. This condition is at least applicable to euhedral grains.

In aggregates with a fairly uniform grain size it is probably reasonable to assume that all grains were nucleated simultaneously and grew under similar conditions. Neighbouring grains accrete material contemporaneously and finally impinge, first at a point and then over an increasing surface area. This surface is the grain boundary and is determined by the competitive growth of adjacent grains, and not independently by each grain.

The relationship between a competitively derived grain boundary and the actual growth surface is important. The compositionally distinct zonation of

single grains indicates that the predominant growth surface consists of a number of plane grain faces corresponding to low-index lattice orientations (see the following sub-section). The existence of plane growth surfaces is not inconsistent with the development of the curved and other complex forms of grain shape and grain boundary morphology described above. Because of their compositional distinctiveness, which is effectively correlable with a time scale, internal growth zones indicate that the mode of accretion to the crystal was through a layer growth mechanism. This involves accumulation of atomic or multi-atomic layers which themselves grow by lateral spreading from one or more points of nucleation (Bunn and Emmett, 1949, p. 119; Buckley, 1951, p. 206). The more rapidly the layers spread, the more rapidly the crystal grows at right angles to the growth face.

Rapidly spreading growth layers in one grain will reach the grain boundary ahead of layers spreading less rapidly in an adjacent grain. This means that the grain boundary will be displaced towards the slower growing grain. If the growth rates are reversed, the grain boundary migrates in the opposite direction for the period of time that this rate is sustained. Hence the grain boundary configuration depends entirely on the relative growth rates, at different times, of adjacent grains. When the growth rates remain fairly constant, the grain boundary will be correspondingly regular. When the growth rate of one grain changes, or both growth rates change differently, the grain boundary will tend to become irregular.

Especially in uniform grain size aggregates, where the assumption of contemporaneous growth is most valid, the coexistence of non-plane grain

boundaries and euhedral zone structures must be attributed to some kind of changing growth rate mechanism. Restricted changes due to highly localised effects (e.g. inclusion inhibition, and accessibility of the ore solution to different growth planes) may frequently be operative. However, in the natural environment, there are probably two main factors which are important in producing frequent and perhaps even constant changes of growth rate.

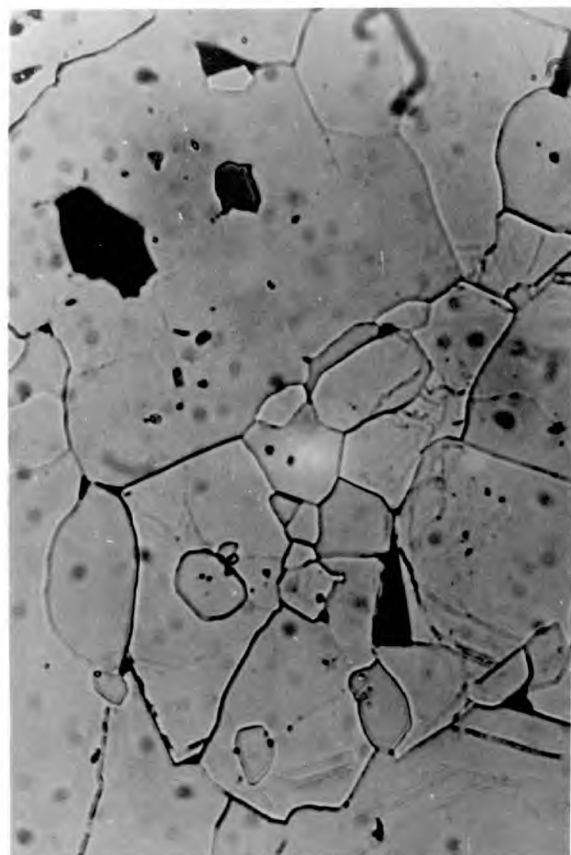
The effects of changes in the supersaturation level of the depositing solution are well known (Buckley, 1951, p. 138). Compositional variations of the accreting material are also likely to be important since they could have a major effect on the bonding and therefore the stability of the surface layer (compare for example the marked inhibition of growth, and habit modifications, induced by the addition of impurities to crystallising solutions, Buckley, 1949, p. 243; Cabrera and Vermilyea, 1958, p. 400). Since the growth rate of different lattice planes is variable (Bunn, 1949, p. 134), compositional changes will almost certainly produce different growth rate changes for different growth planes. From experimental observations it is known that changes in the supersaturation level lead to different changes in the growth rates of different lattice planes (Buckley, 1951, p. 138). For randomly oriented nucleation, adjacent grains will frequently impinge so that crystallographically different growth planes come in contact. Alternatively, different growth planes may impinge at a later stage of growth. Thus compositional and supersaturation changes would produce differential changes in the growth rates of the impinging grain surfaces.

The presence of intragranular growth zones

demonstrates that compositional variations actually occurred during the growth event (see the following sub-section), but there appear to be few examples where the boundary morphology is distinctly related to individual zones. Two such examples are illustrated in Plates 4.33 and 4.34. The central grain in each of these illustrations contains euhedral zone structures whose optical manifestation indicates that there were several short or more extended periods of growth characterised by a particular and fairly constant composition of the accreting material. Several of these growth stages show a marked correlation with irregularities in the boundary against one of the neighbouring grains.

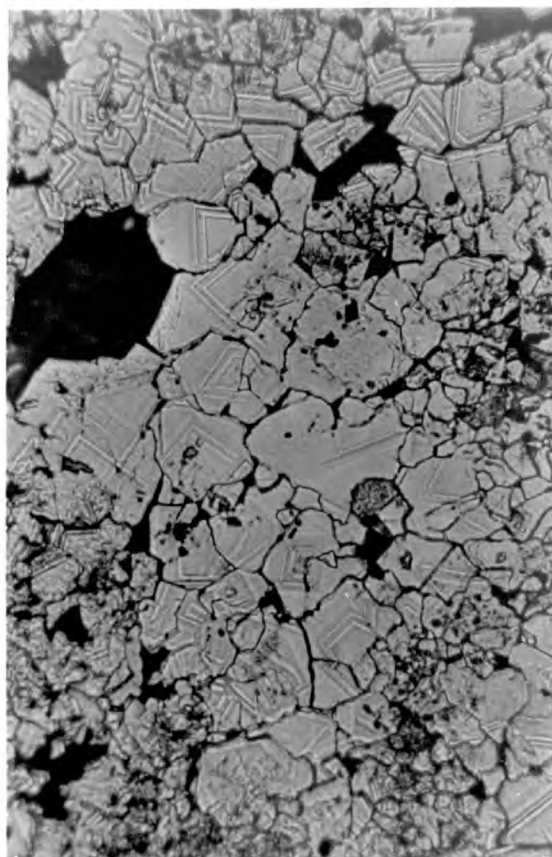
It is also noteworthy that the general frequency with which compositional variations (i.e. zoning) are developed shows a broad relationship to the associated grain boundary morphology. That is, grains in which growth zones are poorly developed or absent frequently have much more regular boundaries than those in which the zone frequency is high (compare for example Plates 4.36, 4.37 with Plates 4.38, 4.39).

However, the infrequent occurrence of well defined correlations between the boundary morphology and individual zones suggests that changes in the supersaturation of the ore solutions have a major effect in causing growth rate variations. If the supersaturation changes were gradual, they would not, alone, produce sharp boundary irregularities. However, superimposed on effective compositional changes, which are manifestly discontinuous, they would tend to blur the sharp irregularities due to the latter. Various combinations of the relative effectiveness of these two factors can probably account for most



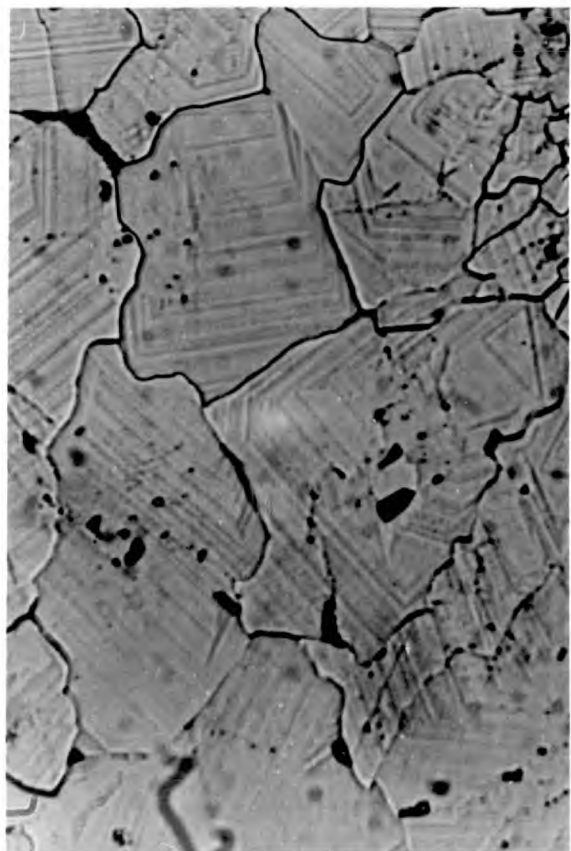
4.36

25 μ



4.37

50 μ



4.38

10 μ



4.39

25 μ

Plate 4.36 Aggregate containing several unzoned grains which show smooth grain boundary morphologies.

Plate 4.37 Open, euhedral zone structures. The incidence of discrete zones in each grain is fairly representative of most examples of the massive fabrics. Note that the zone pattern in each grain is essentially the same, and that there are many grain boundaries where equivalent zones are continuous from one grain to the next.

Plate 4.38 Open, euhedral zone structures reflecting a high frequency and marked uniformity of the compositional variations. Note the irregularity of the grain boundary morphology, in contrast to that shown in Plate 4.36.

Plate 4.39 Closed euhedral zone structures reflecting a high frequency of the compositional changes. Note the irregularity of the grain boundary morphology, in comparison to that shown in Plate 4.36

of the grain boundary morphologies observed.

4.1.4 (3) Internal Grain Structure

Three features characterise the internal structure of pyrite grains, namely, compositional zoning, inclusion concentration, and in some instances, a radial substructure.

A Zone Structures

In etched aggregates a striking property of all fabrics is the high incidence of intragranular zone structures. In the massive fabrics, these features are not manifest in every grain (Plate 4.36), but their distribution is such that in one form or another they are rarely absent from more than two or three contiguous grains. The real incidence of zoned grains is probably higher than estimated from sectional observations, since an apparent absence of zoning may be a spurious effect due to (i) a special position of the zone structure in relation to the plane of observation, or (ii) a low etching rate for the particular grain surface exposed.

Zone structures are sometimes evident after careful polishing, but are most clearly defined by the sharp relief and reflectivity differences produced on etching (see for example Plates 4.37 to 4.39). When polished surfaces are heavily etched at a high rate, regularly shaped etch pits are developed. Within the limits of a single grain, these artefacts have a constant orientation which is independent of the zonal structure. Since it is reasonable to assume that the etch pit shape is determined by the lattice structure, the constant orientation of the artefacts must mean that individual zones have the same crystallographic orientation. Thus the physical distinction between different zones is apparently related to

compositional variations. This conclusion has not been directly confirmed, but scanning of single grains on a microprobe analyser indicates that there are significant compositional changes. Variable trace amounts of copper were indicated by the scanning analysis.

In describing the structure of zoned grains, it is convenient to use the following system of terminology, diagrammatically illustrated in fig. 4.2. The bulk assemblage of zones within the limits of a single grain is referred to as a zone structure. When the latter is asymmetrical, three regions are distinguished, namely, the apical, basal and lateral regions. The whole of a compositionally distinct volume is referred to as a zone or discrete zone, whose margin is the zone boundary. Two main types of zone boundary are distinguished: (1) irregular or anhedral boundaries, which define anhedral zones, and (2) plane, or euhedral boundaries, which define euhedral zones. The structure of euhedral zones can be summarised as follows. A zone sector is each area in which the zone boundaries have a constant or preferred orientation. Each zone in the area is referred to as a zone segment. The major boundaries of euhedral zones are termed euhedral boundaries, and the short boundary that results when a single zone does not extend to the grain boundary is referred to as a terminal boundary. An assemblage of terminal boundaries constitutes a truncation surface. Closed zones occur where a single zone boundary closes on itself. Open zones occur where the zone boundary intersects the grain boundary, and truncated zones, where the zone boundary does not intersect the grain boundary. The region between the grain boundary and a truncation surface usually has an irregular form,



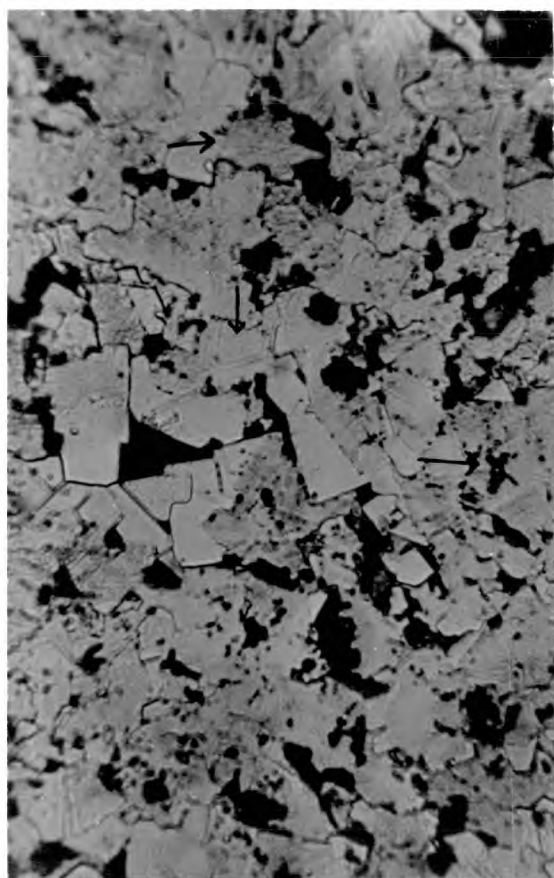
4.40

50 μ



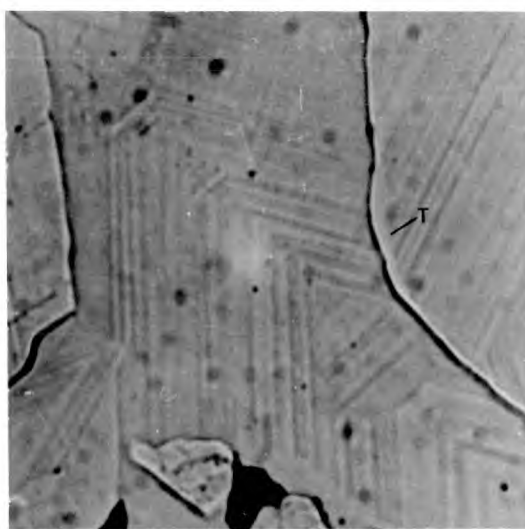
4.41

25 μ



4.42

25 μ

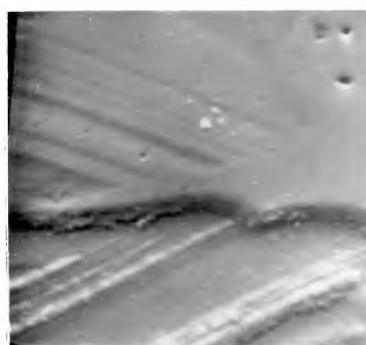


4.43

5 μ

4.44

1 μ



Plates 4.40, 4.41 and 4.42 Modifying features associated with euhedral growth zone structures.

Plate 4.40 Bulbous zones which exhibit a colloform appearance are superimposed on euhedral zone structures.

Plate 4.41 Gross euhedral structures formed by groups of interconnected, undulose zones. The central grain also contains several euhedral zones proper. Note that the inclusion concentrations occur in several discrete zones.

Plate 4.42 Euhedral to subhedral zone structures characterised by a central zone which exhibits a distinctly brownish colour and a rough surface texture. Arrows indicate grains in which the central region contains a separate assemblage of euhedral zones.

Plate 4.43 Truncation of euhedral zones reflecting changes of growth habit. The same zone orientations are truncated at several different levels in the zone sequence, and the habit changes were cyclic. Note that both extremities of the truncation surface marked T intersect the same grain boundary.

Plate 4.44 Electron micrograph illustrating the terminal boundaries of discrete euhedral zones, and the overall planarity of the truncation surface. (The grain boundary is the dark escarpment trending horizontally). Note also the sharp definition of the euhedral zone boundaries.

and is referred to as an anhedral zone, or anhedral region.

By far the most common zone structures are those composed entirely or almost entirely of euhedral zones (Plates 4.37, 4.38, 4.39). The zone boundaries are nearly always strictly planar, though local irregularities are often developed in the form of minor indentations and interconnecting zones. Where the grain boundary is euhedral (e.g. at interstices), euhedral zones are usually conformable or symmetrically oriented with respect to the grain boundary (see for example some of the interstices in Plate 4.37). In many instances, euhedral zones occupy the entire grain and occur with a high frequency and/or regular spacing (Plates 4.38, 4.39). More commonly their distribution tends to be sporadic, and the width of the zones variable (Plate 4.37). The number of zones decreases with decreasing grain size, and in the smallest grains the number of zones is frequently reduced to one or two.

There are ^{few} examples in which euhedral zone boundaries degenerate to typical anhedral boundaries. However, there are two distinctive modifications of strictly euhedral zone structures:

- (i) Zones with a marked colloform appearance are produced where bulbous irregularities are superimposed on a grossly euhedral structure (Plate 4.40). Zonal structures of this type coexist with the euhedral zones proper, but occur only rarely and are always confined to the marginal region of the largest grains.
- (ii) The most frequent modifications of euhedral zones is illustrated in Plate 4.41. These structures are difficult to characterise, but essentially they consist of a number of undulose, semi-

continuous sub-boundaries which tend to be interconnected and grouped together in the form of an overall euhedral structure. Coexisting and strictly euhedral zones are conformable with the sub-boundary assembly.

There is one other type of euhedral to subhedral zone structure which is fairly common and merits separate consideration. Grains in which this structure occurs (Plate 4.42) are composed of two main parts separated by a sharply defined boundary whose shape may be either euhedral or partly subhedral. Where the central zone is euhedral, its overall shape is often markedly tabular or lath-like. The central zone usually occupies more than half the grain and exhibits a distinctly brownish colour and a rough surface texture. Both components of the grain may be internally homogeneous, but the interior region frequently contains a separate assemblage of euhedral zones (see the arrowed grains in Plate 4.42).

The simplest euhedral zone structures consist of an assemblage of strictly conformable zones (see Plate 4.37, and many of the grains in Plates 4.38, 4.39). Patterns of this type are modified by the dismissal of some zone orientations, or by the introduction of new orientations at one or more points in the structure (Plate 4.43). New orientations, once introduced, may become predominant or replaced by earlier orientations. These changes may be cyclic and repeated frequently (Plate 4.43), or sporadic.

In the interior of a grain it is relatively uncommon for euhedral zones to be discontinuous. Even then, the discontinuity is frequently only a local feature, and does not extend through the entire succession of zones. Interior discontinuities appear in the form of unzoned and irregular bulbous areas



4.45

25 μ



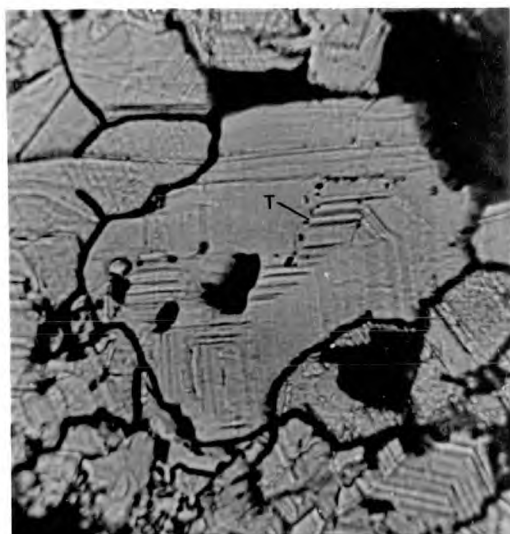
4.46

10 μ



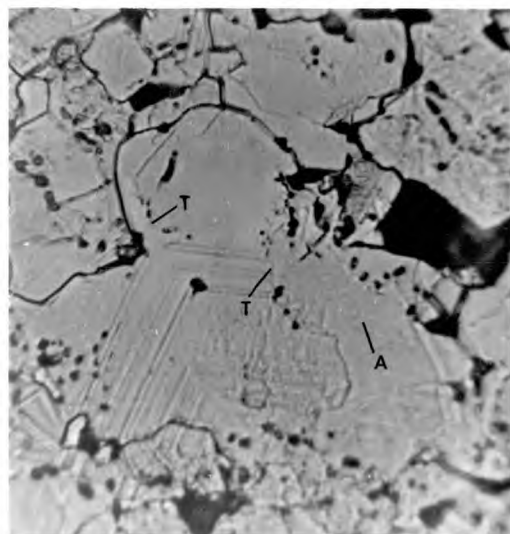
4.47

25 μ



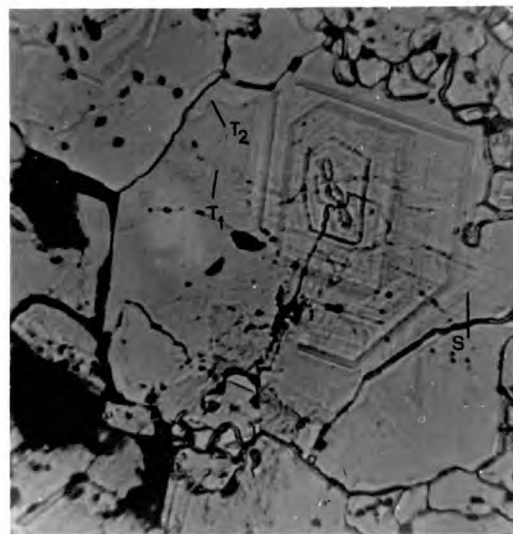
4.48

25 μ



4.49

10 μ



4.50

10 μ

Plates 4.45 to 4.50 Truncated euhedral zone structures.

The truncation surfaces are indicated by the symbol T.

Plate 4.45 The truncation surface is confined to the interior of the grain, and does not transect the entire succession of zones.

Plate 4.46 The main euhedral zone structure appears as a relict in the centre of the grain, and is bordered by two anhedral zones which are the dominant features of the internal grain structure. A few inclusions occur along the truncation surfaces. Indistinct zone patterns occur in the anhedral region at the areas indicated A.

Plate 4.47 Only some of the truncation surfaces are indicated, but in all grains the main euhedral zone structures are disconnected from the grain boundaries over a large part of their perimeter. In several grains the euhedral zone structures are almost completely isolated from the grain boundaries. Note the plane segments of the truncation surfaces in the areas indicated T_1 .

Plate 4.48 The truncation surface is also delineated by an array of inclusions, and is itself terminated by a sequence of parallel sided zones which are conformable with part of the main euhedral zone structure.

Plate 4.49 A few inclusions are concentrated at or near both truncation surfaces. An irregular zonal structure in the anhedral region is indicated by the symbol A.

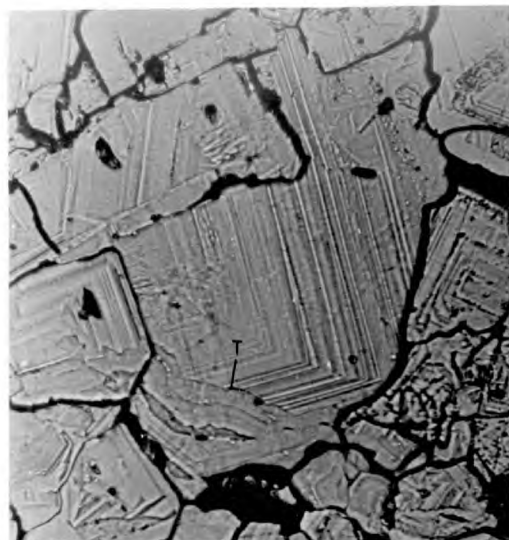
Plate 4.50 The truncation surface marked T_1 is much less distinct than that marked T_2 . A few inclusions are concentrated along the surface marked T_1 . A radial substructure occurs in the area indicated S.

which transect an otherwise integral zone pattern (Plate 4.45). These structures may be complex in detail, but it is noteworthy that they are not associated with offsets or other modifications to the orientation of the enclosing euhedral zones.

Almost invariably at least some of the zones comprising an open euhedral zone structure extend to and terminate at the grain boundary. In a large number of cases, both extremities of all, or nearly all, the zones belonging to a single assemblage terminate at the grain boundary (Plates 4.37, 4.38). However, there are many instances of intragranular truncation and the resulting internal grain structure may exhibit one or a combination of several different forms.

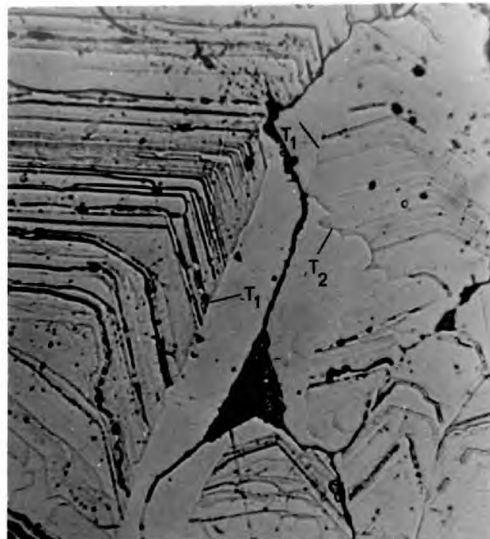
There are some instances where the grain structure is dominated by features associated with the truncation of euhedral zones. For example, in a few single occurring grains and small clusters of grains, the main euhedral zone structures are largely obliterated and appear as insular relicts which are almost completely isolated from the enclosing grain boundary (Plates 4.46, 4.47). From these occurrences, there is a complete gradation (Plates 4.48 to 4.53) to the most common case where the truncation surface occurs close to the grain boundary and isolates a relatively narrow region which extends for only a short distance around the perimeter of the grain (Plates 4.54, 4.55, 4.56).

In grains containing closed euhedral zone structures, the truncation surface may occur at any point around the margin of the grain, and its location appears to show no preferential relationship to the internal zone structure. In grains containing open euhedral zones, truncation is frequently restricted to the lateral regions of the zone structure



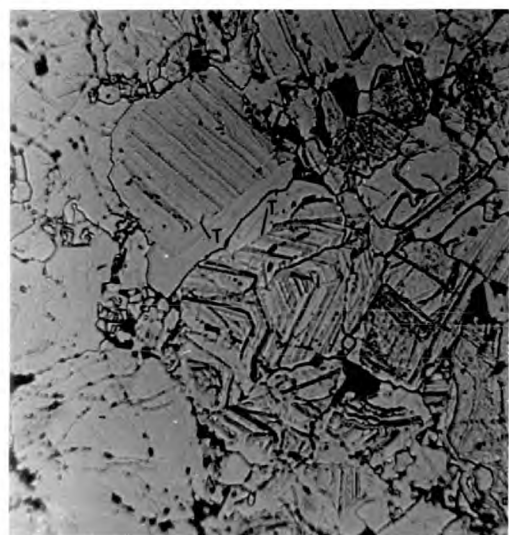
4.51

25 μ



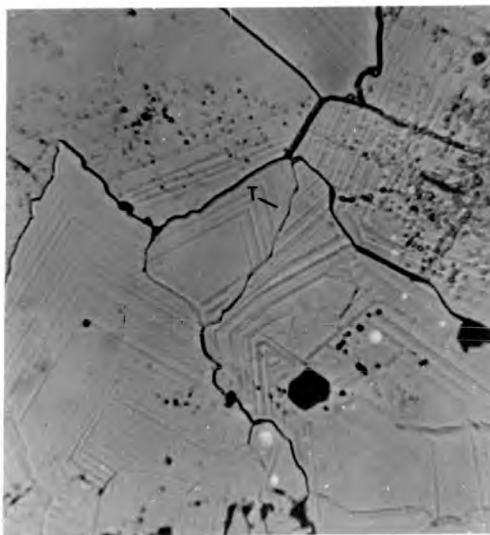
4.52

25 μ



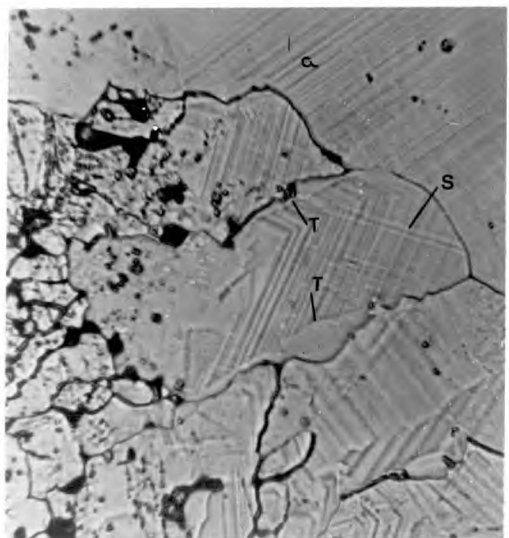
4.53

25 μ



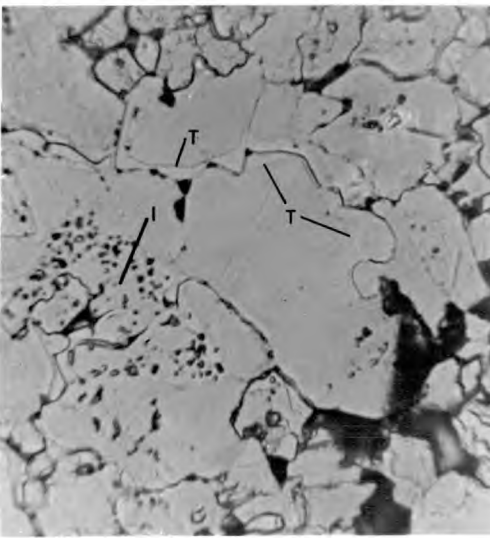
4.54

10 μ



4.55

10 μ



4.56

10 μ

Plates 4.51 to 4.56 Truncated euهدral zone structures. The truncation surfaces are indicated by the symbol T.

Plate 4.51 A sequence of conformable zones is superimposed on the truncation surface. The innermost zones are undulose, corresponding to the shape of the truncation surface, but the outermost zones are euهدral and conformable with the main interior zone structure.

Plate 4.52 The surfaces marked T_1 exhibit an overall planar configuration, but also contain a number of small indentations. The surface marked T_2 is composed of several cusped segments ^{and coexists} with a plane grain boundary.

Plate 4.53 The euهدral zone structures are truncated on both sides of the grain boundary, and broadly conformable zones are superimposed on the truncation surfaces in the anهدral region.

Plate 4.54 The euهدral zone structure in the central grain is truncated along a plane surface which coexists with an irregularly shaped grain boundary.

Plate 4.55 The euهدral zone structure in the central grain is truncated in both of the lateral regions. Local segments of both truncation surfaces are approximately plane, but the overall shape is irregular. A radial substructure occurs in the area indicated S.

Plate 4.56 The main euهدral zone structures are represented by the indistinct, parallel sided zones in the interior of the central grains. These zones are truncated by surfaces which are mainly composed of a number of plane segments. Note that the inclusion concentration indicated I is transected by a grain boundary and exhibits a sharply defined, angular shape.

(Plates 4.52, 4.53, 4.55).

The truncation surface itself is nearly always sharply defined and is sometimes delineated along part of its length by small concentrations of inclusions (Plates 4.46, 4.48, 4.49, 4.50). In a few instances, the truncation surface is indistinct, and at some of the euhedral zones which it intersects the terminal boundaries may be difficult to locate (see the surface indicated T_1 in Plate 4.50).

The morphology of the truncation surface is characteristically irregular or undulose, but there are a few instances where the surface configuration is almost perfectly plane. Irregular truncation surfaces tend to show their maximum development when the euhedral zones are terminated well within the interior of a grain, and are typical of the euhedral zone structures which have been reduced to insular relicts (Plates 4.46, 4.47). Irregular surfaces also occur close to the grain boundary (Plates 4.49, 4.50), but there is a fairly general tendency for the morphological irregularities to become less marked as the truncation surface approaches the grain boundary and becomes less extensive (compare Plates 4.46 and 4.53, and also the surfaces marked T_1 and T_2 in Plate 4.52). Irregular surfaces are characterised by cusped forms, and by blunt or sharp embayments or protrusions; local segments of the surface may be remarkably planar (see the surfaces indicated T_1 in Plate 4.47).

Many truncation surfaces close to the grain boundary exhibit an overall planar configuration. Usually the gross planarity is disrupted by minor indentations or protrusions (see Plates 4.53, 4.55 and the surfaces indicated T_1 in Plate 4.52). In a few instances the plane configuration is maintained over the entire surface (Plate 4.54). Electron

microscope observations on one specimen indicate that the terminal boundaries of the euhedral zones are plane and parallel, and are aligned along an almost perfectly plane surface (Plate 4.44). Thus there is no structural distinction between the plane surfaces which truncate euhedral zone structures near the margin of a grain and those which truncate the same structures in the grain interior, where new zone orientations are superimposed on the truncation surface (Plate 4.43).

There are also a few cases where the interior euhedral zone structure is reduced to the form of a few isolated zones which are truncated by an extensive surface composed of several plane segments. The truncation surface may degenerate by developing local irregularities, but its overall form is basically euhedral (see the surfaces indicated T in Plate 4.56). The comparatively marked euhedralism of surfaces of this type suggests that it is probably more significant to regard the truncation surface as an integral part of the main euhedral zone structure, rather than as a separate entity in itself.

Since most truncation surfaces are either irregular or undulose, the region intervening between the grain boundary and the truncation surface is referred to as anhedral zone, or anhedral region. Apart from occasional inclusion concentrations, this zone is usually homogeneous (see for example Plates 4.47, 4.52, 4.54, 4.55, 4.56). However, the anhedral region sometimes contains a separate zonal pattern. In most grains this pattern is irregular or indistinct (see the areas indicated A in Plates 4.46, 4.49), but there are a few instances where the zonation of the anhedral region is conformable with the truncation surface, and may even be combined with a set of

euهدral zones which are conformable with the main interior zone structure (Plates 4.51, 4.53). In some grains the anهدral zone does not extend completely to the grain boundary, and the truncation surface is itself terminated by a second truncation surface, or by an assemblage of euهدral zones which are conformable with the main interior zone structure (Plate 4.48).

In the description presented above the main object has been to extract the principal relationships between the predominant types of zoning. The most important aspect of the overall zonal assemblage is the distinction between a predominant, interior, euهدral zone structure, and an exterior and essentially discontinuous anهدral zone. In large grains this simple two-fold structure is often modified by local superposition of additional groups of zones. However, as the grain size decreases there is a marked simplification of the zone structure. The simple two-fold structure is most prevalent in grains of intermediate size, but even here there is a large proportion of grains in which the entire zonal structure consists of an integral assemblage of euهدral zones. In the smallest grains the exterior anهدral zone is nearly always completely absent.

Zone structures are a record of the growth history of single grains, and reflect the sequence of compositional changes which occurred during the growth event. Euهدral zone boundaries can be interpreted as representing the free surface of grains at different stages of growth. By analogy with the euهدral shape of single crystals in hydrothermal veins, it is reasonable to assume that euهدral zones have rational crystallographic

orientations which correspond to either cube, pyritohedral or octahedral planes. Because of their conformable or symmetrical relationship, the euhedral surfaces of grains exposed at interstitial sites is equivalent to similar, internal zone boundaries. The succession of euhedral zones indicates that the preferred growth planes are not always the same at different stages of growth. The various combinations of mutually truncating euhedral zones can be interpreted in terms of growth habit changes.

Since the size of a crystal increases with time, the smallest zones will be located closest to the nucleus. This generally means that the bulk growth direction of a grain is determined as the direction in which the zone perimeter increases. However, in the case of open zone structures, the site of the nucleus is unknown and consequently this criterion can lead to an incorrect conclusion. The local growth direction (which is the only direction that can be estimated from sectional observations) corresponds to the direction in which the zone structure shows an overall convexity.

The interpretation of truncation surfaces and anhedral zones is much more difficult. Truncation surfaces associated with conformable or homogeneous overgrowths may represent a progressive change to conditions during the main growth event, where accretion on low-index lattice planes was no longer favourable. This could become possible when growth is rapid, or may even become necessary when the growing grain replaces a host matrix whose dissolution determines the sites at which new material can be deposited. The morphological features associated with irregular truncation surfaces strongly suggest that the surface configuration was derived by leaching. If this is

so, then the anhedral zones represent retrogressive stages in the main growth event, and their relationship to euhedral zone structures can be interpreted in the following way: (1) growth of euhedral grains, followed by (2) marginal dissolution of these grains, followed by (3) rejuvenation of growth with or without further compositional variations. If repetitive growth and leaching is admitted, then even the most complex growth structures can be accounted for in terms of this basic sequence of events.

The effects of non-supergene leaching in producing macroscopic pore spaces in the massive ore are both widespread and penetrative (see sect. 3.2.5 and 4.6.2). The importance of this phenomenon suggests that intermittent periods of active dissolution might be closely associated with the depositional process. It is perhaps even necessary to suppose that conditions sustaining constant growth could not have been maintained during a prolonged depositional history, or at all points within such a large volume of ore as that contained in the San Dionisio lode. Equilibrium conditions are not likely to persist for long periods of time, and where large volumes of ore are concerned, it seems highly probable that many of the fluctuations which determine the equilibrium displacement will be local. Under these circumstances, it is reasonable to suppose that growth and leaching proceeded simultaneously at different points in the lode.

The relative frequency of closed and open zone structures cannot be easily established because the two types coexist in single grains, where they have a continuously variable incidence. In the fine grain size range closed zones tend to predominate. In the intermediate and coarse range, the trend illust-

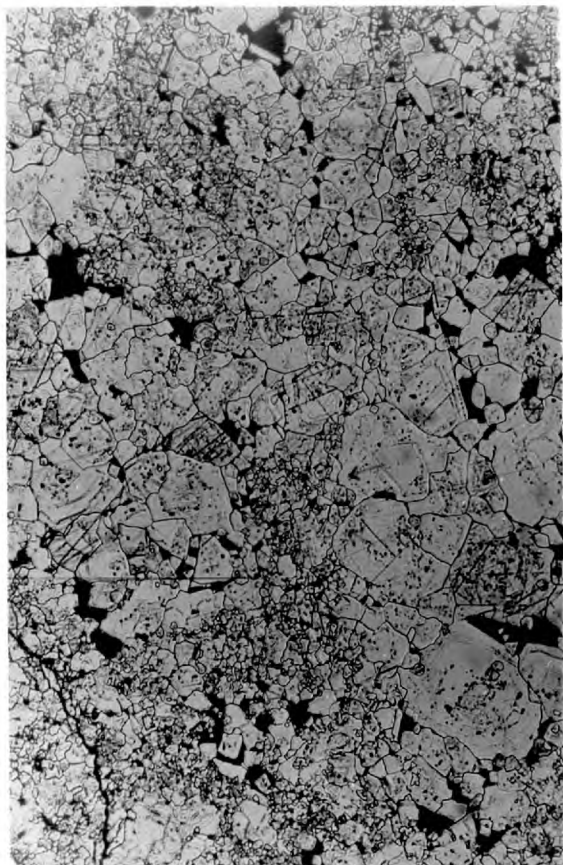
rated in fig. 4.3 is well developed. Closed zone structures are least prevalent and tend to be concentric about the centre of the grain. More frequently a considerable part of the grain is composed of open zones, and the centre of the closed zone structure is displaced towards the grain boundary. Assemblages composed entirely or almost entirely of open zones are the commonest. Since the zone structures are three-dimensional features, their appearance in section is subject to an orientation effect. If this is taken into account, then the relative incidence of the three main structures shown in fig. 4.3 can be interpreted as indicating that each grain contains a set of closed zones, whose centre - the growth nucleus - is significantly displaced towards the grain boundary. In the fine grain size range, where closed zones tend to predominate, the growth nucleus coincides with the grain centre.

The probability that single grains were nucleated at more than one site is clearly unlikely, though a mechanism of highly controlled nucleation (governed by a pre-existing lattice structure for example) could allow this to occur. The occurrence of anhedral zones, which sometimes contain an independent zonal assemblage, does not necessarily imply contemporaneous multi-site nucleation, since the anhedral zone can reasonably be interpreted as an overgrowth (see above). Complex zone structure can also be explained without the necessity of invoking multi-site nucleation. Even where the complexities are marked, an overriding or gross structure can be discerned, and this structure indicates the integrity of the grain as a whole. The increasing complexity of internal structure with increasing grain size can

be reasonably interpreted in terms of the growth history alone. If the larger grains are assumed to have grown for a longer time, then these grains will have been subjected to more of the total changes in the depositional environment. The increasing variability of the growth conditions will be reflected as an increase in the complexity of the grain structure.

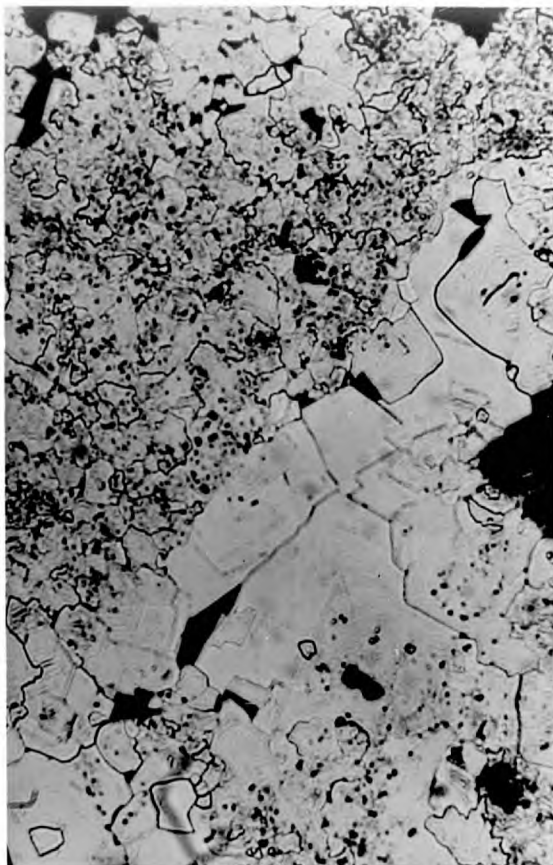
Three other features substantiate the conclusion that each grain is an integral growth unit.

- (i) Open euhedral zone structures tend to be symmetrically related to the overall grain shape. For example, a central zone sector is frequently bordered by lateral sectors whose boundaries are equidistant from the grain boundary. Alternatively, there may be only two lateral sectors, and in this case their boundary tends to divide the grain into two symmetrical halves. If the grain shape is elongate, the boundaries between the zone sectors are approximately parallel to the grain elongation. These features strongly suggest that the complete volume of material which originally accreted to the zone structure is now contained within the enclosing grain boundary.
- (ii) The observed high incidence of open zones may not be representative of the number of these structures which would actually be associated with a closed structure, if closely spaced zones were manifest over the entire surface of observation. Where there are no compositional variations, no zones appear. Hence, if the nucleus is not located immediately at the grain boundary, the chance of observing closed structures becomes increasingly small as the distance between the



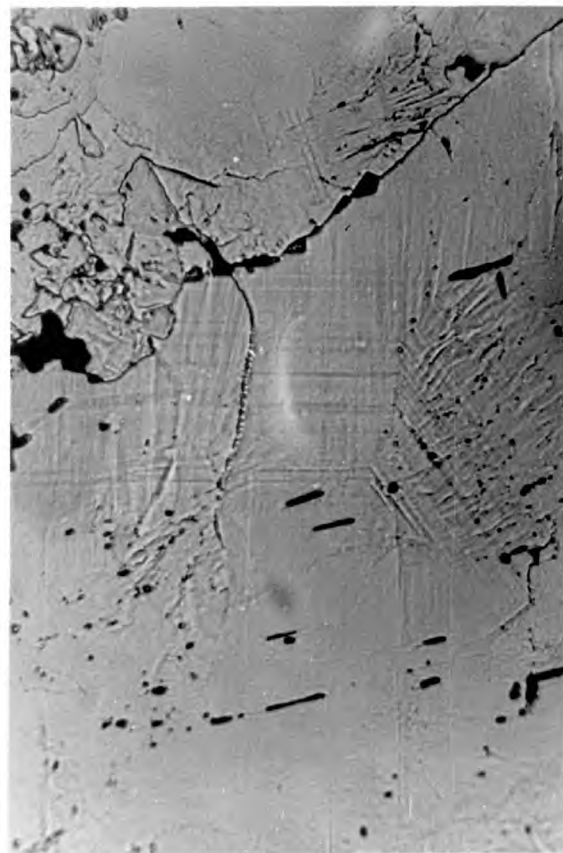
4.57

100 μ



4.58

50 μ



4.59

25 μ



4.60

50 μ

Plate 4.57 Aggregate showing inclusions concentrated at the nucleus regions of the grains and along certain euhedral zones.

Plate 4.58 Part of the aggregate contains a high and fairly uniform inclusion density, and is separated from a relatively inclusion-free area by a sharply defined boundary. The inclusion concentration appears to be superimposed on the granular structure since several of the grain boundaries transgress the contact between the areas of high and low inclusion density.

Plates 4.59 and 4.60 Radial substructures defined by groups of alternating grooves and ridges which trend at right angles to, and transgress the euhedral growth zones. In Plate 4.60 several of the growth zones are slightly tilted between adjacent grooves or ridges.

- nucleus and the first compositional variation increases. Thus there is always a tendency to underestimate the number of grains which potentially have closed structures and whose integrity is therefore directly established.
- (iii) Inclusion concentrations frequently show a strongly preferred distribution in single grains (see the following sub-section). In many instances, the inclusions are also closely related to the zone structures. Where the latter are difficult to interpret, it is probably reasonable to infer the integrity of the grain structure from the fact that the inclusions are frequently concentrated in small groups which are isolated within the grains and do not transgress the grain boundaries.

B Inclusions

The composition of inclusion particles is difficult to establish, especially where they are small and below the limit of optical resolution. Many of the large inclusions reflect light and therefore consist of solid particles (Plate 4.36). Among these, sphalerite and pyrrhotite and/or bravoite, have widespread occurrence. However, the majority of inclusions appear black in polished section and can safely be regarded as surface pits (see for example Plates 4.57 to 4.60), the significance of which is not fully understood. These pits may represent real voids, or the former sites of solid particles which have been removed during polishing. The density measurements described in sect. 6.2 indicate that most of the microscopically observed pore spaces are real, thus suggesting that the inclusions are voidal. Small inclusions are equant and their shape is spherical (see for

example Plates 4.59, 4.60), or approximately square. Large inclusions exhibit sub-spherical (Plate 4.58) and strongly elongate (Plate 4.59) shapes, but are usually fairly equant or irregular (Plate 4.57).

In local parts of polygranular aggregates, the inclusion concentration is frequently distributed with more or less uniform density. That is, the distribution of inclusions is largely independent of the granular structure, and areas of high and low concentration transgress the grain boundaries (see for example some parts of the aggregate in Plate 4.11). However, strictly uniform distributions are extremely uncommon, and there is nearly always a distinct tendency for inclusions to concentrate in local high density groups - denoted inclusion arrays - which coincide with single grains (see for example Plates 4.9, 4.12, 4.14, 4.21). Where the inclusion arrays are sharply defined, they nearly always occur at or near the basal region of open zone structures, and at the centre of closed zone structures - i.e. inclusions are preferentially concentrated in the nucleus region (Plate 4.57). In some instances, high inclusion densities delineate part of the internal zone structure (Plates 4.41, 4.57).

Apart from the typical intragranular inclusion arrays, polygranular aggregates also exhibit one other special type of inclusion distribution. In these occurrences part of the aggregate is comparatively free of inclusions and is separated from a high inclusion density area by a sharply defined boundary which is either plane or composed of several plane segments (Plate 4.58). The inclusions in different grains in the high density area make up a combined and substantially uniform assemblage which appears to be superimposed on the overall grain

structure. Similar inclusion-rich areas sharply distinguished from the surrounding aggregate also occur at a much smaller scale than that illustrated in Plate 4.58. For example, the inclusion concentration indicated in Plate 4.56 appears to be superimposed on the grain structure and exhibits a sharp, angular boundary.

C Radial Substructures

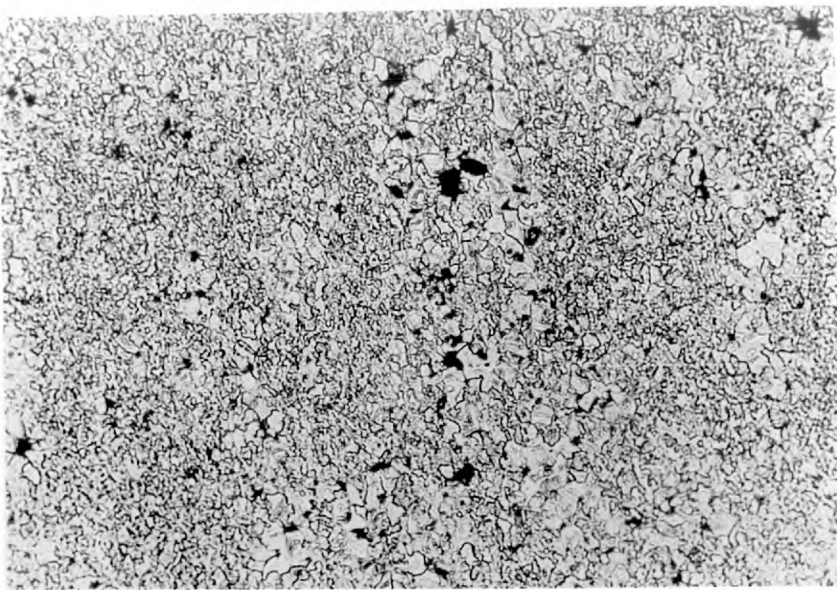
Zoned grains are sometimes characterised by the substructures illustrated in Plates 4.59 and 4.60. On etched surfaces the substructure is manifested by numerous undulose or strictly linear grooves and ridges which trend at right angles to, and transgress the euhedral zone boundaries. The grooves and ridges are arranged in groups which are usually confined to the central part of the zone sector and which increase in width towards the grain boundary. In single grains the substructure is nearly always restricted to areas of high frequency zoning and generally does not extend either to the centre of the grain or to the grain boundary. In most instances the zone boundaries are not offset or otherwise reoriented (Plate 4.59), but in a few cases the zones are slightly tilted between adjacent grooves or ridges (Plate 4.60).

The substructures indicated in Plates 4.50 and 4.55 are also manifested as alternating grooves and ridges, but in these occurrences the radial arrangement is incompletely developed and the linearity of the surface markings is more pronounced. The grooves and ridges are characteristically parallel in different parts of the grain and intersect the zone boundaries in two or more sectors at oblique angles.

The groove and ridge structures described above

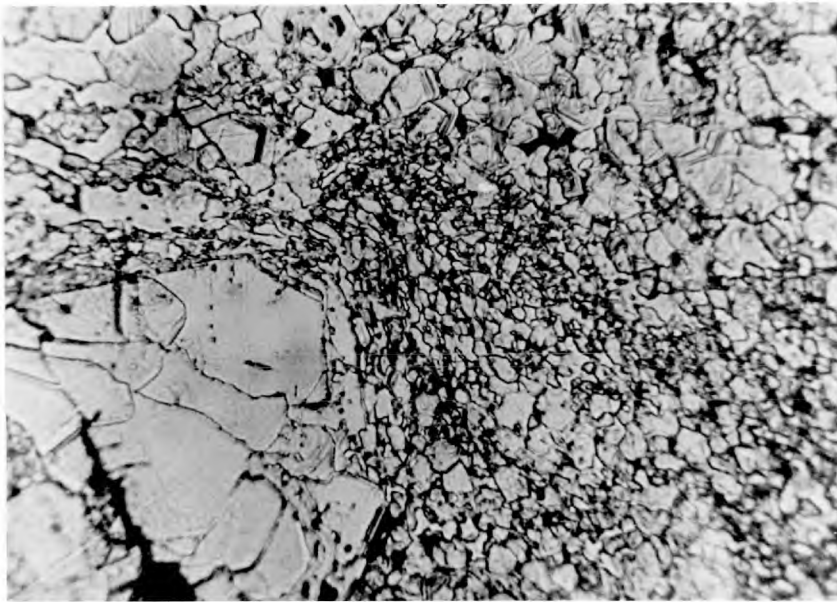
4·61

100 μ



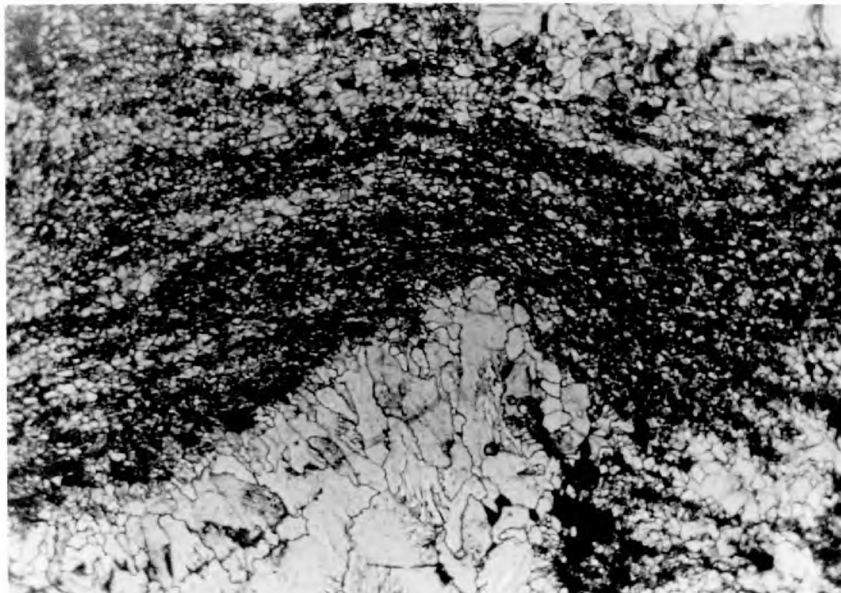
4·62

25 μ



4·63

100 μ



Foliate Fabrics

Plate 4.61

Aggregate showing the marked grain size uniformity and the layering structure of the foliate fabrics. The grain shapes are difficult to discern at this magnification, but the long axes of the grains are oriented approximately parallel to the discontinuous coarse grained bands.

The aggregate shown here is part of a larger sample in which a relatively coarse grained band defines a similar-fold structure; the lamination in the foliate fabric is parallel to the axial plane of the fold.

Plates 4.62 and 4.63

Foliate aggregates showing distortion of the layering structure at large and small scale irregularities in the configuration of the boundary surface between the foliate and massive fabrics.

cannot be interpreted in terms of translation or twin gliding phenomena, since they are rarely associated with reorientation of the euhedral growth zones. Even if the observed tilting effects (Plate 4.60) were derived mechanically, the bulk deformation of the grain is obviously insignificant. It seems most likely that the radial substructures are primary growth features and correspond to the lineage structure reported by Smith (1942).

4.2 Foliate Fabrics

Aggregates in which the component grains are elongate and exhibit a preferred dimensional orientation are distinguished as foliate fabrics, (Plates 4.61 to 4.66).

Comparatively homogeneous aggregates, such as that shown in Plate 4.61, are known to extend continuously over at least the area of a conventional polished section. Oriented samples indicate that the grain elongation of the foliate fabrics is parallel to the regional slaty cleavage orientation (sect. 3.2.2).

Apart from the preferred orientation of the elongate grains, some type of banding is always developed in the foliate fabrics, and trends parallel to the grain elongation. A well defined layering is frequently manifested by the lenses and bands composed of substantially equant grains (Plates 4.61, 4.64). A lamination may also be defined by grain size changes in the elongate grains themselves; these changes are usually fairly continuous, and the banding correspondingly vague (Plates 4.63, 4.64).

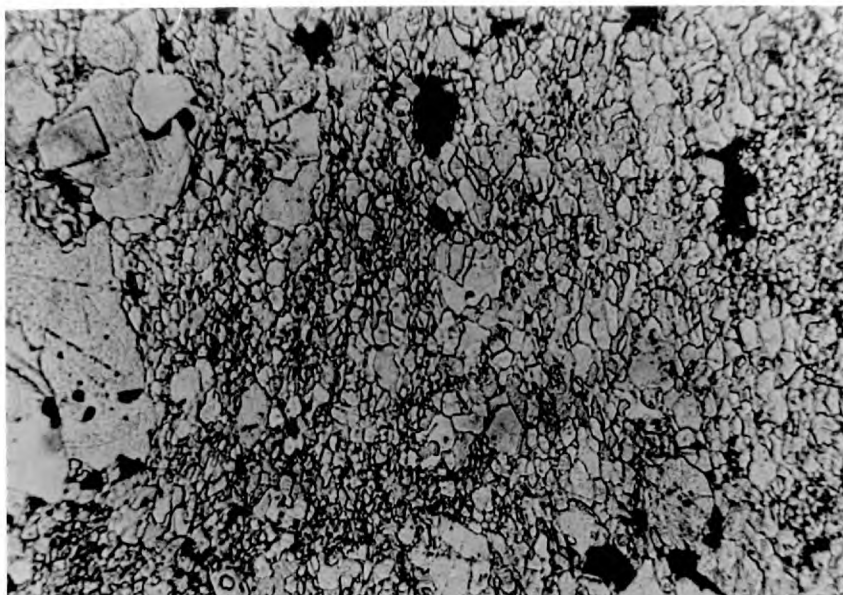
The shape of small-volume foliate aggregates is elongate and conformable with the average grain elongation. Where the aggregate contains only a few or a few tens of grains, its form is distinctly lenticular. These occurrences grade into more extensive bands, which may be either undulose or comparatively irregular. Disseminated lentic-

ular aggregates commonly represent an observable transition between an entirely massive aggregate and an entirely foliate aggregate. Undulose bands, only a few grains wide, may extend over distances of several millimetres, and are frequently linked with neighbouring bands or small lenses. Groups of interconnected lenses and bands may occupy broadly conformable zones up to several millimetres wide and with unknown extension parallel to the zone.

The transition from foliate aggregates to the enclosing massive fabric may be gradational, by decreasing grain elongation and/or decreasing incidence of elongate grains, but is generally abrupt. When the boundary is sharp, there is always a conformable relationship between the boundary orientation and the local direction of grain elongation. Away from the marginal region, the orientation of the layering structure in the foliate fabric is usually constant, and although the lamination is generally parallel to the overall trend of the boundary, there are no undulations corresponding to the details of the boundary configuration. As the marginal region is approached, the orientation of the layering structure becomes increasingly distorted, and exhibits marked flexures which are correlable with irregularities in the boundary surface (see Plates 4.62, 4.63 and the lower left corner of Plate 4.64). The orientation of the grain elongation is nearly always distorted where the morphological features of the boundary surface are developed at a relatively large scale (Plate 4.63). Detailed boundary irregularities, due to single grains or groups of grains projecting from the neighbouring aggregate, are less frequently associated with noticeable flexures in the layering structure. However, in several instances the grain elongation is distorted at even the smallest irregularities (see Plate 4.62 and the lower left corner of Plate 4.64). It is noteworthy that in some occurrences the flexure of the layering structure is

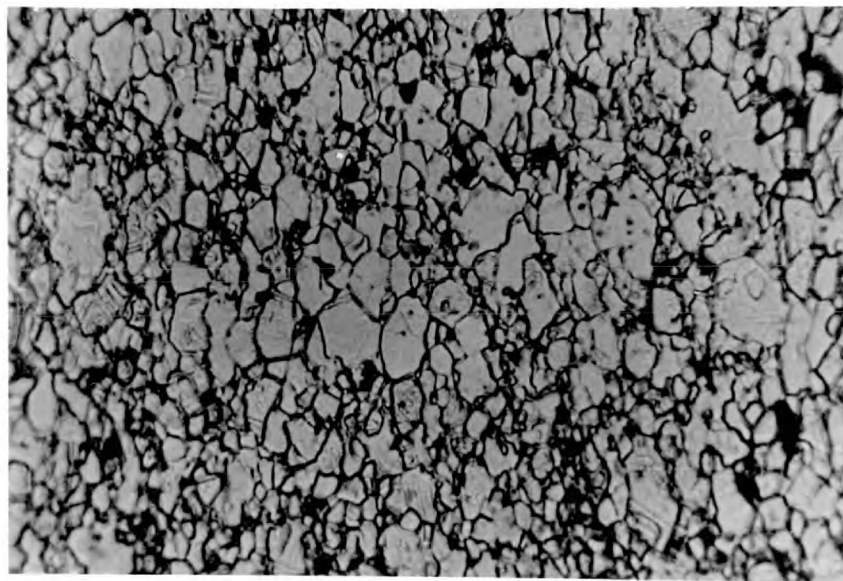
4.64

50 μ



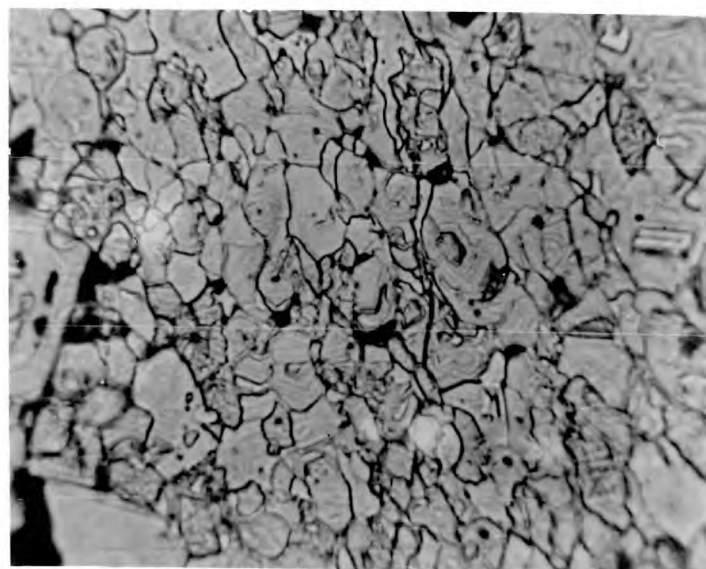
4.65

25 μ



4.66

10 μ



Foliate Fabrics

Plates 4.64, 4.65 and 4.66 Aggregates showing the detailed microstructure of the foliate fabrics.

Plate 4.64 The layering structure defined by the grain elongation is enhanced by subtle grain size variations, and by elongate clusters of comparatively equant grains.

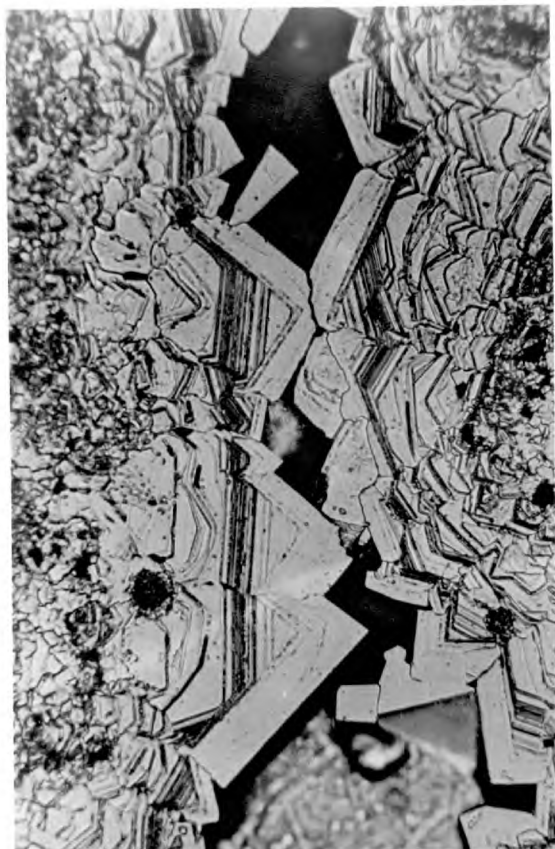
Plates 4.65 and 4.66 Aggregates illustrating the range of shapes exhibited by the elongate grains, the simple euhedral zone structures and the low density of inclusions.

related to projecting grains which exhibit euhedral or subhedral terminations (Plate 4.62).

In comparison to the massive fabrics (where the grain diameters range up to 1 or 2 cm., and the commonest grain size is approximately 10 to 100 microns), the grain size in the foliate fabrics is extremely uniform and much smaller. Grain widths range from 1 or 2 microns up to a maximum of approximately 10 microns, and most grains are approximately 5 microns wide. The average grain elongation is estimated at about 2:1. Many grains are equant or only slightly elongate (see for example Plate 4.65), but in some fabrics the grain elongation is abnormally marked (Plate 4.66), and reaches a maximum where the axial ratio is about 5:1.

The range of shapes exhibited by the elongate grains are illustrated in Plates, 4.65 and 4.66. Most grain boundaries are plane or gently curved, and fine scale serrations are absent. The comparatively regular grain shapes shown in Plate 4.65 are by far the most common. Those illustrated in Plate 4.66 are characterised by protrusions or tenuous extensions which frequently tend to transgress the layering structure.

The internal structure of the elongate grains is effectively the same as in grains of similar size in the massive fabrics. Growth zones are predominantly euhedral, and are rarely truncated by anhedral zones (Plates 4.65, 4.66). Zone frequency decreases with decreasing grain size, and the smaller grains contain only one or two discrete zones. Many zone structures are symmetrically oriented about one of the grain axes, and structures composed mainly of closed zones tend to be concentric about the grain centre. The density of inclusions is low, but in many instances one or two inclusion particles occur at or near the nucleus region of the grain (Plates 4.65, 4.66).



4.67

50 μ



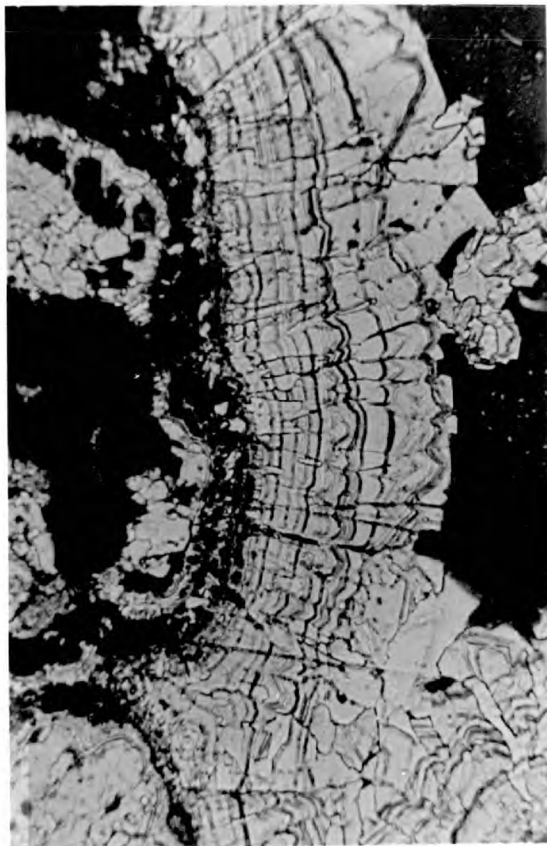
4.68

100 μ



4.69

100 μ



4.70

50 μ

Vein Aggregates and Colloform Structures

- Plate 4.67 Vein composed of two opposing layers of sub-equant grains. The growth zone patterns in the component grains of both layers are similar. In any two adjacent grains there is nearly always at least one equivalent zone which is continuous across the grain boundary.
- Plate 4.68 Closed colloform structures consisting of homogeneous or multi-layered spheres enclosed by successive botryoidal layers.
- Plate 4.69 Open colloform structure consisting of a conformable sequence of botryoidal layers. The arrow indicates a coexisting closed colloform structure.
- Plate 4.70 A colloform layer showing the identity of growth zone patterns in different grains, and the continuity of equivalent zones along the length of the layer.

4.3 Vein Aggregates

Many samples of ore contain narrow, relatively coarse grained bands of pyrite which are composed of two symmetrical layers (Plate 4.67). The orientation of the intragranular growth zones indicates that the grains in each layer were nucleated at the margin of the band, and grew towards its centre. Bands of this type are referred to as veins, and are essentially transgressive features, exhibiting irregular or undulose orientations.

The outer margin of a vein may be gradational to the host fabric, or marked by a sudden change in grain size (Plate 4.67) or by discontinuous aggregates of abnormally fine grained pyrite. In most instances the central region is voidal and defined by euhedral terminations of the marginal grains (Plate 4.67).

The microstructure of the layers composing each of the vein walls is extremely variable. In the simplest veins (Plate 4.67) each layer is only one grain wide, and the grain shape may be either equant or elongate. More complex veins are composed of several layers of grains which may differ in their shape, size, internal zone structure or inclusion density.

Despite the overall complexity of the shape or layering structure in many veins, the component grains in each layer always exhibit distinctive growth zone patterns. The main features of a particular pattern of zoning are repeated in adjacent grains over the entire length of a vein, but the details of the pattern often show minor changes due to the progressive dismissal or introduction of discrete zones. The structure of each layer in the vein is characterised by longitudinal continuity of the growth zone structures. That is, at least some of the equivalent zones in a particular pattern intersect at the grain boundary between neighbouring grains. The same discrete zone is usually not continuous over more than a few grain diameters, but the structure of the layer is

such that in any two adjacent grains there is nearly always at least one equivalent zone which is continuous across the grain boundary. These features are illustrated in Plate 4.67 where the equivalent zones are manifested as discrete euhedral bands of similar reflectivity, thickness or relief.

4.4 Colloform Structures

Colloform structures were observed in a few samples of ore, and even here their distribution is localised. The pyrite grains composing these aggregates are frequently characterised by a brownish colour and a rough surface texture.

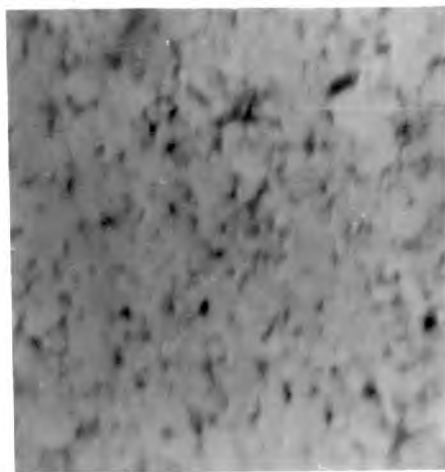
Two types of colloform aggregate can be distinguished: Closed colloform structures consist of discrete spherical aggregates which are clustered together and enclosed by successive botryoidal layers (see Plate 4.68 and the arrowed structure in Plate 4.69). The spheres are either composed of a simple assemblage of radially arranged elongate grains, or are multi-layered, in which case the component grains of different layers are distinguished by difference of size, shape, elongation or internal structure.

Open colloform structures appear as a conformable sequence of botryoidal layers which extend more or less continuously over distances ranging up to at least approximately a centimetre (Plate 4.69). The layering sequence is defined by microstructural variations similar to those in the multi-layered colloform spheres.

In both closed and open colloform structures, there is always at least one band in the layered succession where the component grains exhibit distinctive euhedral growth zone patterns (Plate 4.70). Equivalent zones in adjacent grains intersect at the grain boundary, and the continuity of the zones along the length of the layer is even more

4.71

100 μ

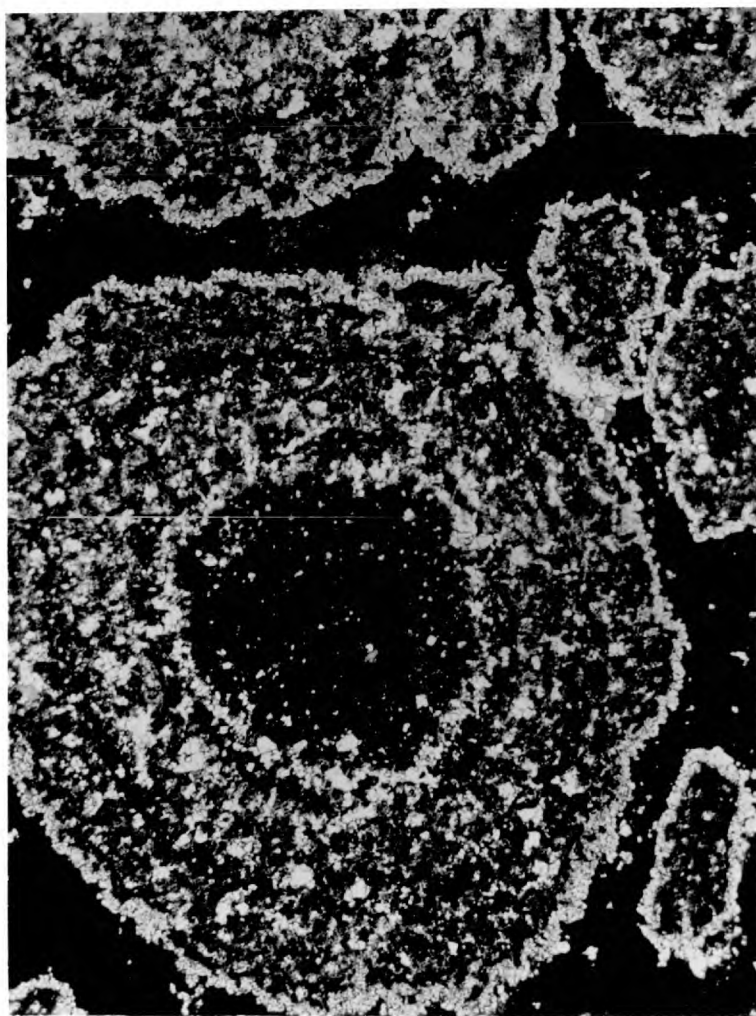


4.72

1 μ

4.73

250 μ



Other Special Microstructures

Plate 4.71 Ultra-homogeneous, fine grained pyrite aggregate containing lenses of sphalerite (low-reflecting) and a few large, subhedral grains of pyrite (high-reflecting).

Plate 4.72 Electron micrograph showing the indistinct granular structure on etched surfaces of the ultra-homogeneous pyrite aggregates.

Plate 4.73 Heavily etched, multi-layered structures showing spherical and elongate shapes. The centre of the large sphere and the matrix are composed of ultra-homogeneous pyrite. The high-reflecting layers contain relatively large grains which exhibit euhedral growth zone structures.

marked than in the vein aggregates described above (Plate 4.70).

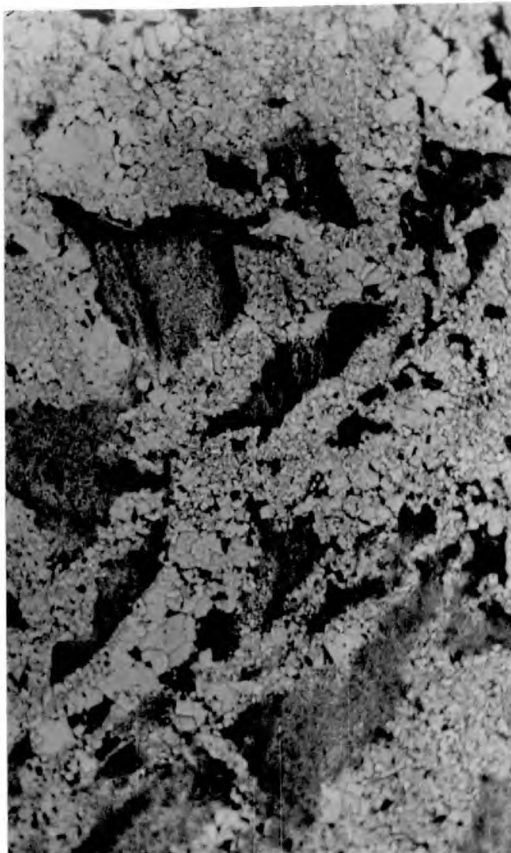
4.5 Other Special Microstructures

- 4.5.1 One sample of ore collected from ~~near~~ the upper contact of the lode contained extensive laminar and curved bands of ultra-homogeneous pyrite (Plate 4.71), the microstructure of which is not properly known. Direct electron micrographs reveal an indistinct granular fabric, but details of the grain shape, internal structure and packing cannot be recognised (Plate 4.72). The low-reflecting centres observed by optical microscopy suggest that the aggregates contain considerable porosity.
- 4.5.2 Many of the aggregates described in 4.5.1 contain poly-granular lenses of sphalerite and chalcopyrite (Plate 4.71). These lenses have a preferred orientation parallel to the trend of the containing band, and exhibit finely serrate boundaries.
- 4.5.3 The homogeneous aggregates described in 4.5.1 grade into and constitute part of multi-layered spherical and elliptical structures (Plates 4.73, 4.74). Other layers in these structures are composed of radially arranged, equant or elongate grains, and the grains in some layers contain euhedral zone structures.
- 4.5.4 Sub-angular banded structures (Plate 4.75) are frequently associated with the aggregates described in 4.5.1. Some of these structures appear to be randomly distributed, whilst others are strictly confined to certain zones in the host fabric. The banding (Plate 4.76) in different structures is nearly always discordant to local banding in the matrix and is defined by abrupt and gradational grain size, grain shape and porosity changes.
- 4.5.5 Fine grained aggregates closely allied to those described in 4.5.4 occupy sharply defined elongate structures whose boundaries are typically curved and undulose (Plate 4.77).



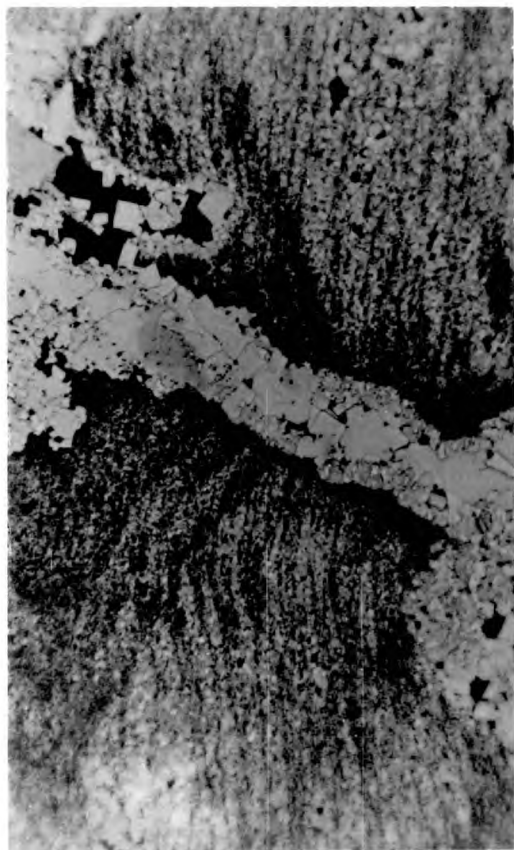
4.74

250 μ



4.75

100 μ



4.76

50 μ



4.77

100 μ

Other Special Microstructures

Plate 4.74 Multi-layered elliptical structures containing coarse grained layers (high-reflecting), but composed mainly of ultra-homogeneous pyrite.

Plates 4.75 and 4.76 Sub-angular structures composed of fine grained pyrite. Definition of the internal banding is mainly due to changes in pore space density. The microstructure of the pyrite aggregate is partly evident in Plate 4.76; in this illustration a coarse grained vein intervenes between two adjacent structures.

Plate 4.77 Elongate structures composed of fine grained pyrite. The internal microstructure is similar to that illustrated in Plate 4.76.

These structures are fairly common and widespread. They always occur in laminar zones and exhibit a preferred orientation parallel to trend of the zone.

- 4.5.6 Coarse grained aggregates occupying bands which define fold structures exhibit growth features which are worthy of separate mention. The microstructure is usually characterised by a preferred orientation of the grain boundaries at right angles to the boundary surface of the folded layer. The dependence of grain structure on the configuration of the layer is best illustrated by the radial arrangement of elongate grains in the crests of folds (Plates 3.18, 3.19). The orientation of internal zone structures, or the elongation of the grains, indicates that the predominant or only growth direction was approximately at right angles to the boundary of the folded band. In all cases at least one of the boundaries was a major nucleation surface for the subsequent growth.

4.6 Structure of Interstitial Sites in Pyrite Aggregates

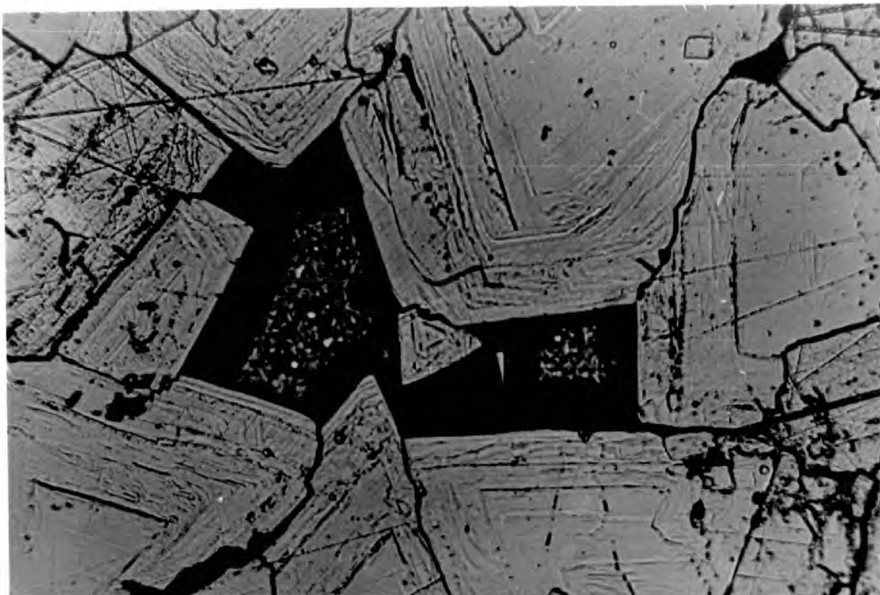
Fully dense, monomineralic pyrite aggregates do not generally persist over distances of more than a few tens of grain diameters. Larger volumes of pyrite contain interstitial regions which may be either voidal or occupied by another mineral (principally chalcopyrite and sphalerite). There are two types of interstitial sites, namely, euhedral interstices, which are primary growth features, and leached interstices, derived by later dissolution.

4.6.1 Euhedral Interstices

Euhedral interstices are defined by euhedral terminations of the marginal pyrite grains, and are an integral part of all fabric types. The interstitial sites are disconnected and their separation, which increases with increasing grain size, is usually in the order of a few to a few tens of grain diameters. Typical examples of the density and distribution of euhedral interstices are shown in Plates

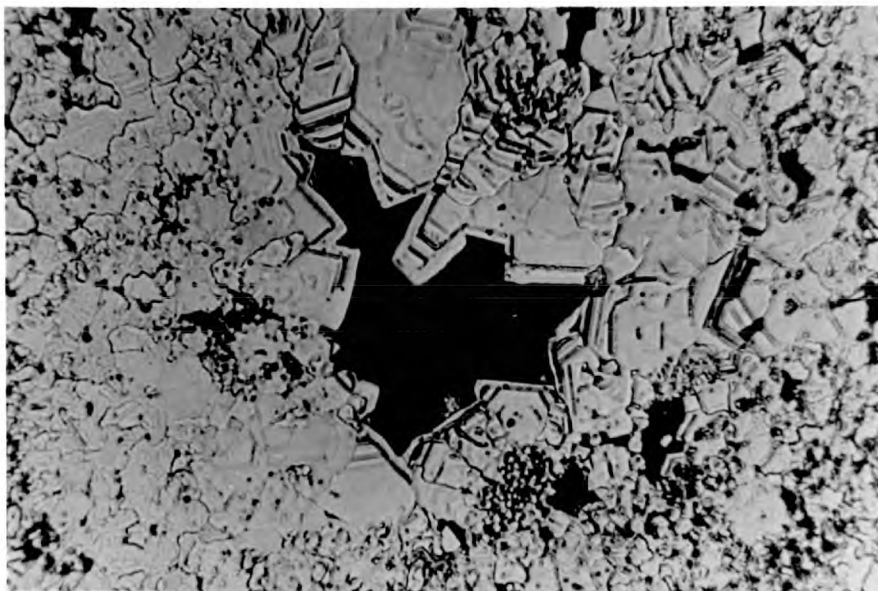
4.78

50 μ



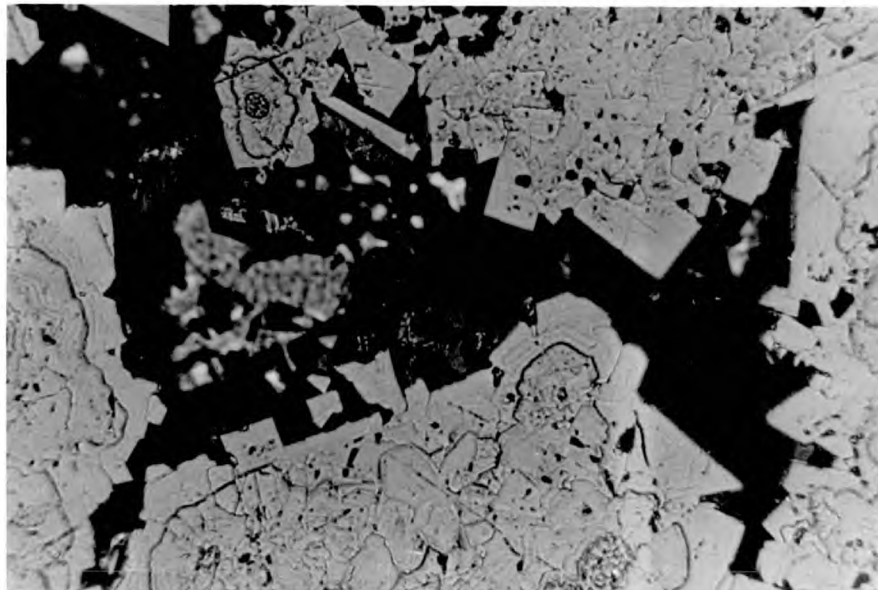
4.79

25 μ



4.80

50 μ



Euhedral Interstices

- Plate 4.78 Simple, euhedral interstice, partly occupied by chalcopyrite. A wide growth zone occurs near the free faces of all the marginal grains, and is continuous across each of the grain boundaries.
- Plate 4.79 Additional-growth, euhedral interstice (voidal). The marginal grains exhibit distinctive growth zone patterns near their free faces, and equivalent zones are continuous around almost the entire perimeter of the void.
- Plate 4.80 Complex, euhedral interstice, partly occupied by chalcopyrite. Distinctive growth zone patterns are continuous around the upper and lateral margins of the interstice.

4.10, 4.11, 4.13 and 4.19.

Voidal or occupied euhedral interstices can be grouped into three main categories:

- (1) Simple Interstices are distinguished where the size of the grains at the margin of the interstice is approximately the same as the average grain size in the surrounding aggregate. Several typical examples are illustrated in Plate 4.10, and the detailed microstructure at the interstitial site is shown in Plate 4.78. Since the size of the marginal grains is approximately the same as the grain size in the compact aggregate, the interstitial site must have formed at substantially the same time that the surrounding aggregate became fully dense.
- (2) Additional-Growth Interstices are distinguished where the size of the grains at the margin of the interstice are noticeably greater than the average grain size of the surrounding aggregate. Interstices of this type are illustrated in Plate 4.13, where a number of voids are preferentially centered at the coarse grained clusters, and in Plate 4.79. The increased grain size associated with the margin of the interstice is taken to indicate that considerable amounts of growth occurred at the free grain surfaces after the surrounding aggregate became fully dense. The period of additional growth is also represented by one or more growth zones which occur near the terminal regions of the marginal grains but which do not appear in the compact aggregate (Plate 4.79). Where the overgrowth layer is substantial, the marginal grains tend to be elongate and radially arranged (Plate 4.79). The transition from the grain surfaces which form the initial margin of the interstice to the overgrowth layer is frequently accompanied by a growth habit change.
- (3) Complex Interstices occur where the boundary of the

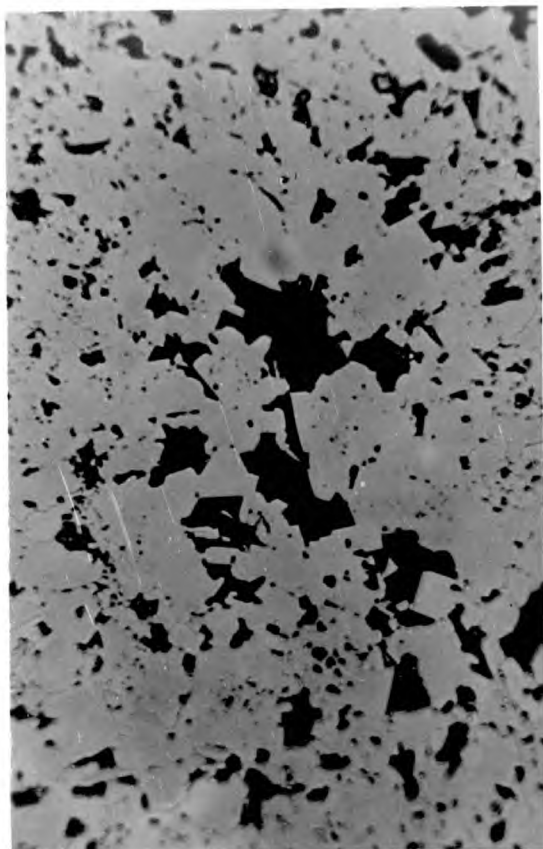
interstitial region is defined by the margins of grains belonging to a number of independent clusters. The shape and degree of impingement of these clusters may take many different forms, and the microstructure of particular interstices is correspondingly variable. An example is illustrated in Plate 4.80 where a large void is almost completely surrounded by groups of grains belonging to sub-spherical growth structures.

Interstices of the simple and additional growth types range in size from a few microns up to several times the average grain size in the surrounding aggregate. A large number of these interstices have dimensions which are similar to, or greater than the average grain size. The overall dimensions of complex interstices are controlled by the impingement of independent grain clusters, and are considerably greater than the average grain size.

Euhedral interstices are characterised by the occurrence of distinctive patterns of growth zoning near the free faces of the marginal grains (Plates 4.78, 4.79, 4.80). Similar or identical patterns are repeated in adjacent grains, and the equivalent zones in a particular sequence invariably intersect at several of the grain boundaries. At many interstices, equivalent zones are continuous around almost the entire perimeter (Plates 4.78, 4.79, 4.80).

4.6.2 Leached Interstices

Leached interstices are most conspicuous as semi-connected voids which occur in localised patches and discontinuous bands of megascopic dimensions. These large scale occurrences are associated with fragment zones and have rather special features, already described in sect. 3.2.5. The following descriptions are confined to interstices which are essentially isolated and appear as an



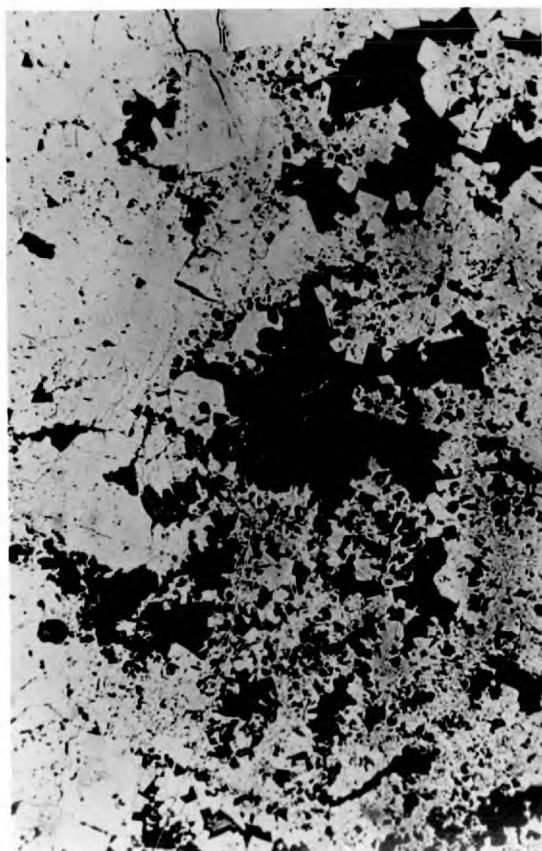
4.81

25 μ



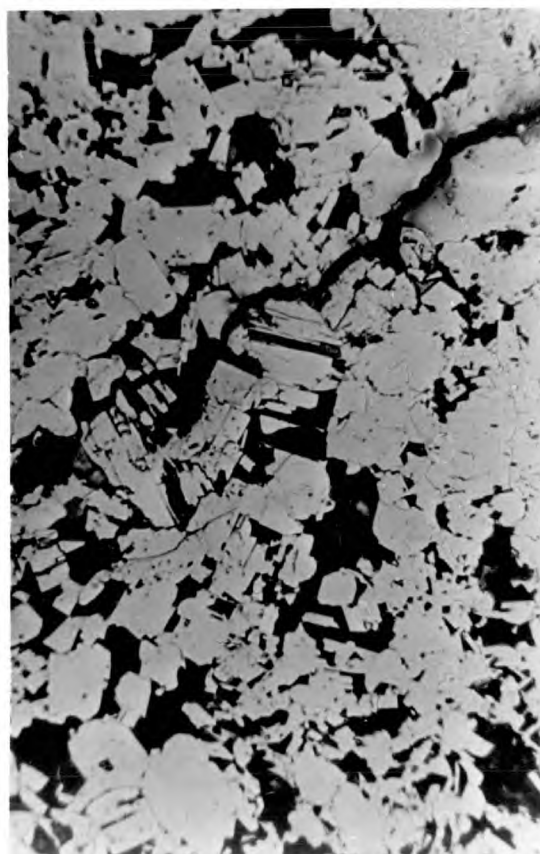
4.82

50 μ



4.83

100 μ



4.84

50 μ

Leached Interstices

Plate 4.81 Typical development of leached interstices (voidal), showing the coexistence of euhedral grain faces with the characteristic embayments, projections and rounded surface features.

Plates 4.82 and 4.83 Advanced development of leached interstices (voidal). Euhedral grain faces are absent, and the surface configuration of the voids is extremely complex. The most advanced stage of leaching is illustrated in Plate 4.82 where previously isolated voids (Plate 4.81) have become interconnected along the grain boundaries, leaving only remnants of the initially compact aggregate.

Plate 4.84 Lamellar grain shapes associated with pronounced leaching activity.

integral part of the microstructure.

The morphological features associated with the interstices illustrated in Plates 4.81 to 4.84 are generally considered to be indicative of leaching activity in the supergene environment of sulphide ore bodies. On this basis it is concluded that the interstices described below are also indicative of dissolution phenomena - hence, the term leached interstice.

The typical development of leached interstices as observed on unetched polished surfaces (where the existence of artificial dissolution features can be discounted) is illustrated in Plate 4.81. Several of the free grain faces are generally euhedral, but a large part of the exposed surface is characterised by embayments, delicate projections, and by a marked tendency for the morphological irregularities to exhibit rounded shapes. In some instances, there are no euhedral terminations at the margin of the interstice, and the configuration of the boundary surface is extremely complex (Plate 4.82). Interstices of this type are usually extensive and tend to be interconnected along the grain boundaries. At an advanced stage, the interstitial volume is predominant; and the pyrite aggregate is highly dissected (Plate 4.83). In several instances the interstitial regions are associated with grains which exhibit distinctive lamellar or recticulate shapes (Plate 4.84). Where leached interstices are infilled by other sulphide minerals, the infilling minerals themselves frequently show leaching effects. Chalcopyrite is most susceptible to these effects, and is sometimes associated with covellite and/or bornite.

The frequent coexistence of plane and irregularly shaped surface configurations at the same interstitial site suggests that in many instances the leaching effects were only incipient. For example, it seems reasonable to suppose that the euhedral terminations which occur at many

of the interstices shown in Plate 4.81 were retained from pre-existing euhedral interstices. However, in the case of lamellar and recticulate grains, which only occur in regions where an aggregate is leached, there can be little doubt that the plane grain faces are actually surfaces of dissolution.

The development of plane and irregular surface morphologies probably depends on the rate at which the grain faces are dissolved. At low dissolution rates, the maximum response to leaching occurs by removal of the least strongly bonded atoms. Since these are sited at the grain edges and corners, the latter tend to be removed, and the effect of the dissolution process is to produce rounded grain faces. Under the requisite conditions, high dissolution rates are achieved by increasing the area of the dissolution surface, and therefore the total volume of material available for solution. The removal of grain edges and corners becomes less important, but embayments and other irregularities are developed because these shapes increase the surface area. At intermediate dissolution rates, a compromise is reached whereby leaching becomes most favourable at a particular lattice plane. This plane is preferred because of its low stability compared with other lattice orientations; at the same time, a relatively large surface area is maintained, especially where lamellar or recticulate grains are developed.

It should be emphasised that leached interstices are equally prevalent in samples of ore taken from both the upper and lower levels of the lode. In fact, all the leaching phenomena observed in the massive ore occur below the zone of secondary alteration. This suggests that the leaching effects were not produced in a near-surface, supergene environment, and that they may be connected with the primary mineralisation itself. In this regard it is noteworthy that important hydrothermal leaching

activity has previously been recognised in several sulphide ore deposits, at central or lower levels in the lodes where the influence of the near-surface environment can be neglected (Lacy and Hosmer, 1956; Turneaure, 1960; Sims and Barton, 1961; Barton, Bethke and Toulmin, 1963). Moreover, as pointed out by Barton, Bethke and Toulmin (1963, p. 183), several changes can reasonably be expected to occur in the physiochemical environment of hydrothermal deposition which would lead to the onset of intermittent leaching.

4.7 Accessory Sulphide and Gangue Minerals

In the massive ore the principal accessory sulphide and gangue minerals are chalcopyrite, sphalerite, tetrahedrite-tennantite, galena and quartz. These minerals occur predominantly at euhedral interstitial sites in otherwise compact pyrite aggregates. Since the boundaries of the interstices are determined by the growth surfaces of the marginal pyrite grains, the deposition of the accessory sulphides must post-date the growth of the surrounding pyrite aggregate. This conclusion is strictly valid only in the case of euhedral interstices. However, the fact that these interstices accommodate most of the accessory minerals strongly suggests that the general deposition of these minerals occurred later than, though perhaps in continuity with, the main pyrite mineralisation.

None of the accessory minerals shows intragranular structures resembling those of the pyrite aggregates. At least in the case of chalcopyrite, which reacts to the etching process, the absence of internal zoning is almost certainly a real feature. Sphalerite grains are rarely twinned, but almost invariably contain oriented chalcopyrite inclusions, and in some instances, irregularly shaped inclusions of an unidentified grey mineral. Etched chalcopyrite grains frequently exhibit broad twin

lamellae. Some chalcopyrite grains show diffuse rims, where the usual pale yellow colour of the mineral acquires a pinkish tinge. Other than the properties listed above, the internal structure of the accessory minerals is essentially homogeneous.

CHAPTER 5

PYRITE SPHERES AND ELLIPSES

The special microstructures described in this chapter are composed of spherical, sub-spherical and elliptical aggregates of fine to sub-microscopic pyrite grains and are either equivalent or closely allied to the familiar structures known as pyrite spheres (see, for example, Love, 1962; Love and Amstutz, 1966; Kalliokoski, 1966). Although it is generally agreed that pyrite spheres were derived from a colloidal precipitate, the conventional inference that the initial spheroidisation occurred under the influence of their surface tension is open to question. Spherical aggregates occur in the massive-discrete fabrics, for example (sect. 4.1.1), and the size and internal structure of these aggregates suggest that they grew by uniform accretion to a continuously advancing spherical surface. A similar mechanism, involving the accretion of colloidal or ionic material, might be applicable in the case of the pyrite spheres. If this were so, then by analogy, the development of elliptical structures could be attributed directly to the initial growth process, and could be explicable in terms of anisotropic accretion. But if surface tension is the shape controlling factor, then the elliptical structures must originate by distortion of pre-existing spheres.

Thus, although pyrite spheres and ellipses are estimated to occupy less than 5% of the total ore, the occurrence of elliptical structures is obviously important since they may imply that deformation has occurred. Moreover, even if the elliptical structures are distorted equivalents of the spheres, it still remains to decide whether, at the time of the deformation, the spheres were in a colloidal or a crystalline state. This question is important because, if the latter case is true, there could be significant implications for the potential

mechanical behaviour of the normal massive ore under conditions of natural deformation.

The object of this chapter is to demonstrate that the elliptical structures are deformed equivalents of the spheres, and that at the time of distortion the parent spheres were still composed of a colloidal precipitate. Although for the spheres themselves there is no question of deformation, a large part of the present discussion is necessarily concerned with the origin of these structures. Conventional interpretations of the spherical shape are re-examined in relation to the internal structure of the spheres, and the full implications of the microstructure are discussed.

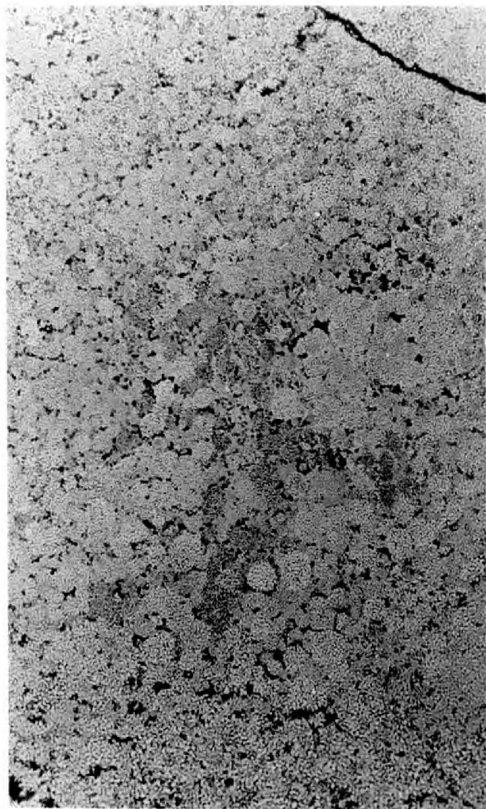
The chapter is divided into two parts; the first contains most of the description, and the interpretation is presented in the second part.

PART A DESCRIPTION

5.1 Modes of Occurrence

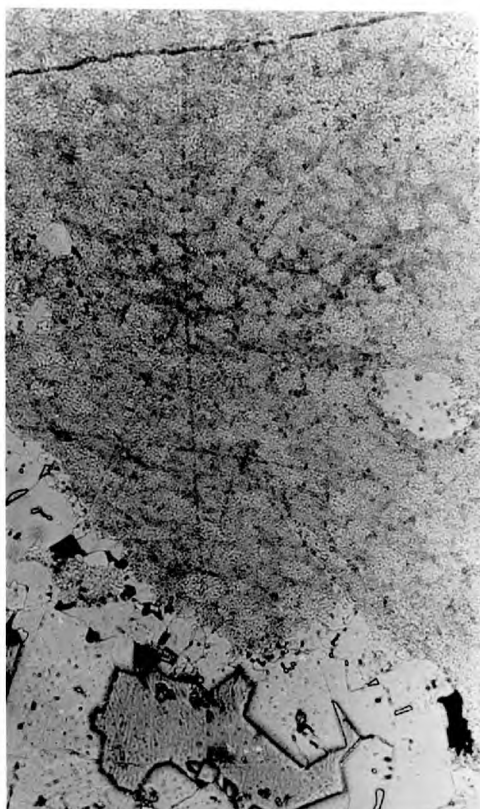
From the genetic viewpoint, spherical and elliptical structures are quite inseparable, and distinctions relating to their degree of distortion do not provide a suitable basis for classification. The occurrence of elliptical structures has not previously been widely recognised (see, however, Barringer, 1954, p.57), but in fact their incidence is probably as great or greater than that of the spheres. The interrelationship of spherical, sub-spherical and elliptical structures is important from the genetic viewpoint, and for this reason it is emphasised in the following description.

(1) Aggregates composed largely or entirely of spheres exhibit a high degree of packing (Plate 5.1). This usually involves at least point impingement of neighbouring spheres; frequently the contact area is much greater, and the spheres correspondingly distorted. Close-packed spheres may occupy volumes containing up to at least a few thousand individual structures: the largest continuous



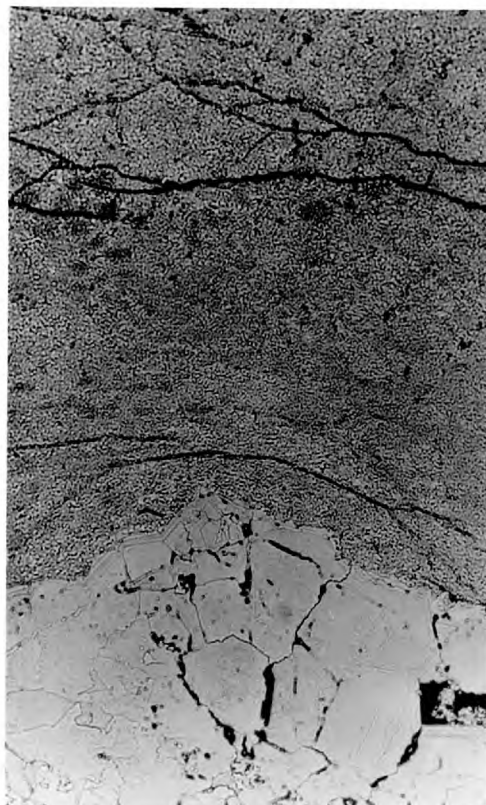
5.1

100μ



5.2

100μ



5.3

100μ



5.4

100μ

Plate 5.1 Close-packed sphere aggregate showing the degree of sphericity of single structures and the normal variation of the sphere size. Note the tendency for spheres of a particular grain size to be concentrated in separate groups. The spheres shown here occur in the centre of the widest part of the aggregate marked S_2 in Plate 3.15 (a), and grade into the marginal zone of ellipses shown in the centre of Plate 5.3.

Plate 5.2 Elliptical structures concentrated near the margin of the neighbouring coarse grained aggregate, and showing decreasing elongation away from the boundary region. The area shown here occurs at the lower margin of the right-hand aggregate marked S_1 in Plate 3.15 (c); the centre of this aggregate is composed of close-packed spheres.

Plate 5.3 Zone of ellipses occurring at the margin of the aggregate whose central region is shown in Plate 5.1. Spherical structures are developed near the top of the illustration. Note that the elongation direction exhibits a flexure which is conformable with the margin of the neighbouring coarse grained aggregate.

Plate 5.4 Band of ellipses (low-reflecting) showing strong elongation and a high degree of preferred orientation. The identity of single structures is difficult to recognise since most ellipses have coalesced with their neighbours, producing a marked laminar structure parallel to the trend of the band.

volumes have average dimensions of more than a centimetre. Almost invariably the margin of a sphere aggregate is sharply defined, and the transition to the enclosing coarse grained pyrite matrix is correspondingly abrupt. To some extent the shape factor provides a suitable basis for distinguishing different modes of occurrence, and it is largely on this basis that the following descriptions are sub-divided.

- (a) Many aggregates exhibit shapes which are grossly equant but whose detailed boundaries are characteristically irregular and determined by single grains or groups of grains projecting from the enclosing coarse grained fabric. Several disseminated aggregates may occupy a broadly defined laminar zone, and in some cases the aggregates themselves often tend to assume an elongate form. More commonly, however, the aggregates form extensive complex assemblages which are essentially transgressive to local structures, such as banding and other types of fabric discontinuity. Elliptical structures are frequently developed near the margin of an aggregate, and may also persist into the interior region where they define characteristic patterns of preferred orientation (see (4) below). Although the development of elliptical structures may locally become a dominant feature, they constitute an integral part of the complex assemblages and cannot be singled out as an independent mode of occurrence.
- (b) Approximately equidimensional aggregates may have boundaries which are conspicuously planar. Typical examples are illustrated by the areas marked S_1 in Plate 3.15. The margins of the aggregate are macroscopically planar, but at the scale of the microstructure they are modified by minor irregularities corresponding to the grain structure of the enclosing coarse grained fabric.

In both of the aggregates shown in Plate 3.15 there is a similar and strongly preferred distribution of spheres and ellipses. A semi-continuous zone of ellipses up to approximately 20 diameters wide occurs along the boundary against the host fabric. The remaining parts of the aggregates are composed of spheres, and these show gradational shape changes to the most strongly distorted ellipses which occur immediately against the host fabric. The micro-structure of the marginal zone of ellipses is shown in Plate 5.2. Close to the margin of the host aggregate the long axes of the ellipses are parallel to the overall trend of the boundary, and frequently show inflexions which are correlable with the details of the boundary morphology.

- (c) Discrete, irregularly shaped aggregates are illustrated by the area marked S_2 in Plate 3.15. These aggregates are distinguished separately, but exhibit properties (notably irregularity and the local development of plane boundaries) in common with those described in (a) and (b) above. Their shape is characterised by tenuous interconnections and marginal apophyses. Especially near their extremities, the apophyses become partly or completely discontinuous, and exhibit sharp constrictions which result from local impingement or near-impingement of coarse grains in the surrounding fabric.

The central, and largest part of these aggregates is composed entirely of spheres (Plate 5.1). At some places these extend to the margin of the aggregate, but there is generally a marked development of ellipses over most of the boundary region (see the zone immediately above the coarse grained host aggregate in Plate 5.3). The long axes of the ellipses are conformable with the boundary of the aggregate,

and show inflexions at minor irregularities, and especially at constrictions.

- (d) Semi-continuous aggregates of spheres sometimes comprise a matrix to single or small groups of coarse grains.
 - (e) Spheres are sometimes grouped together in narrow bands which are only 2 or 3 diameters wide, but which may extend over distances of several tens of diameters. These bands may be conformable or transgressive to the surrounding structures, and ellipses are often developed locally.
 - (f) Occasionally small groups of spheres are immediately surrounded by radially arranged grains whose internal zone structures indicate a preferred growth direction away from and at right angles to the margin of individual spheres. The growth of the marginal grains post-dates the deposition of the spheres, and their comparatively large size and gradational transition to the host fabric suggest that they are an integral part of the latter.
- (2) Singly occurring spheres are rare, and are always closely associated with larger groups of either spheres or ellipses. Disseminated groups containing one to a few spheres occasionally occupy interstitial sites in coarse grained aggregates (Plate 5.19), and in a few instances single grains of pyrite actually enclose isolated spheres.
- (3) Aggregates composed largely or entirely of ellipses occur in a wide variety of banded structures. In many of these aggregates the ellipses are strongly elongate and tend to coalesce. Where the elongation is extreme the structure of the aggregate exhibits a marked laminar appearance (Plate 5.4). The trend of a band may be constant or undulose, but in all cases its orientation is broadly conformable with the local layering structures.

Band widths vary from 1 or 2 ellipse diameters up to several tens of diameters, but the full longitudinal extension of the widest bands is unknown.

In all cases the long axes of the ellipses are oriented parallel to the trend of the containing band. However, in the marginal regions of the bands two orientation relationships can be distinguished. (a) Where discrete grains belonging to the host fabric project into the ellipse band and define its margin, the long axes of the ellipses conform with major orientation changes of the boundary of the band, and frequently show inflexions which are correlable with minor irregularities. (b) In several occurrences the margin of an ellipse band is defined by a continuous rim of grains whose zone structures and radial arrangement indicate that they have grown on already existing elliptical structures.

(4) Ellipses are frequently grouped in narrow bands which define fold structures, and are oriented with their long axes parallel to the axial planes of the folds (see Plates 3.18, 3.19). Where the neighbouring aggregate is coarse grained, the marginal ellipses are surrounded by clusters of radially arranged grains (Plate 3.19 (b)). This relationship indicates that the development of the elliptical structures pre-dates the deposition of the coarse grained aggregate.

5.2 Sphere and Ellipse Size, and Component Grain Size

The size distribution of spheres, ellipses and their component grains, and the mode of variation of these factors in particular aggregates, has not been established on a statistical basis. The following observations are intended to draw attention to the range and general mode of variation encountered.

The commonest sphere sizes fall in the range approximately 30 to 40 microns. A minimum limit appears to be

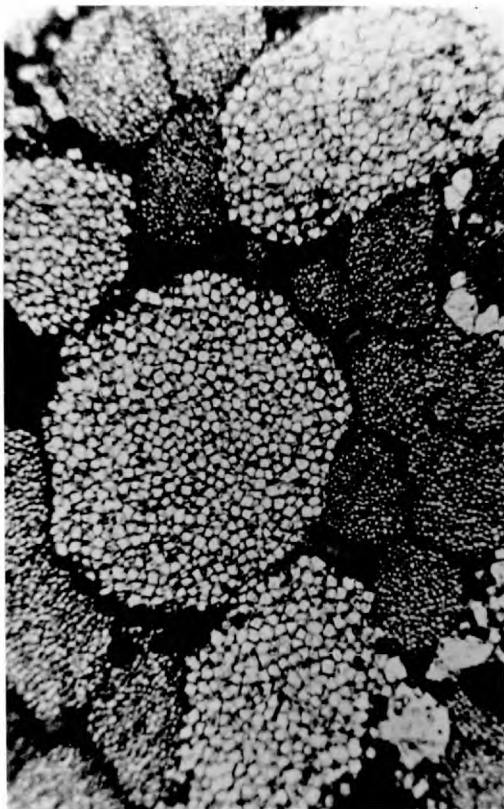
around 10 microns, and the maximum size around 60 microns. The largest spheres occur with the lowest frequency. The commonest component grain sizes fall in the range approximately 0.5 to 1.5 microns. The lower limit, determined by replica electron microscopy, is around 0.2 microns, and the maximum grain size is approximately 5 microns. Despite the difficulty of estimating sphere size from sectional observations, it is fairly clear that there is a broad correlation between increasing sphere size and increasing component grain size.

The size range of spheres and ellipses has not been directly compared on a volume basis. However, visual comparisons leave little doubt that the volumes of ellipses fall in approximately the same range as those of the spheres. The axial ratio of ellipses shows a continuous variation up to an unknown limit, and where the ratio exceeds a value of about 5:1, the identity of the elliptical form is virtually lost. Neighbouring ellipses frequently coalesce and give rise to semicontinuous, parallel bands separated by coarse grained laminae. In several instances the ellipses coalesce over an extensive area, producing a uniform aggregate which is characterised by a marked laminar structure (Plate 5.4).

The distribution of spheres or ellipses of different size or different grain size usually does not define any regular structural pattern in the aggregate as a whole. However, there is frequently a tendency for spheres or ellipses with different size characteristics to be concentrated in separate groups (Plate 5.1).

5.3 Packing and Types of Distortion

(1) Spheres In most occurrences there are parts of an aggregate where the individual spheres are not in contact (Plate 5.1). The interstitial space may be voidal or occupied by another sulphide mineral. At least part of



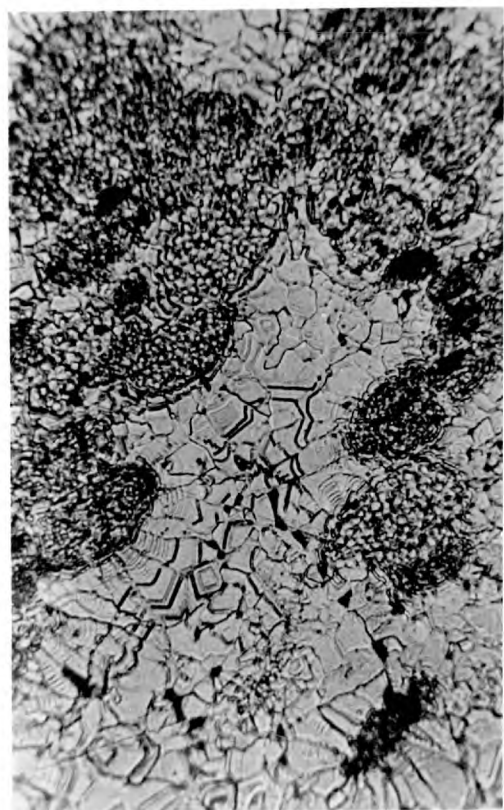
5.5

10μ



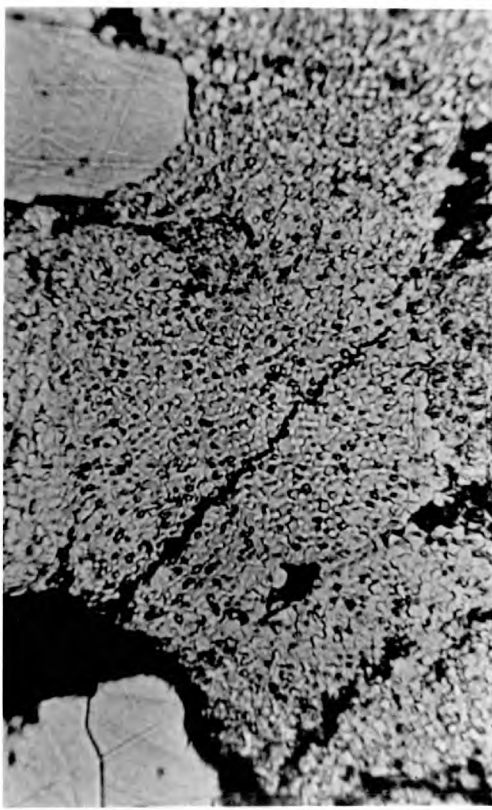
5.6

10μ



5.7

25μ



5.8

10μ

Plate 5.5 Sub-spherical structures showing the typical shapes developed in close-packed aggregates. The large spheres exhibit disordered packing of their component grains, but ordered grain arrangements are locally developed in several of the smaller spheres.

Plate 5.6 Distorted spheres occurring near the margin of the coarse grained host aggregate (bottom of illustration). The structures at the centre and the upper left exhibit disordered packing of their component grains.

Plate 5.7 Part of an extensive band of ellipses showing the microstructure of the intervening coarse grained matrix. Note the radial grain arrangements controlled by the elliptical shapes, and the continuity of the euhedral growth zone patterns in the rim grains and in the interior of the matrix aggregate.

Plate 5.8 Close-packed spheres of uniform grain size. The sphere boundaries are not immediately obvious, and are mainly defined by the different patterns of grain arrangement in different spheres.

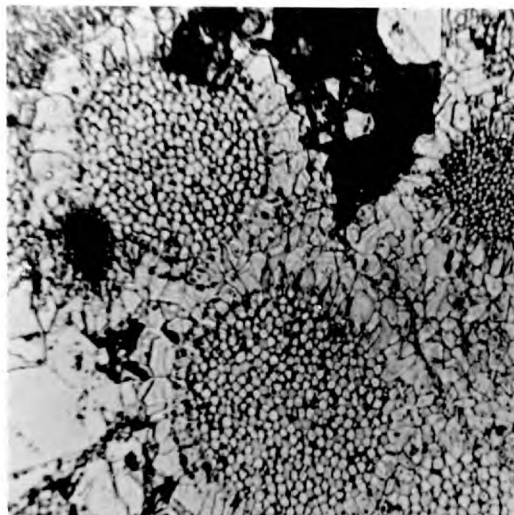
this space is frequently occupied by equant or elongate grains which form rims around the individual spheres (Plate 5.9).

Most sphere aggregates involve at least point impingement of neighbouring structures. Usually, however, the spheres impinge over a considerable area, and are correspondingly distorted (Plate 5.5). In these circumstances, interstices may be completely absent so that parts of an aggregate are fully dense (Plates 5.1, 5.6). Where compaction has occurred, the smaller and finer grained spheres have usually suffered the greatest distortion (Plate 5.5). The marginal spheres of an aggregate tend to be flattened against neighbouring coarse grains (Plate 5.6) and often distorted so as to accommodate sharp irregularities in their boundaries.

In fully compacted groups of spheres of uniform grain size, it is sometimes exceedingly difficult to recognise the spherical forms. Disseminated pore spaces or inclusions may reveal the position of parts of the sphere boundaries. In some cases the identity of separate spheres is reflected by different patterns of ordering of the component grains (Plate 5.8).

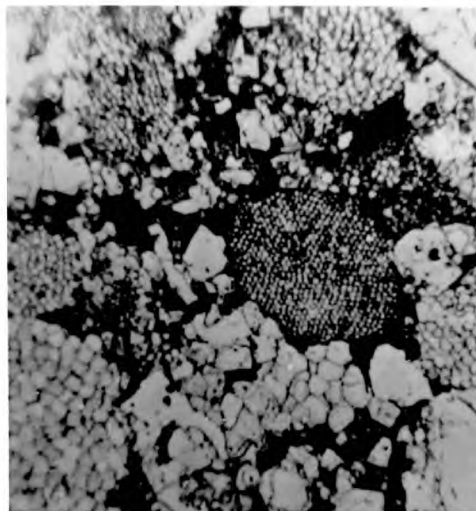
(2) Ellipses Although distorted shapes occur in compacted sphere aggregates, these can be readily distinguished from typical elliptical structures. In aggregates of ellipses there is usually local impingement, at least in small groups (Plates 5.7 and 5.21). Discrete structures and their elliptical shapes can generally be easily recognised (Plates 5.7, 5.20, 5.21 and 5.23). In many instances, however, individual structures are difficult to distinguish, and their shapes may be considerably modified either as a result of non-uniform distortion or because of the impingement of neighbouring structures (Plate 5.4).

Where ellipses are not in contact the individual



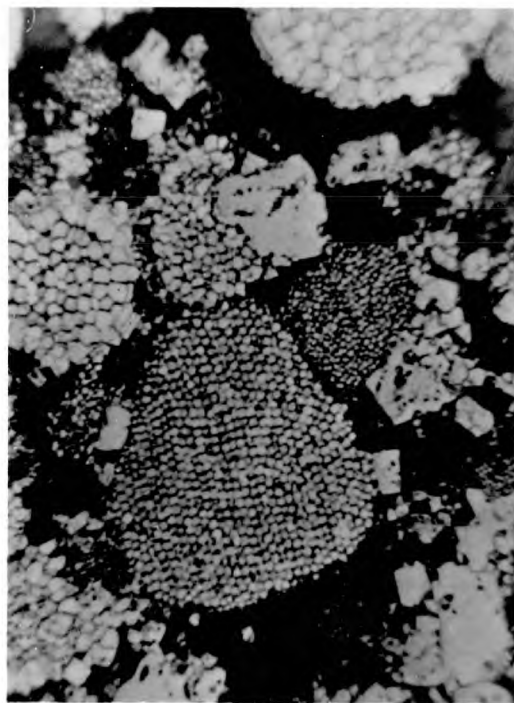
5.9

10 μ



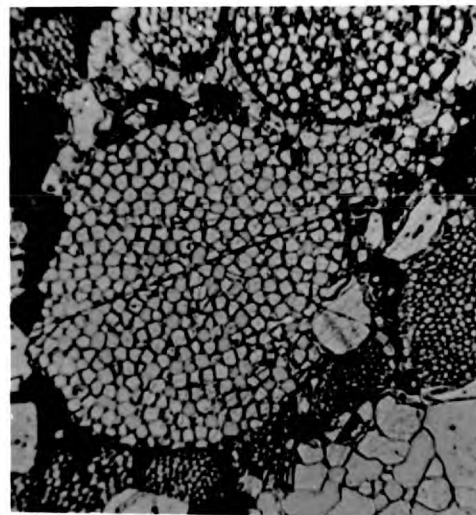
5.10

10 μ



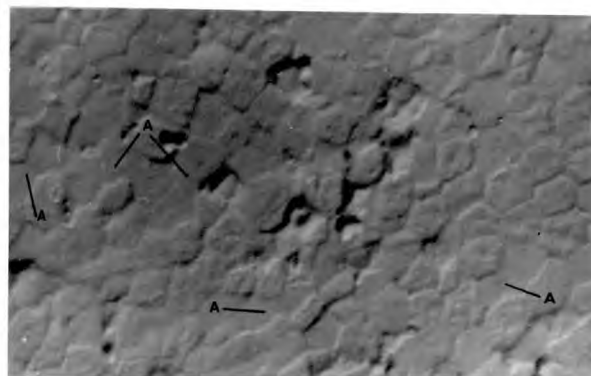
5.11

10 μ



5.12

10 μ



5.13

1 μ

Plate 5.9 Unimpinged spheres separated by rims composed of relatively large, radially arranged grains. The component grains of the upper sphere exhibit a concentric packing arrangement.

Plates 5.10 and 5.11 Sub-spherical structures showing well ordered arrangements of their component grains. The packing patterns are characterised by linear groups of grains defining two or three dominant and fairly uniform orientations.

Plate 5.12 Sphere showing local development of an ordered grain arrangement. The most conspicuous linear groups are those at the upper left, but the component grains are arranged in less distinct or less continuous rows at several other places in the sphere.

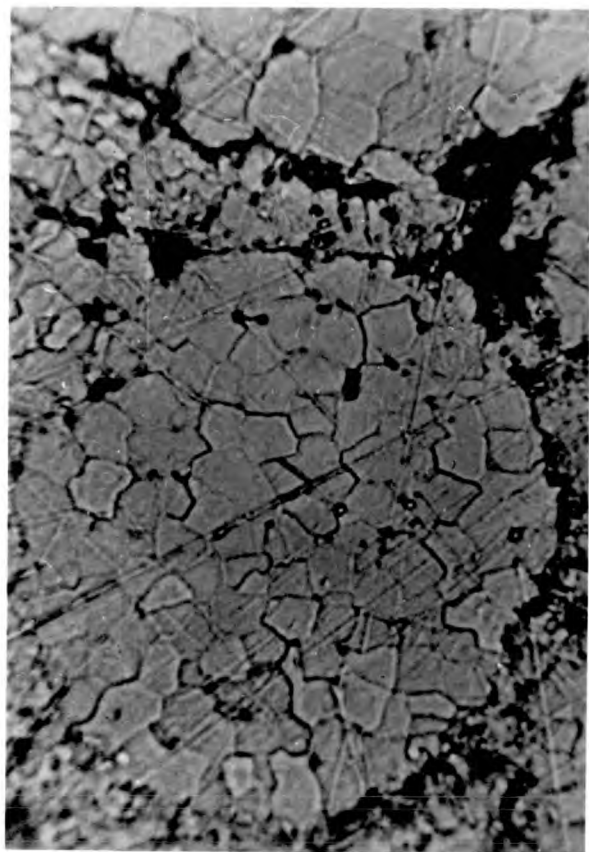
Plate 5.13 Electron micrograph (shadowed carbon replica) showing the typical development of partly ordered grain arrangements in spherical structures. The most conspicuous ordering is defined by the rows of hexagonal grains at the centre right. In the areas indicated A the surface relief (low in comparison to the surrounding grains) of two or more grains is almost identical, and the grain boundaries are either unobservable or difficult to discern. Note also the uniform surface relief of the rows of hexagonal grains at the centre right.

structures are usually surrounded by a rim of radially arranged grains (see Plate 5.20 and part of the margins of ellipses shown in Plates 5.7 and 5.21). The remaining interstitial space is generally composed of relatively coarse grains whose zone structures indicate a continuance of growth in the direction away from the nearest ellipse (Plates 5.7 and 5.20).

5.4 Arrangement, Shape and Internal Structure of Component Grains

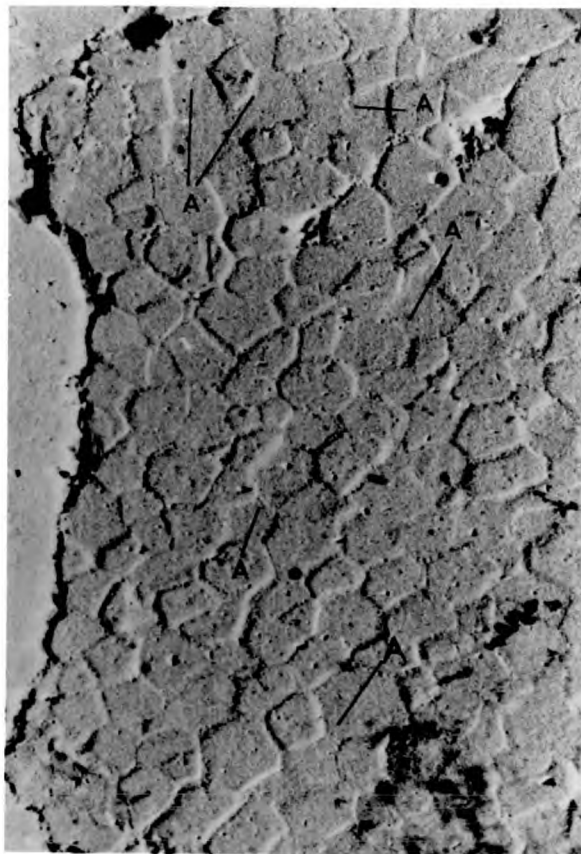
(1) Spheres A major feature of the internal structure of spheres is the development of an ordered arrangement of the component grains. This characteristic is most apparent in spheres whose component grains fall in the intermediate and lower grain size range (see for example Plates 5.8 to 5.12). With increasing grain size, there is a general tendency for the ordered structure to degenerate, and in the coarsest grain size spheres there are no special patterns of grain arrangement (Plate 5.14).

The internal sphere structure is sometimes manifested by a concentric arrangement of the component grains (Plate 5.9), but the most common form of ordering is defined by linear groups (a layered grouping in three dimensions) of two or more grains of similar shape or orientation. In many spheres, and especially those in the lower part of the grain size range, plane or gently curved linear groups of this type are regularly packed and continuous over the entire surface of observation (Plates 5.10, 5.11). From these, the most highly ordered structures, there is a continuous gradation (Plates 5.8, 5.12) to isotropic aggregates where the component grains show no regular patterns of ordering (see Plate 5.15, the central sphere in Plate 5.5, and the spheres in the centre and upper right of Plate 5.6). The most common spheres are only partly ordered and consist of semi-isotropic



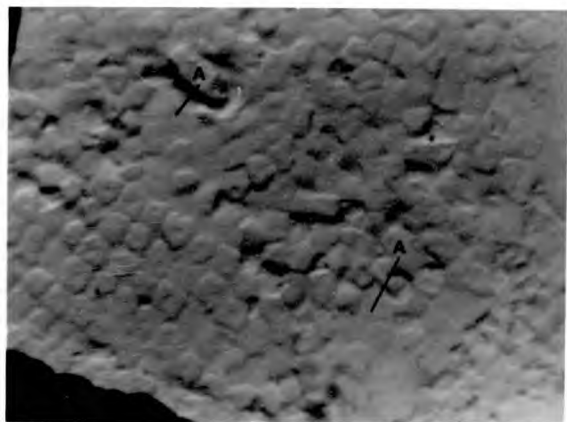
5.14

10 μ



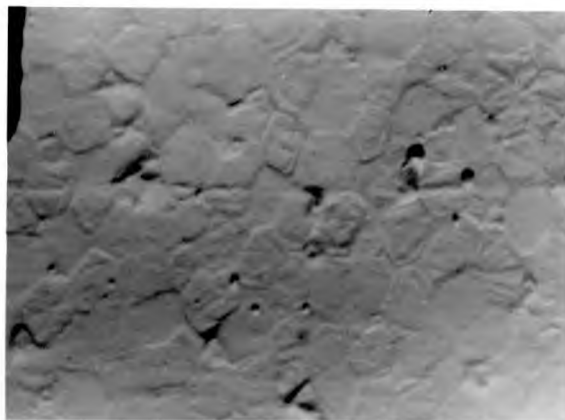
5.15

1 μ



5.16

1 μ



5.17

1 μ

Plate 5.14 Abnormally coarse grained sphere showing comparatively irregular shapes and disordered packing of the component grains.

Plate 5.15 Electron micrograph (shadowed carbon replica) showing the characteristic non-regular, hexagonal grain shapes, the plane or smoothly curved grain boundary morphology and the internal homogeneity of the component grains of a sub-spherical structure. The packing of the aggregate is disordered. The areas indicated A are referred to in the caption to Plate 5.13.

Plate 5.16 Electron micrograph (shadowed carbon replica) showing the local development of highly ordered packing of the component grains of a sphere. The ordered region in the lower left is composed of approximately square grains; at several points the corners of these grains are truncated, and there appears to be a continuous transition to non-regular and regular, hexagonal grain shapes. The areas indicated A are referred to in the caption to Plate 5.13.

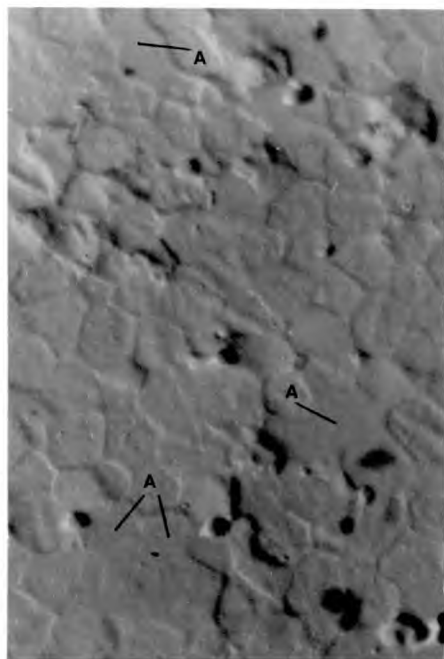
Plate 5.17 Electron micrograph (shadowed carbon replica) showing the simple euhedral zone structures developed in the component grains of a sphere. The zone structures are broadly conformable with the shape of the containing grains, but almost all the zones intersect the grain boundaries.

aggregates, containing several linear groups whose orientations tend to define a uniform structure for the sphere as a whole (see Plates 5.12, 5.16 and the rows of hexagonal grains at the centre right of Plate 5.13).

The number of differently oriented linear groups in a single sphere is variable. In the most highly ordered spheres, two or three major orientations predominate. In the less ordered types several discontinuous groups tend to have slightly different orientations, but statistically there are a much smaller number of preferred orientations. In aggregates of spheres there is no preferred orientation of the linear groups in different spheres.

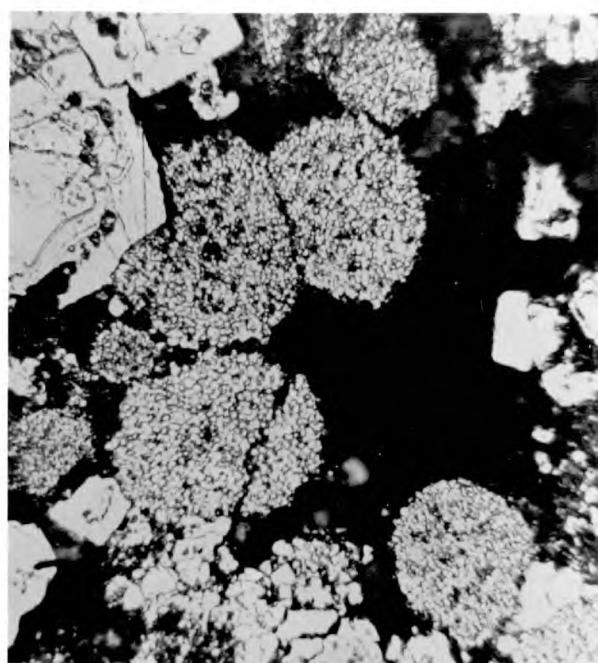
The coarsest grained spheres exhibit fairly irregular though equant grain shapes (Plate 5.14). For the remainder of the size range (including spheres with near-maximum grain sizes) the component grains are characteristically polygonal and have plane or slightly curved boundaries. The most common grain shapes are approximately non-regular hexagons (Plates 5.13, 5.15, 5.16, 5.18), but isolated clusters are sometimes composed of approximately square grains (lower left of Plate 5.16) or regular hexagonal grains (central right of Plate 5.13). A major contribution to the internal structure of spheres is due to the linear grouping of grains of similar shape.

On etched surfaces of carefully polished spheres, small or large groups of contiguous grains are often characterised by their remarkably uniform surface relief (see for example the alternating rows of high- and low-reflecting grains in Plate 5.8, the hexagonal grains at the centre right of Plate 5.13, the square grains in the lower left of Plate 5.16, and the areas indicated by the arrows A in Plates 5.13, 5.15, 5.16, 5.18). In some cases there appear to be only two or three major relief levels over the entire surface. The degree of uniformity of the surface level of single groups of grains is best illustrated



5.18

1 μ



5.19

25 μ



5.20

10 μ



5.21

10 μ

Plate 5.18 Electron micrograph (shadowed carbon replica) of the component grains in part of a spherical structure. In the areas indicated A small groups of grains exhibit a uniform, low surface relief; several of the grain boundaries in these areas are unobservable. Note that this mode of ordering persists despite the absence of regular patterns of packing of similarly shaped grains.

Plate 5.19 Spheres attached to the margin of a coarse grained host aggregate and facing a voidal interstitial region. The sphere margins in contact with the coarse grains are distorted, but the free surfaces facing the void tend to exhibit a spherical form.

Plate 5.20 Unimpinged, low elongation (1.5:1) ellipses rimmed by radially arranged grains. Note the diagonally trending row of high-reflecting grains near the centre of the upper ellipse. In the central and upper parts of the lower ellipse the component grains show incipient elongation.

Plate 5.21 Impinged and unimpinged ellipses showing moderate elongation, and partly rimmed by radially arranged grains. The ellipse at the upper centre (elongation 2.8 : 1) is composed of substantially equant grains. In the large ellipse at the centre of the illustration (elongation 2.5 : 1) many of the grains are elongate and exhibit a preferred orientation parallel to the major axis of the ellipse; a local concentric grain arrangement is developed in the lower left of this structure.

in those groups for which the surface dissolution (during etching) has been greatest. The surface of these grains appears at the lowest level, and the grain boundaries are frequently either unobservable, or only faintly evident (see the areas indicated by the arrows A in Plates 5.13, 5.15, 5.16, 5.18). Since a grain boundary is effectively subject to an independent dissolution rate, its manifest absence as a relief feature means that the contiguous grain surfaces are at the same level. Where the grain boundary is absent, this is an unambiguous interpretation; where the grain boundary is manifest, the grain surfaces may be at different levels. Linear groups of grains with similar surface relief constitute the second manifestation of the internal structure of spheres, and reinforces the effect due to shape orientation (see for example the alternating rows of high- and low-reflecting grains in Plate 5.8, the rows of hexagonal grains at the centre right of Plate 5.13, and the rows of square grains in the lower left of Plate 5.16).

The dissolution (or etching) rate of different lattice planes is variable, and depends directly on changes of bond strength, or stability, with crystallographic orientation. For low-index, close-packed planes, the dissolution rate is minimal, and increases to one or more maximum values at intermediate, high-index orientations. The dependence of etching rate on lattice orientation means that there is a preferred crystallographic orientation in clusters of grains whose etched surfaces are at the same level. The actual orientations that are preferred are not known, and cannot be reasonably inferred in the absence of fairly detailed knowledge of the relationship between dissolution rate and lattice orientation. However, some general conclusions can be drawn. For example, groups of grains with the highest relief etch most slowly and therefore, as a group, are characterised

by surface orientations which are closer to a low-index lattice plane (planes) than the surfaces of all other grains in the sphere. Similarly, groups of grains which etch to the lowest level are characterised by surface orientations which are closest to the maximum dissolution rate, high-index lattice planes. A definite preferred orientation exists in each of these groups, at least to the extent that members of one class of orientations do not coexist with members of the other class.

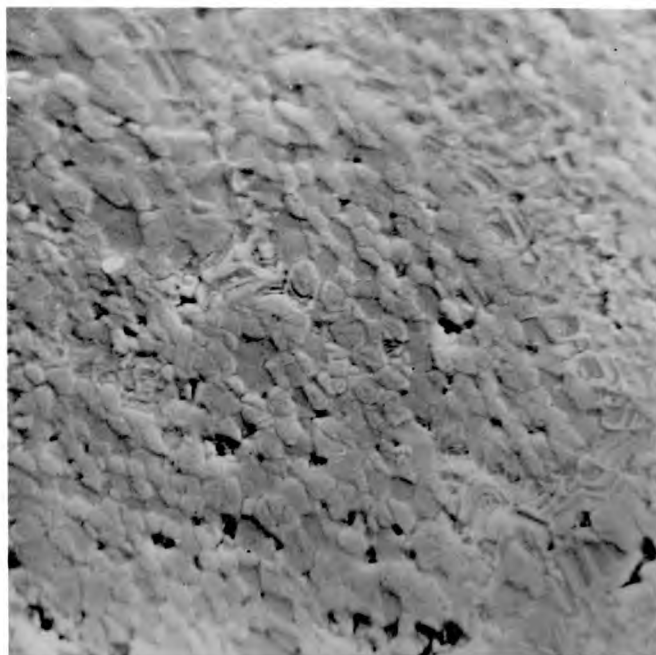
The component grains of most spheres are essentially homogeneous. The fine-scale surface texture observed on carbon replicas (Plate 5.15) is probably an artificial feature, though the sharp indentations which appear as pits are more likely to represent real voids. The component grains of many spheres exhibit simple, euhedral zone structures (Plate 5.17). In coarse grained spheres there are frequently several discrete zones in each grain. However, most zone structures consist of a single, narrow band which occurs near the margin of the grain and divides the latter into two main components (Plate 5.17). The zones are partly conformable with the enclosing grain boundary, though invariably they intersect it at some point.

Many spheres are almost fully dense. In most occurrences, intergranular pore space is less than about 10%, and some of this could represent damage produced during the polishing process.

(2) Sub-Spherical and Elliptical Structures The granular structure already described for spheres is also present in non-spherical structures which are only slightly or moderately distorted from the spherical form (Plates 5.5, 5.11). The same features, notably equant grain shapes, are usually observed in ellipses with axial ratios of up to about 2:1 (see for example the comparatively disordered packing of equant grains in the central ellipse in Plate

5·22

2 μ



5·23

1 μ

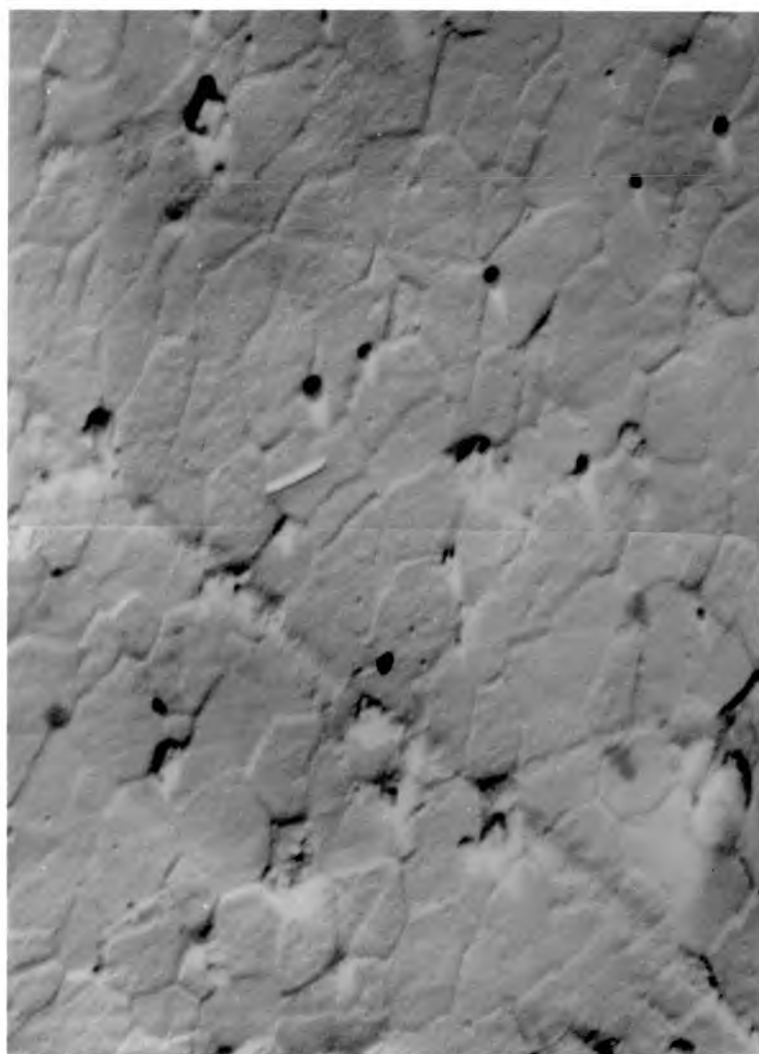


Plate 5.22

Direct electron micrograph showing a group of unimpinged ellipses. Elongate grains are well developed in the ellipse at the upper right (elongation 3:1), especially near its lower apex. Elongate grains also occur in the central ellipse, and in several other structures only parts of which appear in the illustration. Many of the elongate grains (notably those in the central ellipse and near the lower apex of the ellipse at the upper right) exhibit simple euhedral zone structures, which are manifested as fine, low-reflecting lines.

Plate 5.23

Electron micrograph (shadowed carbon replica) showing the approximately 6-sided grain shapes, the plane or smoothly curved grain boundaries and the internal homogeneity of the elongate grains composing an elliptical structure. Note also the absence of linear packing arrangements, other than that which is parallel to the grain elongation.

5.6, and the diagonal row of high-reflecting grains in the upper ellipse in Plate 5.20).¹

However, a major characteristic of elliptical and sub-elliptical structures is the development of elongate grains whose long axes are parallel to the major axis of the ellipse. Elongate grains occur in some ellipses with axial ratios of less than about 2:1 (see the ellipse in the centre of Plate 5.22, and also the incipient development of elongate grains in the lower ellipse in Plate 5.20), but are usually inconspicuous until the axial ratio of the ellipse exceeds about 3:1. However, even where the ellipse elongation is greater than 3:1, a few ellipses are composed of disordered, equant grains (see the ellipse in the upper centre of Plate 5.21). An intermediate stage in the development of elongate grains is illustrated by the ellipse in the centre of Plate 5.21, and an advanced stage is illustrated in Plate 5.23 and by the ellipse in the upper right of Plate 5.22.

At ellipse elongations of less than about 3:1, the linear microstructure defined by the elongate grains is frequently superimposed on recognisable patterns of grain arrangement corresponding to those observed in the spheres (see the diagonal row of grains in the centre of the ellipse in the centre of Plate 5.21, and the local concentric pattern in the lower left of this structure). At higher elongations, the linear microstructure predominates, and other patterns of ordering are either absent (Plate 5.23), or subordinate.

The elongation of all grains in a particular ellipse is approximately the same, and ranges up to a maximum of about 4:1. There is a general, but not entirely consistent, correlation between increasing elongations of the component grains and increasing distortion of the ellipse. In truly symmetrical ellipses, the long axes of the grains

generally exhibit a constant orientation in all parts of the ellipse. For less symmetrical shapes the major axes are often curved, and in these instances, the grain orientation exhibits a similar, curved trend.

Elongate grains have plane or slightly curved boundaries, and tend to be approximately 6-sided (Plates 5.22, 5.23). They may be internally homogeneous (Plate 5.23), or exhibit simple, euhedral zone structures (Plate 5.22).

PART B INTERPRETATION

From the foregoing descriptions it is evident that: (1) there is a continuous gradation of shape and internal structure between spheres and ellipses, (2) discrete spherical and elliptical structures have volumes which fall in approximately the same range, and (3) the component grain size range for spheres and ellipses is approximately the same. The continuity of the trends in (1), and the basic similarity of their structural features suggest that the origin of the spherical structures is closely related to that of the ellipses. Moreover, it seems probable that the most primitive form of these structures is represented by spheres, the sub-spherical and elliptical structures being modified or derived forms.

5.5 Significance of the Spherical Form

The separate identity of individual spheres and ellipses is represented by their discrete form, their component grain size uniformity, and their component grain arrangement. The independence of single structures is a fundamental property, and implies that the growth process was characterised by accretion or rearrangement of material around well defined, independent centres. Although truly spherical shapes are uncommon, a close approach to sphericity is a marked feature of many aggregates. This implies

that their growth history involved a special type of shape-determining mechanism, related to a fundamentally spherical form.

There are three possible ways in which spherically shaped aggregates could evolve, namely, (1) through ~~pseudo~~-morphism, (2) through shape adjustments controlled by surface tension, and (3) through diffusion controlled accretion.

(1) Pseudomorphism In principle, pre-existing spherically shaped structures could determine the mode of precipitation during their replacement by pyrite. Both the gross form of the spheres and their internal micro-structure might thus reflect, either directly or indirectly, equivalent properties of the original structures.

This mechanism has been proposed on several occasions in the past to account for both the **pyrite** spheres found in sediments (see for example Love, 1957) and the spheres associated with stratiform sulphide deposits (see for example Love and Zimmerman, 1961). The ~~pseudo~~morphed structures were ~~thought~~ to be bacteria, whose existence was inferred from the reducing environment of sedimentation or sulphidation, and from their supposed capacity to produce sulphur. However, it is now conceded that this explanation is inadequate, because there is no direct evidence of organic bacteria in the pyrite spheres of Recent sediments (Love, 1964, p. 14).

Replacement of other types of spherical structures remains a possibility. For example, volcanic rocks are well known to contain spherules, although these are usually large in comparison to pyrite spheres. Unavoidably, the possible connection of the spheres with volcanic structures must remain in doubt, since there are no relicts of volcanic material in the massive ore. However, the structural properties of the pyrite spheres in the Rio Tinto ore are essentially identical to those of spheres

found in Recent sediments, for which there can be virtually no question of pseudomorphism. For this reason, a pseudomorphic origin is discounted in the case of the pyrite spheres in the Rio Tinto ore.

(2) Shape Adjustments Controlled by Surface Tension

Since the structure of an amorphous precipitate is isotropic its free boundary surface is associated with a surface tension which is constant for all orientations of the boundary. This means that a discrete deposit of the substance achieves a minimum surface free energy when the deposit has a spherical shape. The boundary adjustments required to achieve this shape occur when the viscosity of the substance is sufficiently low to be overcome by the surface tension forces. At low (room) temperatures, these adjustments are spontaneous in immiscible liquids and in coacervate-type colloids (Kruyt, 1949, p. 433). They may also occur in the solid state, provided the temperature is sufficiently high to activate diffusion. Spheroidisation may even occur in crystalline materials (where one grain is completely isolated within another), but again the ~~temperature must be sufficiently high to~~ activate diffusion.

The importance of surface tension in determining the shape of pyrite spheres is widely acknowledged (see for example Chukrov, 1966, p. 339; Papunen, 1966, p. 124; Park and MacDiarmid, 1964, p. 128), and the capacity for spheroidisation to occur has led to the generally accepted theory that the spheres were initially in a colloidal state.

As a possible mode of origin for the pyrite spheres, solid state adjustments imply relatively high temperatures. The occurrence of spheres in low temperature, near-surface environments (e.g. Recent sediments) almost certainly implies that spheroidisation did not involve a crystalline or solid-amorphous substance. Indeed, the capacity for shape adjustments to occur at all in low temperature

environments indicates that the colloidal substance was characterised by a low rather than a high viscosity.

The initial substance of the spheres cannot have taken the form of an assemblage of bonded, or closely associated, crystalline particles of colloidal dimensions. In a colloidal suspension of this type, the surface area of the component crystallites is very much greater than that of the boundary surface of the macroscopic volume of precipitate. Hence, the surface area, and the free energy reduction achieved by spheroidisation of the bulk precipitate is negligible compared to that obtained by growth of the component crystallites. A controlled reduction of the area of the boundary surface of the precipitate (e.g. spheroidisation) only becomes possible when the internal phase (grain) boundary area is similar to the area of the boundary surface of the precipitate. However, if crystallite growth leads to the evolution of one or a few large crystals, subsequent surface adjustments will not occur by spheroidisation. The ordered structure of a crystal lattice means that the surface free energy of an isolated crystal is anisotropic, and therefore, that the equilibrium form is non-spherical.

Thus, it is evident that the initial sphere must consist of an amorphous substance, since an isotropic structure is required to ensure that the boundary free energy is uniform for all orientations of the boundary. However, the initial sphere cannot be composed of an aggregate of discrete particles of an amorphous substance. The energy associated with the boundaries between these particles is again very much higher than that of the free surface of the aggregate as a whole, and in this condition, the external surface of the aggregate cannot undergo shape adjustments controlled by surface tension. Even when there are only two particles, shape adjustments will not lead to spheroidisation if the boundary between these

particles intersects the external boundary surface. Only when the external surface is isolated, and has a significantly greater area than internal boundaries, will spheroidisation occur. In reality, this probably means that the amorphous substance is physically continuous within the limits of discrete volumes of precipitate.

In view of the above discussion it is evident that the terms colloid, gel or sol (Kruyt, 1949, p. 2) do not properly describe the structure of a substance which can spheroidise under the influence of its own surface tension. In the context of colloids this substance is described by the term coacervate (Kruyt, 1949, p. 6), and its essential property is an amorphous structure. In the present discussion the main concern is with the amorphous quality of the structure, and for this reason, the explicit terms amorphous substance, amorphous structure etc. will be used in preference to the term coacervate, whose usage appears to be generally restricted to organic colloids.

(3) Diffusion Controlled Accretation In a semi-rigid supporting medium (e.g. a gel), direct sedimentation of a precipitate is inhibited. If the precipitate is not entirely adsorbed, a diffusion field will develop, and particles of the precipitate will diffuse to, and accrete at a number of isolated centres. If the diffusion field is isotropic, the accreting bodies will be spherical. A number of experimental studies suggest that diffusion controlled accretion is an important factor in the growth of multigranular spherical bodies in porous gel media (e.g. Bradford, 1926, p. 790; Kinoshta, 1931, p. 303; Watanabe, 1942, p. 168).

Since the sphericity of bodies growing by diffusion controlled accretion is not determined by surface tension, the spherical form can develop independently of the internal structure of the body. For example, the accreting particles may be discrete crystallites or particles of

amorphous colloid. The latter could retain their identity after incorporation in the spheres, or they might coalesce spontaneously with the main spherical body.

In the natural environment it is conceivable that the requisite conditions for a diffusion controlled mechanism could exist. An isotropic supporting medium could be provided by deposits of silica gel or other fine grained decomposition products derived during leaching and replacement of a host rock. Relatively static conditions could exist in these media where they were protected from high velocity ore-bearing solutions. However, the uniformity of the diffusion field that could actually be attained under natural conditions might be a major limitation. Three main factors could lead to non-uniformity: (i) the presence of heterogeneties in the structure of the fine grained supporting medium, (ii) a non-uniform distribution of the growing spheres, and (iii) directed flow of the nutrient solutions. Although the influence of these factors is probably always present, their actual importance in causing significant modifications to the diffusion field is largely a matter of speculation.

In summary it is concluded that:

- (1) The spherical form is not a pseudomorphic feature, but
- (2) was determined either
 - (a) by surface tension, in which case the initial sphere was composed of a physically continuous amorphous substance,
 - or (b) by diffusion controlled accretion, in which case the initial sphere was composed of either
 - (i) a physically continuous or discontinuous amorphous substance,
 - or (ii) an assemblage of discrete crystallites of colloidal dimensions.

5.6 Significance of the Sphere Microstructure

When the particles accreting to a sphere are rigid crystallites of different shapes, their arrangement in the sphere must be largely fortuitous, although a concentric pattern may develop as a result of particles being incorporated at an advancing spherical surface. Inter-particle attractions tend to maximise the packing density, but the extent to which this occurs is greatly limited by the particle shape and by the non-orienting capacity of the inter-particle forces (see the discussion by Chalmers, 1958, p. 293, who points out that metals crystallising from their melts cannot grow by accretion of multi-atomic growth units (domains)). The dense packing of the component grains in pyrite spheres means that these grains cannot be identified with the accreting crystallites.

Even if the original crystallites were extremely small, and subsequently grew, their initial random arrangement (and perhaps a concentric pattern) is likely to persist in the final microstructure. However, in many of the observed spheres, the microstructure is characterised by marked ordering, which takes the form of (1) a linear, and less frequently a concentric, arrangement of the component grains, and (2) the occurrence of preferred crystallographic orientations in small groups of grains. Except possibly for the concentric microstructures, neither of the features under (1) and (2) can be readily explained in terms of crystal growth in an assemblage where there is no initial linear arrangement or preferred crystallographic orientations of the crystallites. It is therefore concluded that the initial spheres were not composed of an assemblage of discrete crystallites, and that the original composition of the spheres involved an amorphous substance.

However, the component grains of the spheres cannot be identified with discrete particles of an amorphous substance. Adjustments leading to full compaction of the

amorphous particles must occur under the influence of the surface tension associated with each particle, and since these adjustments will probably also occur after coalescence is complete, the final aggregate should exhibit an equilibrium boundary configuration. Although there is a high incidence of grain boundaries intersecting at 120° , triple-point junctions, the presence of square grain shapes (Plate 5.16) cannot be reconciled with surface tension adjustments. Moreover, since the growth structure which develops through the accumulation of independently accreting particles could only be spherical and concentric, the observed patterns of linear grain arrangement cannot be accounted for. On the other hand, the commonly observed continuity of the regular patterns of grain arrangement over the entire surface (section of observation) of a sphere strongly suggests that the amorphous substance was physically continuous throughout the sphere volume. In fact, there is considerable supporting evidence for this, and the evolution of a polycrystalline microstructure from a pre-existing physically continuous amorphous precipitate is discussed below.

The Growth Process The capacity for amorphous compounds to crystallise is well known, and is exemplified by the devitrification of glasses. Neglecting for the moment the nucleation step, the transformation involves growth of discrete crystals at the expense of the parent amorphous matrix.

As implied by the presence of euhedral zone structures, (Plate 5.17) the growth habit of the component grains of the observed spheres was crystallographically determined. Moreover, the zone structures usually intersect the grain boundaries, indicating that the latter are not growth surfaces, but compound boundaries determined by the geometry of impingement. The development of square grain shapes in groups of grains showing a strong preferred

crystallographic orientation (Plate 5.16) might well represent special conditions where the growth habit is cubic and where the orientation of neighbouring grains is identical; under these circumstances, the impingement surface, or grain boundary, will be parallel to the growth surface, and the resulting grain shapes will be cubic. Elsewhere the grain shapes are approximately hexagonal. The mode of impingement leading to these shapes is not known, but it is significant to point out that similar aggregates of sub-micron sized hexagonal grains, incorporating plane or slightly curved boundaries, are generated as a result of controlled crystallisation in certain glasses (Kingery, 1960; Plate 10.16; McMillan, 1964, p. 125).

In view of the dense packing of the pyrite lattice and the probable presence of water in the initial amorphous precipitate, it is almost certain that the amorphous-crystalline transformation would involve a volume decrease, and hence the generation of pore space. In many spheres there is direct evidence for porosity, though in others pore space is apparently absent or occupies an extremely small volume. Love and Amstutz (1966, p. 291) suggest that the voids are subsequently infilled. This explanation might account for spheres in which the component grains are zoned, and where there is therefore direct evidence for a compositional change. However, the significance of the zoning is difficult to assess, especially because there are spheres containing zoned grains which also contain pore space. Relatively pore-free spheres in which the component grains are homogeneous suggest that densification is achieved by means of a two-way diffusion process operating between the sphere and the external environment during at least part of the crystallisation period - i.e. non Fe,S components (presumably water) diffuse from the sphere, and Fe,S components diffuse into the sphere.

The Nucleation Stage

The uniformity of the grain size in single spheres suggests that for all grains nucleation was simultaneous, and the growth rates equal. Moreover, the grain size uniformity implies that the distribution of the nucleation sites was essentially uniform.

However, in spheres where the grain arrangement is ordered, the distribution of nuclei is not isotropic, but indicates that different sites are inter-related. To account for the simultaneous generation and the distribution of nucleation sites two mechanisms are considered:

- (i) The nuclei could be pre-determined at sites inherently favourable for the initiation of growth (heterogeneous nucleation; Kingery, 1960, p. 297); the heterogeneities which constitute these sites could take the form of impurity particles, or local regions of relatively high atomic ordering.
- (ii) Nucleation could occur at sites determined by diffusion within the sphere. When the amorphous substance exists under conditions of a metastable internal equilibrium, diffusion currents could be established about a number of centres. When disequilibrium conditions are introduced, the resulting nett transfer of material might be initially related to these centres where nucleation would ensue.

If diffusion controls the nucleation process, then at the time of nucleation, single spheres must be regarded as closed systems. It is evident, from the absence of radial grain size variations and radially arranged elongate grains (except in rims (Plate 5.9) which are usually interpreted as secondary overgrowths; see for example Kalliokoski, 1966, p. 880) that the controlling diffusion was not directed into, or out from the sphere.

In a homogeneous amorphous substance it is reasonable to suppose that centres of heterogeneous nucleation (see for example, the glass ceramics described by McMillan,

1964 and Kingery, 1960) and centres of equilibrium diffusion are uniformly distributed. In a general way, this accounts for the grain size uniformity of the pyrite spheres. Moreover, if the amorphous substance is isotropic, it is likely that the distribution of the nucleation sites will be similarly isotropic. This relationship provides a reasonable explanation for the microstructure of spheres or parts of spheres where the component grains have no special ordered arrangement.

However, in spheres where the component grains are ordered, isotropic nucleation does not apply. In order to account for the regular patterns of ordering, it is proposed that at the time of nucleation, the amorphous substance possessed a long-range ordered structure. It is reasonable to suppose that a macroscopic structure would have a strong influence on both the distribution and orientation of nuclei. For example, periodic regions of relatively high atomic ordering or dense packing could directly provide the centres for heterogeneous nucleation. Equilibrium diffusion could be influenced by the anisotropy of the structure.

The most direct evidence for the existence of an ordered structure in the initial amorphous substance is the occurrence of small groups of grains with different preferred crystallographic orientations. Grain orientation is determined at the nucleation stage, and similar orientations imply a common orienting factor. In the stress-free environment implied by the existence of spherical shapes, this factor is most likely to be related to the amorphous structure. In regions where the ordering is sufficiently high, the generation of nuclei will involve significantly less diffusion for some nucleus orientation than for others. Hence, certain nuclei will be created more easily than others, and the resulting grains will have a preferred orientation. Since different regions could have

different types of ordering, the preferred orientations could be dissimilar in different groups of grains.

It is necessary to emphasise that the actual crystallisation of the spheres is only the final stage in what is probably a complex sequence of events, involving changes of composition, viscosity and structure. The pre-crystallisation changes are envisaged as follows.

An isotropic amorphous substance is precipitated, and accumulates into spherical bodies. In its initial form the amorphous sulphide has a low viscosity, and the spheres can distort under the influence of their own surface tension. Following precipitation, diffusion occurs within the spheres and perhaps also to the external environment, leading to increased ordering, densification and increasing viscosity. At an advanced stage, a long-range ordering is developed. At this point, the surface tension becomes anisotropic, and at the same time the viscosity has risen sufficiently high to inhibit changes of shape from the spherical form. The stage at which crystallisation is induced depends on the rate at which the amorphous structure can adjust itself to changing external conditions. If adjustments occur under equilibrium or near-equilibrium conditions, the crystallisation event will represent the final stage in a sequence of continuous changes. On the other hand if ordering proceeds slowly in comparison to changes in the external conditions, crystallisation will tend to occur at an earlier stage, and could be induced before significant development of a long-range structure.

In principle, the grain size variation between different spheres can probably be correlated with variations in the structure or composition of the initial precipitate. For example, precipitates in which the initial ordering is relatively high are likely to provide a greater density of heterogeneous nucleation sites than precipitates with a low initial ordering. This prediction is confirmed by

observations in as much as the most ordered microstructures (reflecting high initial ordering) are confined to the intermediate and fine grained spheres (reflecting comparatively high nucleation density). A decreasing amount of water in the initial amorphous structure could also provide a greater density of heterogeneous nucleation sites, by increasing the volume of regions which are closely packed with respect to iron and sulphur.

The intimate coexistence of spheres with different compositions or structures of the initial precipitate (i.e. spheres with different grain size characteristics) can be explained in two ways. Different types of precipitate might be related to different generations of precipitation. There are no reliable microstructural criteria to test this possibility, but in view of the continuous nature of the grain size variation, its applicability, as the sole controlling factor, seems doubtful.

The alternative explanation is to regard the evolution of different types of precipitate in terms of segregation from an essentially single, homogeneous deposit. Different types of precipitate could be regarded as different phases, and this mechanism would thus be somewhat analogous to the amorphous phase segregation observed in certain glasses (McMillan, 1964, p. 44). Following the phase separation, continued densification would lead to isolation of discrete volumes of precipitate, which would spheroidise under the influence of their surface tension. The size of the spheres would depend on the magnitude of their surface tension (i.e. increasing surface tension forces can support the shape of progressively larger spheres) which in turn depends on the viscosity of the precipitate. Thus, where a particular type of precipitate segregates into a comparatively large, continuous volume, subsequent changes would produce a cluster of spheres of similar size and similar component grain size.

In the observed aggregates, clustering of spheres of similar size and similar grain size is in fact a common mode of occurrence (Plate 5.1). In certain instances, spheres are associated with comparatively extensive and homogeneous, fine grained aggregates in which it is difficult or impossible to recognise spherical forms. These aggregates could represent crystallisation at the stage immediately following the phase separation, but prior to spheroidisation.

5.7 Significance of the Shape and Microstructure of Ellipses

In sect. 5.5 it was concluded that two shape-determining mechanisms could account for the evolution of the spherical structures. Corresponding to these mechanisms, there are two potential modifying factors which constitute the possible modes of origin for elliptical structures:

- (1) Distortion of pre-existing spherical bodies; this mechanism has been suggested by Kormilitzyn (1963) to account for the elliptical shapes of previously viscous bodies of galena and sphalerite.
- (2) Non-uniform, diffusion controlled accretion leading to the direct growth of non-spherical bodies. This mechanism could be operative, for example, in a loosely packed matrix composed of fine grained clay minerals with a preferred dimensional orientation.

Since the observed spheres are the end product of an evolution involving several changes in the state of the initial sulphide precipitate, the question of distortion will obviously be clarified by knowing at what stage the deformation could have occurred. For four reasons it can be shown that the crystalline structure of non-spherical bodies is not distorted:

- (i) In some ellipses, the component grains are equant (see Plate 5.6 and the ellipses in the upper centres of Plates 5.20, 5.21), or have axial ratios which are less than that of the ellipse itself. In these

occurrences the amount of deformation implied by grain elongation conflicts with that implied by the elongation of the overall structure.

- (ii) In non-spherical bodies, both equant and elongate grains frequently contain euhedral zone structures (Plate 5.22). As shown in sects. 8.3.1 (2) and 8.3.2 (2), the plane configuration of the zone segments indicates that the polycrystalline aggregates were not plastically deformed.
- (iii) Distortion of the crystalline structure by cataclastic displacements cannot be reconciled with the dense packing of the component grains (see sect. 8.3.1 (1)). Moreover, the similarity of the grain size range in spherical and non-spherical bodies strongly suggests that fragmentation has not occurred.
- (iv) Distortion by a diffusional mechanism is inconsistent with the presence of euhedral zone structures (see sect. 8.3.1 (3)), and is difficult to reconcile with the similarity of the grain size range in spherical and non-spherical bodies.

It is concluded, therefore, that if initially spherical bodies were distorted, the deformation must have occurred at a pre-crystalline stage - i.e. the initial amorphous substance already occupied elliptical bodies prior to crystallisation.

However, an identical situation could arise if the elliptical structures grew directly and developed their shapes as a result of non-uniform accretion of the initial amorphous substance. Despite the pre-crystalline similarity of bodies derived by distortion and by direct accretion, it is possible to discriminate between the two modes of origin on the basis of the observed internal microstructure.

Diffusional accretion to spherical bodies differs from accretion to non-spherical bodies only in so far as

the amount of material accumulating at different points around the perimeter is constant for spheres and variable for non-spherical shapes. There is no reason to believe that the internal structure of the accumulated material would be different in the two cases. Moreover, the similarity of the grain size ranges implies that the compositional variation for spheres is the same as that for non-spherical bodies. Therefore, since both the internal structure and the composition of the accumulated material is similar for spherical and non-spherical bodies, the internal microstructure should be essentially the same in both cases. In reality, the more strongly distorted ellipses are characterised by the presence of elongate grains, which are always absent from spheres.

The preferred orientation of elongate grains in elliptical and sub-elliptical structures implies that the distribution of nuclei is such that the inter-nucleus spacing is at a maximum parallel to the major axis of the ellipse, and at a minimum parallel to the minor axis. This distribution suggests that the nucleation may have been controlled by a special relationship between the shape of a body and a diffusion field connecting it to the external environment. On this view, diffusion along the minor axis of an ellipse would be more rapid (high nucleation frequency) than along the major axis (low nucleation frequency). In principle, anisotropic diffusion seems feasible, but there are three microstructural observations which indicate that this explanation cannot account for the distribution of nuclei.

- (i) From the microstructure (excluding rims composed of radially arranged grains) of spheres, it is evident that the distribution of nuclei is independent of both the spherical form (except in the case of concentric grain arrangements), and the proximity of the sphere margin. That is, the distribution of the nucleus sites was controlled only by the internal structure

and/or composition of the sphere, and not by a diffusion field connecting it to the external environment. It is reasonable to suppose that the same conditions apply to non-spherical bodies.

- (ii) If diffusion operated to the external environment, the nucleation frequency could be expected to change not only from one diffusion direction to another, but also along these directions. This means that the grain size, and probably also the grain elongation, would vary continuously from the centre to the margin of an ellipse. This prediction is not borne out by observations, which indicate that both the grain size and the grain elongation are markedly uniform in single structures.
- (iii) If diffusion to the external environment operated during nucleation, it would be likely to operate during growth. Under these conditions, the grain shapes would probably be determined by the diffusion directions and would therefore be elongate and radially arranged. Microstructures of this type are not observed in ellipses showing substantial elongation.

From the preceding discussion, it is evident that a diffusional accretion mechanism was not responsible for the development of elliptically shaped structures. The microstructural dissimilarities between spherical and elliptical bodies cannot be explained by this mechanism, either in terms of differences in the structure or composition of the accumulated material, or in terms of the nucleation event.

On the other hand, the distortion mechanism provides a direct explanation for the microstructural differences. If the nuclei are more or less pre-determined in the initial spherical structure, these sites will undergo relative displacements corresponding to the geometry and amount of deformation of the sphere. The inter-nucleus spacing will decrease parallel to the compression axis, and increase

parallel to the tension axis. Subsequent growth at the nuclei will lead to the development of elongate grains with their long axes parallel to the tension axis. For homogeneous deformation, the nucleus displacements will be uniform, and hence the resulting grain elongation will be constant, and the grain size uniformity will correspond to that of the equivalent sphere. With increasing deformation, the nucleus displacements, and therefore the grain elongation will increase. For small deformations, the grain elongation will be small, and the patterns of nucleus distribution determined by a pre-existing long-range structure in the amorphous substance are likely to be partly evident in the final microstructure. For large deformations, the grain elongation will be greater and, together with the preferred orientation, will tend to obliterate the potential pattern of grain arrangement in the parent sphere. These predictions are abundantly confirmed in the observed microstructures.

5.8 Discrimination between Surface Tension and Diffusion Controlled Accretion as the Spherical Shape Determining Factors

Since a diffusion controlled accretion mechanism cannot account for the development of non-spherical structures, it seems highly unlikely that its operation could be confined to spherical structures alone. Coexisting spherical and non-spherical structures commonly exhibit the same grain size, and therefore were probably derived from the same initial precipitate and subject to similar external conditions. It is scarcely credible to interpret these relationships on the basis of two independently operating mechanisms.

It thus becomes evident that the shape determining factor for spherical structures is their surface tension. This conclusion is directly substantiated by the shape

relations observed in a few special occurrences where spheres are partly isolated in voids and partly attached to crystalline grains belonging to the host sulphide aggregate (Plate 5.19). The surface of attachment may be flat or more complex, but the free surface facing the void tends to be spherical. Unlike the distorted forms in close-packed aggregates, these occurrences have a unique implication. The presence of a void means that external stresses could not have been transmitted to the sphere. If the spheres initially had any shape other than that now observed (for example, if they were initially detached from the adjacent rigid grains), then the maintenance of a spherical form for the free surface could only be explained in terms of adjustments controlled by surface tension.

5.9 Age of Sphere Growth and Distortion, and the Causes of Distortion

In considering the environmental factors which led to distortion of the pyrite spheres, it is necessary to anticipate a major conclusion of this study, namely, that primary depositional fabrics are preserved in the massive ore (see Chapters 7 and 8). In relation to distortion of the spheres, this conclusion means that external stresses were not transmitted to the spheres via displacements in the host sulphide aggregate. This condition applies not only to aggregates of close-packed spheres/ellipses, but also to the disseminated occurrences where a relatively coarse grained matrix intervenes between neighbouring spheres/ellipses.

The absence of deformation in the host sulphide aggregate immediately suggests that the deposition of spheres which were later substantially distorted pre-dates the main mineralisation event. The pre-mineralisation age of many ellipses is directly confirmed wherever the micro-structure of the host aggregate (i.e. grain elongation and

internal zoning) indicates that its growth was controlled by the shape of the elliptical structures (see for example Plates 3.19(b) and 5.7).

Elliptical structures which define the axial plane cleavage to first generation folds (Plates 3.18, 3.19) represent the earliest known form of sulphide in the lode. It can be shown that the coarse grained pyrite bands which define these folds are undeformed (see sect. 8.3.4). Together with the main sulphide mass, the growth of these bands post-dates the evolution of the regional first generation fold system. The alignment of elliptical structures parallel to the axial plane of the folds strongly suggests that the distortion of the initial spherical form took place during the development of the original folds, which were subsequently pseudomorphed. Deposition of the initial sphere precipitate is early to the extent that it pre-dates the regional folding, which in turn, pre-dates the main mineralisation event. It is largely speculative to attempt to fix the time of deposition of the spheres more accurately than this.

Other occurrences of elliptical aggregates showing regular preferred orientations may also belong to a pre-folding stage. From one oriented sample it is known that bands of ellipses are aligned parallel to the regional slaty cleavage (sect. 3.2.2). Although fold structures are not associated with these bands, it seems reasonable to infer that the sphere distortion was produced during the first phase folding event.

Sediment consolidation could be an important factor leading to the distortion of spheres. This would imply an effectively syngenetic origin for the initial sphere precipitate. The preferred orientation of the ellipses could be regular or irregular, depending on the homogeneity of the host sediments and the uniformity of the consolidation process. Some occurrences of undulose bands of elliptical structures might be explicable in this way.

Disseminated spheres may represent pre-folding deposits which subsequently crystallised and behaved as rigid bodies during the later deformation. Alternatively, they may be connected with the main mineralisation event.

The configuration and internal structural continuity of laminar and irregularly shaped aggregates of close-packed spheres (Plate 5.1) implies that their deposition post-dates the regional folding. Spheres along the margins of these aggregates are frequently flattened or otherwise distorted against the surfaces of the surrounding coarse grains (Plate 5.6). In certain instances the marginal region is characterised by well developed zones of ellipses whose long axes are oriented parallel to the trend of the margin of the aggregate (Plates 5.2, 5.3). The structures developed in the marginal zone show gradational shape changes towards the centre of the aggregate where the close-packing of spheres involves less regular types of distortion. The localised marginal deformation in these aggregates was probably induced by the growth pressure due to continued accretion on the surfaces of the coarse, marginal grains. Since the spheres are viscous at the time of distortion, the stress applied by the advancing coarse grain surface will be transmitted with decreasing magnitude towards the centre of the aggregate. Thus, the deformation would be concentrated in the marginal zone, and the distortion associated with the close-packing of spheres in the central region may be due to the surface tension forces alone.

CHAPTER 6

EXPERIMENTAL RECRYSTALLISATION OF THE NATURAL PYRITE ORE

6.1 Introduction

Since recrystallisation is mainly a temperature dependent process, it should be possible to gain some understanding of whether the massive ore is recrystallised by comparing the temperature conditions of the regional metamorphism with the recrystallisation temperature for pyrite. The mineral assemblages in the country rocks (quartz-chlorite-epidote-albite) correspond to the lower greenschist facies and indicate that the maximum temperature attained during the metamorphic event was about 350°C (Hietanen, 1967, fig. 1). However, the minimum recrystallisation temperature for pyrite is unknown. Barnard (1967) succeeded in recrystallising pyrite under hydrothermal conditions at temperatures as low as 400°C, but these experiments involved solution of the material, bulk transport along a temperature gradient, and redeposition at a new site. There are no published reports of either in-situ or solid-state recrystallisation of pyrite. For this reason, it was decided to conduct a series of experiments with the main object of estimating the minimum temperature at which detectable recrystallisation occurs in the natural pyritic ore. It was also hoped to confirm certain predictions (see Chapter 7) regarding the basic microstructural changes which should occur when the natural ore is recrystallised.

The presence of undisturbed euhedral growth zones and equant grain shapes in the natural pyrite aggregates indicates that the starting material for the recrystallisation experiments is not plastically deformed (see Chapter 8). Therefore, if recrystallisation occurs in a hydro-

static environment, the driving force must be the reduction in the free energy associated with the grain to grain interfaces. From this point, it was decided to conduct three main groups of experiments and in each of these to study the effects of different environmental factors.

- (i) Dry Static Annealing Experiments If an aggregate undergoing recrystallisation contains no fluid phases then diffusion must occur in the solid state or in the vapour phase.

A series of experiments were conducted with the object of inducing recrystallisation under these conditions. Before sealing, the samples for these experiments were pre-heated, and in so doing, it was hoped to remove all traces of fluid phases trapped at grain boundaries or pore spaces and to obtain completely dry samples (fluid phases could be adsorbed during washing of the specimens, exposure to the room atmosphere, or could even take the form of trapped ore-bearing solutions).

- (ii) Wet Static Annealing Experiments When interstitial fluids are present, atoms are more easily released from the surfaces of grains, provided there is a significant energy of attraction between the solute atoms and the fluid, or solvent phase. When the latter is absent, there can be no additional energy reduction accompanying the release of atoms from the grain surface. Apart from volume diffusion in the crystal lattice, the actual release of atoms from the grain surface constitutes the rate-controlling step for the diffusion process involved in recrystallisation. Since this step can be facilitated by the presence of an interstitial fluid, the temperature required to activate diffusion, and hence recrystallisation, could be significantly lower when interstitial fluids are present than when they are absent.

Experiments were performed with the object of testing the influence of water. In six runs, water was deliberately introduced in the form of water of hydration combined with pyrophyllite and ferrous sulphate. The significance of the experiments performed under these conditions had to be finally re-evaluated since similar low temperature (400°C) recrystallisation effects were induced both in these samples and in others where water was not purposely introduced.

- (iii) Stress-Annealing Experiments When the component grains of an aggregate are plastically deformed, the activation energy for recrystallisation is lowered by an amount which depends on the magnitude of the deformation. Thus, the minimum temperature for strain induced recrystallisation is lower than in the case of solid state changes motivated by a surface free energy reduction.

In an attempt to explore the effects of strain energy, a series of experiments was conducted in which the samples were loaded near their fracture point, and at the same time, maintained at a constant temperature. In these experiments it was hoped to induce at least local and small amounts of plastic deformation, and under these conditions, to observe the temperature at which recrystallisation was initiated.

6.2 Starting Material

Three hand specimens of the natural ore were selected for the recrystallisation experiments. Macroscopically these samples are identical, and they represent the most isotropic type of pyrite aggregate in the lode.

The bulk of the starting material is composed of a fairly uniform aggregate with a grain size range of

approximately 5 to 50 microns. However, abnormally coarse grains are disseminated through much of the aggregate, and also occur in more or less irregular clusters and in veins. Some parts of the material contain lenses of more or less elongate grains, colloform structures, clusters of radially arranged grains and bands or clusters of abnormally fine grains. These miscellaneous aggregates complicate the overall microstructure, and since they can easily be distinguished in the recrystallised fabric, they will not be referred to at further length.

Because of its general uniformity, the main emphasis centres around the predominant fine to intermediate grain size component of the starting material. Typical examples of the microstructure of these aggregates are shown in Plates 6.1 and 6.2.

The grain shapes are irregular and except for some of the finer grained clusters, there is no tendency for polygonal shapes to develop. The shape complexity reaches an extreme where the grain boundaries acquire a fine-scale serrate morphology.

The majority of the grains are zoned, and those that are not are entirely restricted to the fine grain size component. Most zone structures are composed at least partly of alternating euhedral zones which show the normal reflectivity and smooth surface relief of pyrite. However, at the nucleus region of many grains there is frequently a relatively wide zone which exhibits a distinctly brownish colour and a rough surface texture. This part of a grain commonly contains sub-zones and is often associated with sub-microscopic inclusions or pits.

Most grains contain at least a few inclusions and these are commonly concentrated in discrete groups near the nucleus region of the growth zones. Most inclusions appear black in polished section and density determinations (see below) suggest that the majority, if not all,

of these inclusions are real voids and not polishing artefacts at the sites of pre-existing solid particles.

Chalcopyrite, sphalerite (sometimes quartz) and voids occur at interstitial sites and occupy a minor volume in the bulk aggregate. The proportions of the non-pyrite components were determined by point counts on carefully polished surfaces of two specimens. Chalcopyrite and sphalerite combined occupy an average volume of about 5%. The calculated average density of the two specimens is 4.57 gms./cc. A direct density determination (by displacement of water) gave an average value of 4.64 gms/cc. The general agreement between these values indicates that most of the black areas that were point counted as voids on the polished surfaces are in fact real voids, and were not previously occupied by solid particles. Direct density determinations on three other samples of the starting material gave values ranging up to 4.91 gms./cc. These measurements and comparisons between photographs of unetched surfaces of different specimens suggest that the average density of the starting material is around 4.7 gms./cc.

Most voids are essentially euhedral, though many are modified by irregularly shaped boundaries and these frequently reach an extreme development characteristic of leaching. A few small and irregularly shaped pores are frequently disseminated along the grain boundaries.

Weight losses were determined for three specimens of the starting material heated in air at 180°C - 200°C. One of these specimens lost 0.1% of its initial weight after 1 week at temperature. The other two specimens were heated for approximately 4 weeks and were weighed at intermittent stages. Both specimens lost approximately 0.3% of their initial weight after 4 weeks. The rate of loss was approximately linear, though it appeared to show a slight decrease towards the end of the 4 weeks. The fact that the specimens continued to lose weight for such

a prolonged period of time, and at a fairly uniform rate, strongly suggests that the weight loss is due to progressive oxidation of the surface of the specimen, and not to evaporation of interstitial fluids. This conclusion is confirmed by the fact that all three of the heated specimens developed brownish coloured surface films.

Although each of the three hand specimens selected as starting material is fairly homogeneous when considered as a whole, the very much smaller samples (approx. 1 cc.) cut from these specimens for the experiments show noticeable variations both within single samples and from one sample to another. Some properties of the microstructure are effectively constant, namely, the incidence of intragranular zoning, the structure of the zones, the distribution of intragranular inclusions, grain shape, the morphology of voids and the morphology of interstices occupied by chalcopryrite and sphalerite. However, the detailed fabric of the aggregate, the average grain size, the pore space density, the density of inclusions and the proportions of chalcopryrite and sphalerite may all exhibit noticeable variations. For example, in different parts of the same sample, the grain size distribution can vary between uni-modal and bi-modal (Plates 6.1 and 6.2). Thus, although the average grain size for all samples is probably about the same, the local grain size in a given specimen can show considerable differences from one part of the specimen to another. Similarly, the density of intragranular inclusions (compare Plates 6.1 and 6.2) and the pore space volume can show wide variations over a given sample; and from one specimen to another.

The variations in the initial microstructure present considerable difficulties in so far as it is almost impossible to detect any subtle changes induced by recrystallisation. For example, small changes of grain size, pore space volume or inclusion density cannot be established

with certainty. However, the general uniformity of the initial microstructure is quite adequate to serve as a reliable basis for the purpose of judging the more prominent changes accompanying recrystallisation. For example, marked changes of grain shape, internal grain structure, pore space density and morphology, and inclusion density can all be easily recognised in the recrystallised fabric.

6.3 Experimental Procedure

6.3.1 Static Annealing Experiments

The samples for the experiments were prepared by coring 9 mm. cylinders from the hand specimens, and by cutting these cylinders into individual specimens about 1 cm. long. The specimens were sealed in tubes with a close-fitting inside diameter, and for the high temperature, dry experiments, the sealed length was kept as small as possible (approx. 2 - 3 cm) in order to minimise the amount of sulphur vapour evolved from the specimen. In the wet experiments care was taken to ensure that the capsules were sealed at a good distance from the hydrous additives so that water was not lost during the sealing procedure; the capsules were about 8 - 9 cm. long. In both the dry and wet experiments Pyrex glass tubing was used up to 600°C and silica glass at higher temperatures.

Before sealing, the samples for the dry experiments were pre-heated in air at 180° - 200°C for times ranging between 1 and 770 hrs. (table 6.1). Some samples were sealed immediately after removal from the drying oven, others were exposed to the room atmosphere for up to 15 mins. before sealing. Microscopic examination of the dried samples reveals that the pre-heating does not induce any microstructural changes.

In six of the wet experiments water was introduced in the form of finely ground, hydrous pyrophyllite (see table 6.1). However, it was subsequently found more satisfactory

to use freshly precipitated, hydrated ferrous sulphate which releases all seven molecules of water at temperatures above 300°C . The quantity of hydrous substance required to achieve a pre-determined water pressure at a given experimental temperature and estimated volume was calculated roughly. By weighing out this amount a known quantity of water could be introduced to the specimen capsule. After sealing and estimating the internal volume of the capsule, the actual water pressure at the experimental temperature could then be re-calculated (see table 6.1). The estimated water pressures are minimum values and do not take into account the presence of any fluids trapped in the sample itself.

The capsules containing the specimens were wired to the insulating sheath of a thermocouple, and the thermocouple bead was adjusted to record the temperature at the centre of one end of the specimen and at a point less than 1 mm. from it.

The experimental temperatures were continuously controlled to within $\pm 5^{\circ}\text{C}$, and in most runs were monitored on a chart recorder. A furnace with a tube length of 30 cm. and a diameter of 4.5 cm. was used for most experiments. The temperature variation was measured roughly, and it is estimated that the specimens were subject to a maximum temperature gradient (end to end, and diametrically) corresponding to $\pm 5^{\circ}\text{C}$ from the set temperature. Thus the maximum total temperature variation during an experiment is $\pm 10^{\circ}\text{C}$. The only exception to this is the experiment for 45 days at 400°C (SA - 25) where, due to erratic behaviour of the controller, the temperature may have been well below 400°C for up to a week.

In the early experiments the specimens were brought to temperature over a period of several hours, because in trial runs it was noted that several samples shattered if subjected to a rapid increase of temperature. However,

it was subsequently found that the temperature could be increased to 700°C over a period as short as $\frac{1}{2}$ hr. In the early runs, at the completion of the experiment, the specimen was allowed to cool over a period of a few hours; in the later experiments the samples were quenched in an oil-bath and cold water, and reached a temperature of 300°C in less than 20 secs. and room temperature in less than a minute (table 6.1). At the completion of several experiments, note was taken of any condensed fluids or sulphur-bearing vapours contained in the specimen capsule (table 6.1).

6.3.2. Stress-Annealing Experiments

The loading jig employed in these experiments is a large though effective apparatus consisting of one fixed load platten and a movable platten connected through a simple lever system to a load arm. A sliding weight is attached to the load arm which is calibrated, and the position of the weight can be directly adjusted to give the desired load on the plattens. The lower platten is attached to the lever system through a crude universal joint, and when a load is applied, the plattens tend to be self-aligning. The apparatus can be used for loads up to 3000 lbs. All tests were performed in compression.

The problem of loading the specimens at elevated temperatures raised considerable practical difficulties. Owing to the rapid oxidation of pyrite at temperatures above approximately 450°C (Asensio and Sabatier, 1958), and the significant amounts of decomposition to pyrrhotite at temperatures above about 600°C (Kullerud, 1959), it is absolutely necessary (as in the static annealing experiments) that the samples are sealed from the room atmosphere at the same time as the load is applied. In the temperature range of oxidation, an inert gas atmosphere could be used. But at temperatures above 600°C , there is a significant sulphur-metal vapour pressure, and the samples

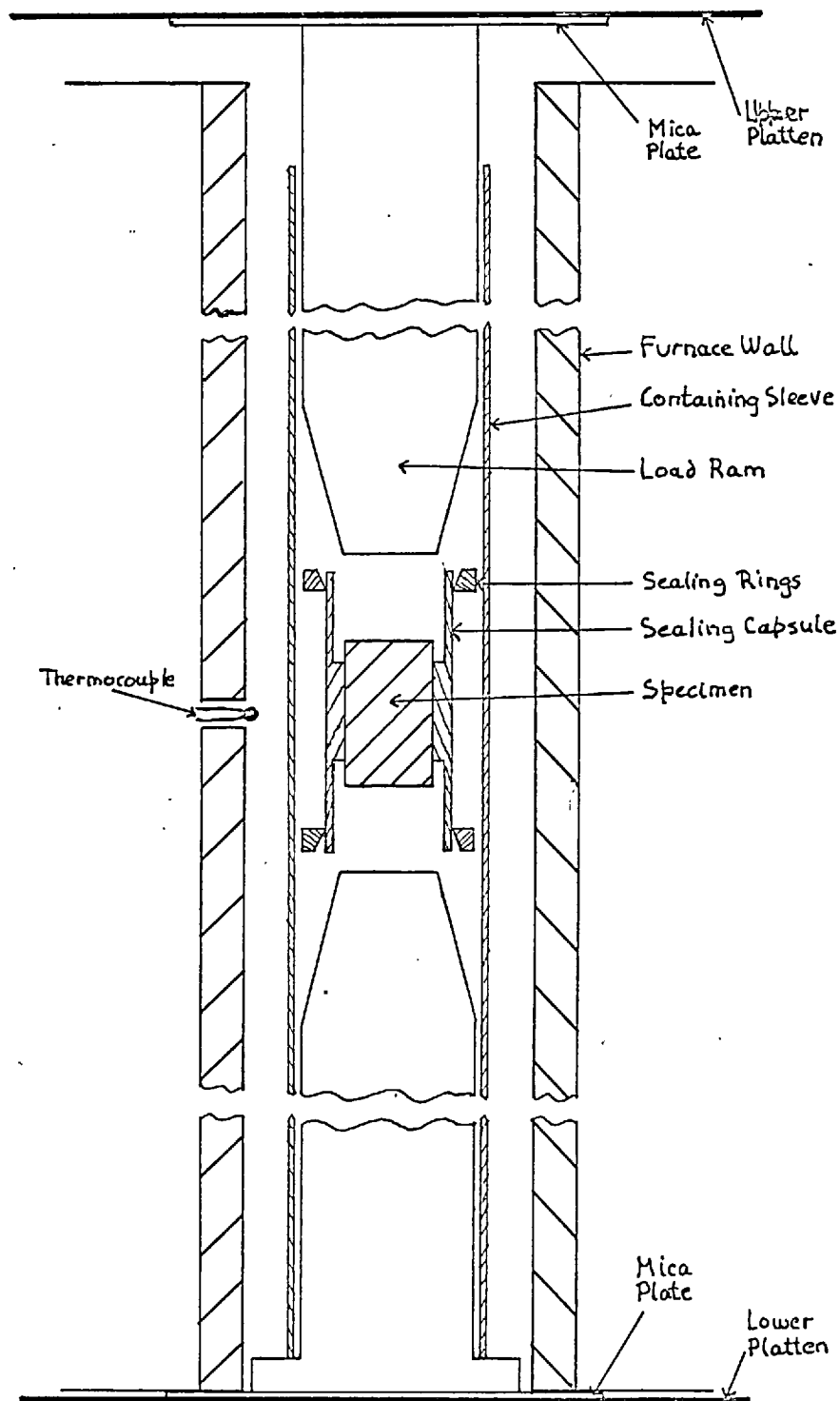


Figure 6.1 Scale drawing (twice actual size) of the loading and heating assembly used in the stress-annealing experiments.

must be completely sealed.

In trial experiments the samples were sealed in glass capsules with a melting point just below the experimental temperature. The capsule and the load rams were inserted in a close-fitting, stainless steel tube and the whole assembly was brought to the temperature of the melting point of the glass. A load was slowly applied and it was hoped to extrude the molten glass between the load rams and the containing tube, thus obtaining a seal. In one experiment, this procedure was partly successful, though the specimen did not align itself parallel to the axis of the load ram. In two other experiments the glass reacted either with the stainless steel casing or the specimen, and was still brittle at the experimental temperature. These difficulties seemed to suggest that it would be a time-consuming task to overcome the experimental problems, and this method of sealing was discontinued.

It was then decided to adopt the sealing technique used by Turner, Griggs and Heard (1954) in their experiments with calcite. This method was at first avoided because the seal is obtained by a strictly mechanical, metal to metal contact, and would therefore be less effective than a seal involving a molten glass to metal contact. However, although the metal to metal contact is not ~~completely~~ gas-tight, it certainly provides an effective seal, and for week-long experiments at 700°C the amount of decomposition is well within tolerable limits.

The final design adopted for the sealing, loading and heating assembly is shown in fig. 6.1. The loading rams were fabricated from an experimental, high temperature, sulphur resistant alloy supplied by International Nickel Ltd. The ends of the rams (diam. 12 mm.) were machined parallel and at right angles to their axis, and finally lapped with a magnesium oxide abrasive. The ends in contact with the specimen have a diameter just exceeding

the specimen diameter (i.e. 6 mm.), and are machined with 15° tapers. The thin-walled sealing capsules are machined from aluminium (for the 400°C experiment) and stainless steel (for the higher temperature experiments); the sealing rings are machined from stainless steel. The specimens fit tightly in the capsules and when the rams are in contact, there is a minimal free volume occupied by air. When a load is applied, the tapers on the rams come in contact with the inside of the capsule and effect a seal before the specimen is stressed. Thus the whole experiment can be brought to temperature before the loading is commenced. As the load is increased the sealing rings finally jam the capsule against the tapers, the capsule distorts and the rams eventually come in contact with the specimen. The whole assembly consisting of the loading rams, specimen and capsule are inserted in a close-fitting stainless steel tube to maintain a general alignment of the components during the setting up of the experiment and the initial loading. Mica plates, approximately 1 mm. thick, are placed between the load platens and load rams to reduce the heat flow from the furnace to the metal loading jig.

A rectangular furnace was constructed to fit neatly between the loading platens, and is supported on the lower platten, though insulated from it by the mica plate between the loading rams and the platten. A thermocouple is inserted through a hole in the furnace tube and the thermocouple records the temperature at the inside of the furnace wall opposite the centre of the specimen. It is estimated that the specimen is subject to a diametrical gradient of around 10°C , and an end to end gradient of probably as much as 20°C . Temperatures were continuously controlled on a chart recorder to within $\pm 5^{\circ}\text{C}$. However, the general uncertainty involved in obtaining reliable

temperature measurements under these conditions probably means that the accuracy of the experimental temperatures is little better than about $\pm 20^{\circ}\text{C}$.

The specimens for the stress-annealing experiments were prepared (by F. Yorke and Partners, London) in the following way. On one of the hand specimens selected as starting material, two parallel surfaces approximately 1 cm. apart were milled and ground flat. The specimen was then set on the bed of a drilling jig, and cores were cut at right angles to the milled surfaces. The resulting cylindrical samples are approximately 1 cm. long and are 6 mm. in diameter. The specimen ends are very close to being parallel, and at right angles to the cylinder axis. Although the loading is not strictly axial, the facility for the loading rams to be self-aligning through the universal joint attached to the lower platten almost certainly means that the ends of the specimen and the loading rams were in complete contact during the experiments. The axial alignment of the components in the specimen-loading assembly are quite adequate for the purpose of the experiments, which was to apply a constant and approximately axial load so that the specimens were stressed close to their fracture point.

An estimate of the fracture strength of the pyrite samples was based on the values given by Robertson (1955, fig. 20) for natural, two-, three- or four-crystal pyrite specimens (20,790 psi. at room pressure, and 70,000 psi. at 6,800 psi. confining pressure). To ensure that the samples remained intact, it was decided to load the 6 mm. diameter cylinders at 2,000 lbs. This corresponds to a stress of 17,700 psi. The samples in all experiments were loaded at the same stress level. The latter remained constant for the total duration of the experiment in all cases, except in the run conducted for 1 week at 700°C (CJ - 06) where the load fell below 17,700 psi. for inter-

mittent periods totalling probably about one third of the duration of the experiment.

Setting up an experiment involved the following procedure. After the loading assembly and furnace were positioned between the platens of the loading jig, the temperature was raised to approximately 200°C. At this point, in three experiments (CJ - 05, CJ - 07, CJ - 06), the temperature was maintained at 200°C for times ranging between 6 to 180 hrs. (see table 6.2) to ensure that the samples were dried in a similar way to the pre-heated specimens used in the dry, static annealing experiments. The samples in experiments CJ - 01 and CJ - 03 were not pre-heated. However, since the mechanical seal is not perfectly gas-tight, a certain amount of drying could probably occur during the experiments.

In all runs a load of between approximately 100 and 500 lbs. was applied at about 200°C, and this is considered to provide a fairly good seal between the capsule and the loading rams. From this point, the temperature was increased to the required level, and at the same time, the load was continuously adjusted to maintain the seal. The times to reach temperature (table 6.2) and the exact procedure followed in each experiment are variable and will not be described in detail.

At the completion of all experiments, there was no evidence of condensed fluids inside the sealing capsule and sulphurous gases could not be detected except in the experiment at 600°C where SO₂ fumes were recognised. By comparing the initial and final lengths and diameters of the cylinders it was found that none of the specimens had been recognisably strained except the sample in the long term experiment at 700°C (CJ - 06) which was shortened by approximately 10%. During this experiment it had been necessary to continuously adjust the load.

Experiment No.	Temperature of Experiment °C	Initial Condition of Specimen	State of Recrystallisation	Pre-heating time in air at 180°-200° (hrs.)	Time to reach temperature (hrs.)	Experiment Duration (hrs.)	Cooling Time (hrs.)	Condensed fluid in spec. capsule end of exp.	Fumes in spec. capsule end of exp.	Estimated pres. of added H ₂ O at temp. of exp. (atms.)	Hydrous additive
SA-06	300	Wet	Nil		7	182	2		Nil	ca. 5	Pyrophyllite
SA-01(a)	400	Natural	Incipient		100	184	5		H ₂ S		
SA-05(a)	400	Dry	Incipient	170	1	170	4		SO ₂		
SA-01(b)	400	Wet	Incipient		100	184	5		H ₂ S	ca. 5	Pyrophyllite
SA-05(b)	400	Wet	Incipient		1	170	4		H ₂ S	8.3	Pyrophyllite
SA-15	400	Wet	Nil		1	170	Quench	Yes	SO ₂	10.9	FeSO ₄
SA-25	400	Wet	Incipient		1/4	45 days	Quench	Yes	H ₂ S	10.6	FeSO ₄
SA-02(a)	500	Natural	Incipient		5	168	1/2	Yes	H ₂ S		
SA-20	500	Dry	Incipient	170	1	170	Quench	No	H ₂ S		
SA-02(b)	500	Wet	Incipient		5	168	1/2	Yes	H ₂ S	ca. 5	Pyrophyllite
SA-12	575	Dry	Incipient	770	1	170	Quench	No	SO ₂		
SA-03(a)	600	Natural	Incipient		9	168	5		H ₂ S		
SA-17	600	Dry	Incipient	1	1/2	170	Quench	No	H ₂ S		
SA-03(b)	600	Wet	Incipient		9	168	5		H ₂ S	ca. 5	Pyrophyllite
SA-21	650	Dry	Moderate	250	3/4	195	Quench	No	H ₂ S		
SA-26	700	Natural	Substantial		6	115	2				
SA-27	700	Natural	Substantial		5	11	2				
SA-07	700	Dry	Substantial	410	24	170	4	No	SO ₂		
SA-11	700	Dry	Substantial	770	3	170	Quench	No	SO ₂		
SA-10	700	Wet	Substantial		1/2	180	Quench		SO ₂	ca. 4	Pyrophyllite

Table 6.1 Details of static annealing experiments. Fine grained Rio Tinto pyrite as starting material.

6.4 Microstructural Observations and Results of the Experiments

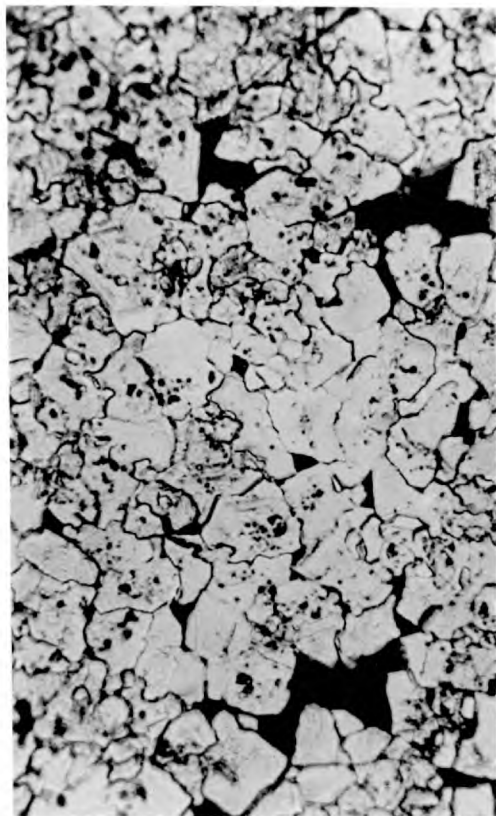
At the completion of an experiment the sample was mounted in cold-setting plastic and polished. After examining the unetched specimen, a representative half of the polished surface was etched. Cylindrical samples were polished on surfaces both parallel and at right angles to their axis to test whether there was any microstructural variations correlable with the temperature gradient in the furnace. In all cases there were no such variations, except that along the upper surface of the high temperature (600°C and above), statically annealed specimens, a few grains of pyrrhotite and a rough surface texture had developed, apparently as a result of the evaporation of sulphur.

The results of the microstructural observations for the static annealing and stress-annealing experiments are presented separately below.

6.4.1 Static Annealing Experiments

Table 6.1 summarises the conditions and results for 20 experiments performed between 300°C and 700°C . Samples denoted wet and dry were prepared and subjected to the conditions described in sect. 6.3. Samples denoted natural were cut from the starting material and allowed to dry in the room atmosphere, but were neither pre-heated, nor annealed in the presence of added water.

In the statically annealed samples, there is a progressive increase in the incidence of microstructural changes with increasing temperature. The fabric of the sample annealed at 300°C in the presence of water (SA - 06) is indistinguishable from the microstructure of the starting material. In describing the changes produced in the specimens annealed at and above 400°C , it is convenient to distinguish three stages of recrystallisation. These are: incipient, moderate and substantial recrystallisation



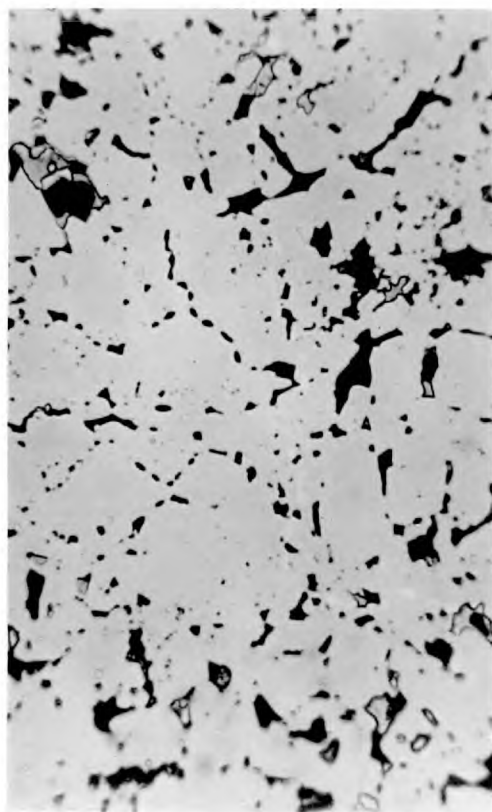
6.1

25 μ



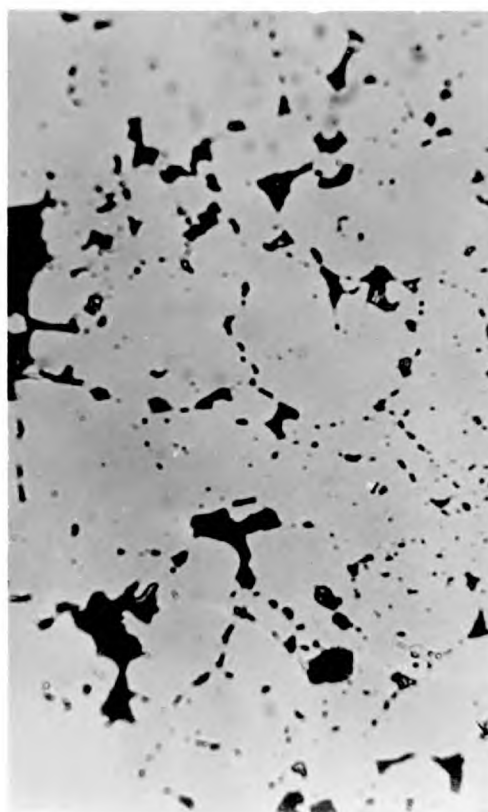
6.2

25 μ



6.3

25 μ



6.4

25 μ

Starting Material:

Plates 6.1 and 6.2 Microstructure of the fine grained, pyritic ore (San Dionisio lode, Rio Tinto) used for the recrystallisation experiments.

The fabric illustrated in Plate 6.1 is fairly representative of aggregates containing a high inclusion density and showing a uniform grain size. Euhedral zone structures are evident, but not clearly defined. Inclusions are generally concentrated near the nucleus region of a grain. Intergranular pore space is euhedral or subhedral.

The fabric illustrated in Plate 6.2 is fairly representative of aggregates containing a low inclusion density and a wide grain size variation. Small and large grains tend to be concentrated in separate clusters. The characteristic euhedral growth zone structures are well defined.

Incipient Recrystallisation

Plate 6.3 Unetched microstructure of the sample annealed in experiment SA - 01 (b), for 1 week at 400°C (wet). The characteristic changes produced during incipient recrystallisation are illustrated here - i.e. lenticular pores are developed along and delineate the grain boundaries, and the free grain faces at pre-existing euhedral voids tend to acquire curved shapes. Note that in this specimen the size and spacing of the grain boundary voids is approximately *the same* as in the specimen shown in Plate 6.4 which was recrystallised at 600°C.

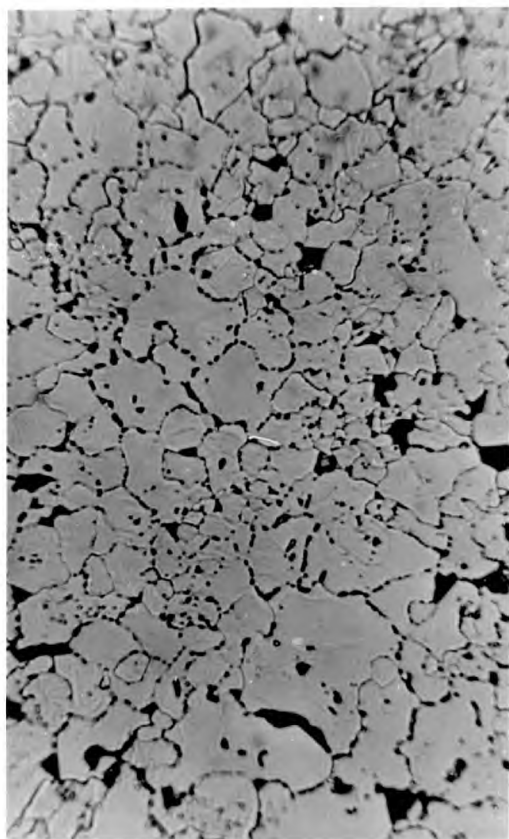
Plate 6.4 Unetched microstructure of the sample annealed in experiment SA - 17, for 1 week at 600°C (dry). The microstructural changes illustrated here, in particular the size and spacing of the grain boundary voids, are approximately the same as in the specimen shown in Plate 6.3 which was recrystallised at 400°C.

(see table 6.1). The microstructural changes occurring in the pyrite aggregates at these three stages are described below. The effects of the annealing on chalcopyrite and sphalerite are described separately in sect. 6.4.3.

- (1) Incipient Recrystallisation occurs between 400°C and 600°C and is characterised by the following microstructural features which are illustrated in Plates 6.3 to 6.7. The main grain size and shape characteristics of the initial aggregate can be easily recognised. Intragranular zone structures and inclusions are retained and show no recognisable modifications. The characteristic changes induced by incipient recrystallisation are the development of lenticular voids along the grain boundaries and a distinct tendency for pre-existing euhedral voids to acquire curved boundary shapes. These features can be discerned most clearly on unetched or lightly etched polished surfaces (Plates 6.3 and 6.4).

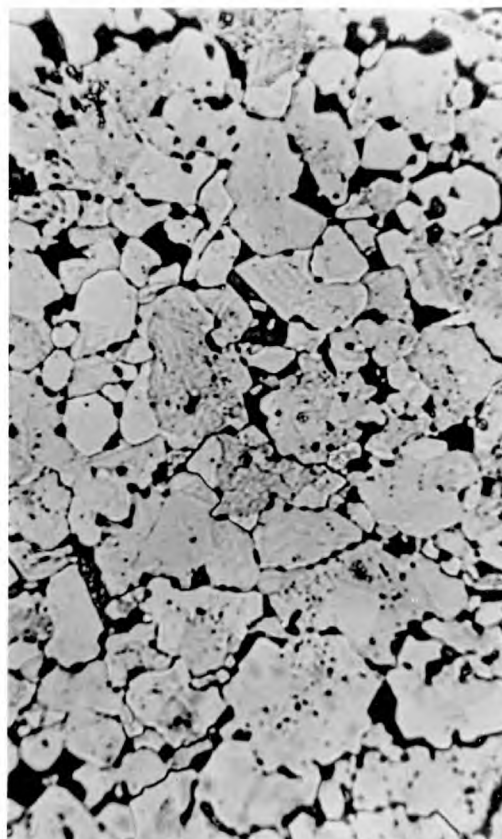
The development of grain boundary pores and the acquisition of curved boundaries at pre-existing euhedral voids tends to simplify the original grain shapes by eliminating irregularities in the grain boundary morphology. The modified grain shapes tend to assume simple curved forms, but the gross shape characteristics (i.e. the main limits of extension of single grains) are those of the initial aggregate (compare Plates 6.1 and 6.2 with Plates 6.5, 6.6. and 6.7). In general, the shape of the voids tends to become increasingly curved as their size decreases, but there are also many large pores with distinctly curved boundaries (Plates 6.3 and 6.4).

In some experiments the pores developed along the grain boundaries are numerous and closely spaced (Plate 6.5), whilst in other samples the grain bound-



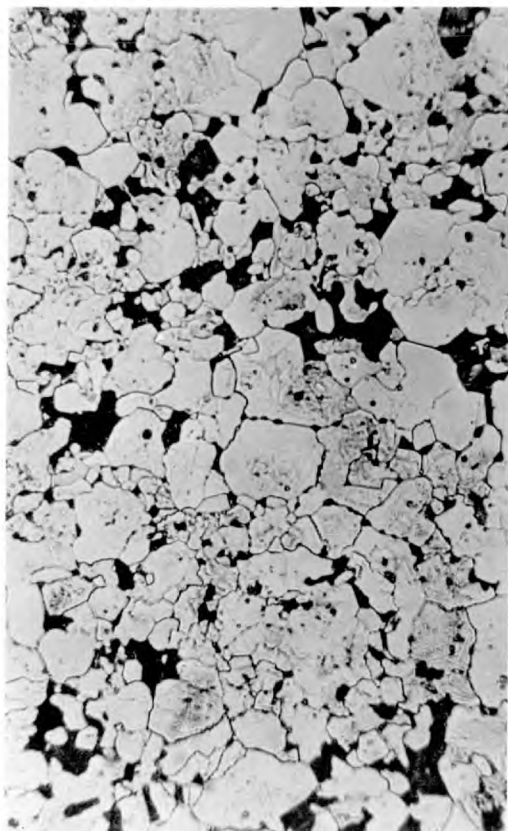
6.5

25 μ



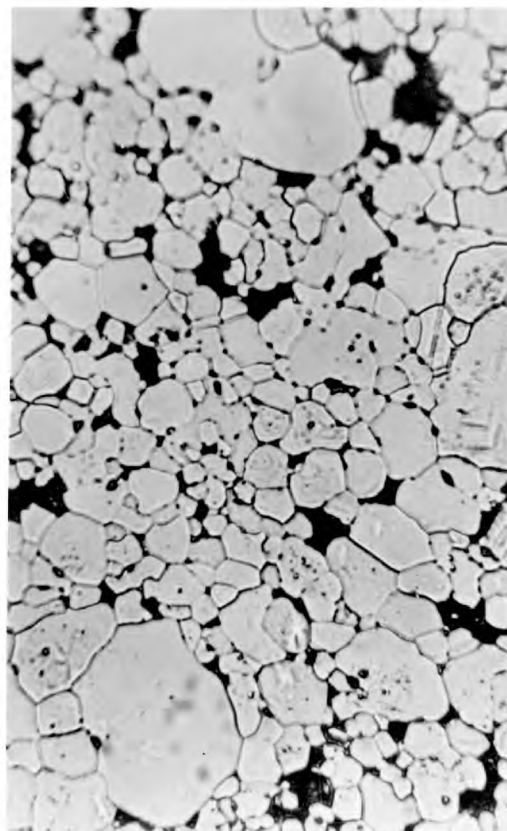
6.6

25 μ



6.7

50 μ



6.8

25 μ

Incipient Recrystallisation

Plate 6.5

Etched microstructure of the sample annealed in experiment SA - 25, for 45 days at 400°C (wet). Lenticular pores are developed along the grain boundaries. Internal zone structures and the initial grain shapes are retained. The inclusion density is low. Note that the size and spacing of the grain boundary pores is considerably less than in Plates 6.3, 6.4, 6.6, 6.7.

Plate 6.6

Etched microstructure of the sample annealed in experiment SA - 01 (b) for 1 week at 400°C (wet). Large, widely spaced, lenticular pores are developed along the grain boundaries. Internal zone structures and the initial grain shapes are retained. The inclusion density is considerably higher than in Plate 6.5.

Plate 6.7

Etched microstructure of the sample annealed in experiment SA - 17, for 1 week at 600°C (dry). The main features of the microstructure are the same as in Plate 6.6.

Moderate Recrystallisation

Plate 6.8

Etched microstructure of the sample annealed in experiment SA - 21, for 1 week at 650°C (dry). The grain size variation is inherited from the primary fabric, and the inclusion density can be matched in typical examples of the starting material. The grain shapes have become polygonal, and most of the recrystallised grains do not contain the 'clear' euhedral zones which are characteristic of the starting material. The core zones which are distinguished by a brownish colour and a rough surface texture are evident in a large number of grains.

ary voids are relatively disseminated (Plates 6.3, 6.4, 6.6, 6.7). In the samples annealed in experiments SA - 05, a and b (400°C), the incidence of grain boundary pores is extremely low. There is a marked correlation between pore spacing and pore size, namely, in specimens where the voids are closely spaced their size is small in comparison to voids which are widely spaced (compare Plate 6.5 with Plates 6.3, 6.4, 6.6, 6.7). The experiments in which small, closely spaced and relatively large, widely spaced grain boundary pores were developed are listed in the following table.

Experiment No.	Temperature $^{\circ}\text{C}$	Initial Condition of Specimen
Small, closely spaced grain boundary pores		
SA - 25	400	wet
SA - 02 (a)	500	natural
SA - 02 (b)	500	wet
SA - 20	500	dry
Large, widely spaced grain boundary pores		
SA - 01 (a)	400	natural
SA - 01 (b)	400	wet
SA - 12	575	dry
SA - 03 (a)	600	natural
SA - 03 (b)	600	wet
SA - 17	600	dry

Although there is some correlation between decreasing incidence of voids and increasing temperature, it is notable that voids of approximately equal size and equal spacing were developed both in two experiments at 400°C (SA - 01, a and b) and in three experiments at 600°C (SA - 03, a and b and SA - 17) (compare Plates 6.3 and 6.4).

The source of the free volume contained in the grain boundary pores is not properly understood. Irregularly distributed grain boundary pore space certainly occurs in the starting material, and presumably these pores undergo shape adjustments and account for at least some of the voids observed after the annealing treatment. However, the incidence of macroscopic grain boundary voids in the starting material appears to be far less than in several of the recrystallised aggregates. In view of this discrepancy, it is suggested that much of the pore space observed after annealing results from the coalescence of sub-microscopic pores contained in the grain boundaries of the initial aggregate.

Density determinations were not carried out for any of the samples before and after an experiment. However, visual comparisons were made between photographs of the unetched surfaces of the recrystallised samples and of a number of specimens of the starting material. By estimating the relative proportions of voids, which appear as black areas on the photographs, it is possible to decide whether there has been any major density changes. In all cases the comparisons suggest that the density of the recrystallised samples was less than that of the starting material. If density changes occurred, they are not uniform, and there is no marked correlation with the temperature of annealing.

Intragranular zone structures and inclusions are retained in all the recrystallised specimens (Plates 6.5, 6.6 and 6.7). The density and distribution of inclusions and the frequency and type of zoning is identical to the equivalent properties of the initial microstructure. In different recrystallised specimens and in different parts of the same specimen, the

density of inclusions frequently shows noticeable variation. However, the variation of inclusion density in the recrystallised samples falls within approximately the same limits as the density variation in different samples of the starting material (compare Plates 6.1 and 6.2 with Plates 6.5, 6.6 and 6.7).

- (2) Moderate Recrystallisation occurs at 650°C. The annealed fabric (Plate 6.8) resulting from the one experiment (SA - 21; dry) conducted at this temperature represents a transition between the stages of incipient and substantial recrystallisation.

Lenticular pores are developed along the grain boundaries, and their distribution, density and size is approximately the same as for the relatively large, widely spaced pores which occur in the samples showing incipient recrystallisation. Many pre-existing euhedral voids tend to assume curved shapes, but the extent to which these forms are developed is similar to that in several of the specimens annealed at lower temperatures.

Density determinations were not carried out before and after the experiment, but visual photographic comparisons indicate that the bulk density of the recrystallised specimen is noticeably less than that of the starting material.

The grain shapes in the recrystallised fabric (Plate 6.8) are quite different in comparison to those in the starting material (Plate 6.1 and 6.2). The fine-scale irregularities which are frequently characteristic of the grain boundary morphology in the initial aggregate are completely absent from the recrystallised fabric. Moreover, the typical, grossly irregular grain shapes of the initial microstructure are largely absent from the annealed aggregate. Most

grains, and especially those in the lower part of the grain size range, exhibit a strong tendency to be polygonal. Their boundaries are generally plane or gently curved, and frequently meet at triple-point junctions where they show a marked preference to enclose 120° angles.

Although the grain shapes are different from those of the initial aggregate, the overall grain size range and spatial distribution is approximately the same. In some parts of the recrystallised aggregate the grain size is fairly uniform. Other parts of the aggregate are relatively heterogeneous, and large grains are either disseminated or occur in small clusters surrounded by a finer grained matrix (Plate 6.8). The overall fabric is matched by aggregates in the starting material which show similar, uni-modal and bi-modal grain size distributions.

Intragranular zone structures are totally absent from a considerable number of grains, but there is no preference for the absence of zoning to be concentrated at either extremity of the grain size range (Plate 6.8). Most grains do not contain the typical clear euhedral zones which are characteristic of the starting material. The most prominent zonal features in the recrystallised grains are the euhedral or sub-hedral areas which occur near the nucleus region and exhibit a rough surface texture and a brownish colour (Plate 6.8).

Intragranular inclusions are totally absent from some grains, but their overall density and distribution can be matched in aggregates of the starting material (compare Plate 6.8 and 6.2).

At this stage of annealing, many of the recrystallised grains have acquired a distinctly cleared aspect in comparison to grains in typical examples of

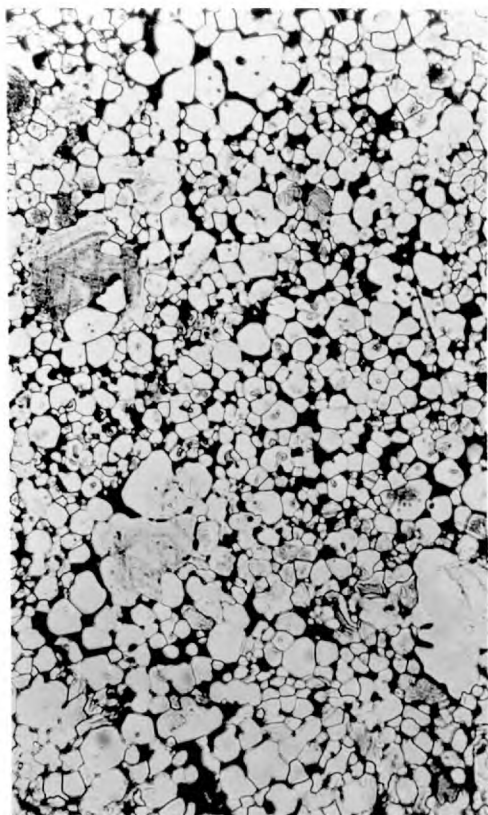
the unrecrystallised material. In specimens annealed at temperatures lower than 650°C , there is no definite evidence to indicate that the internal structure of the grains has been modified. At 650°C , it appears that the internal 'clearing' of grains is due, not to the dispersal of inclusions, but to the obliteration of the typical clear and parallel sided euhedral zone structures which are invariably characteristic of the initial aggregate (compare Plates 6.8 and 6.2).

- (3) Substantial Recrystallisation occurs at 700°C and is characterised by the development of polygonal grain shapes, widespread obliteration of the primary growth zone structures, dispersal of inclusions and a reduction in the bulk specimen density (Plates 6.9, 6.10, 6.11).

Five experiments were performed at this temperature, one for 11 hrs., one for 115 hrs. and the other three for the standard time of approximately 1 week (table 6.1).

The microstructure of the specimen annealed for 11 hrs. at 700°C (SA - 27) is similar to that for the sample annealed at 650°C for 1 week (SA - 21). Lenticular pores are developed along many of the grain boundaries in the specimen recrystallised at 700°C , but these voids are much larger than in the specimen annealed at 650°C . The most prominent difference between the two specimens is the small density decrease in the sample recrystallised at 650°C , compared to a marked density reduction resulting from the 11 hr. annealing treatment at 700°C (see below).

The microstructure of the sample annealed for 115 hrs. at 700°C (SA - 26) is virtually identical to that of the specimens annealed for 1 week at this temperature (SA - 07, SA - 10, SA - 11), and the results for all four of these experiments are des-



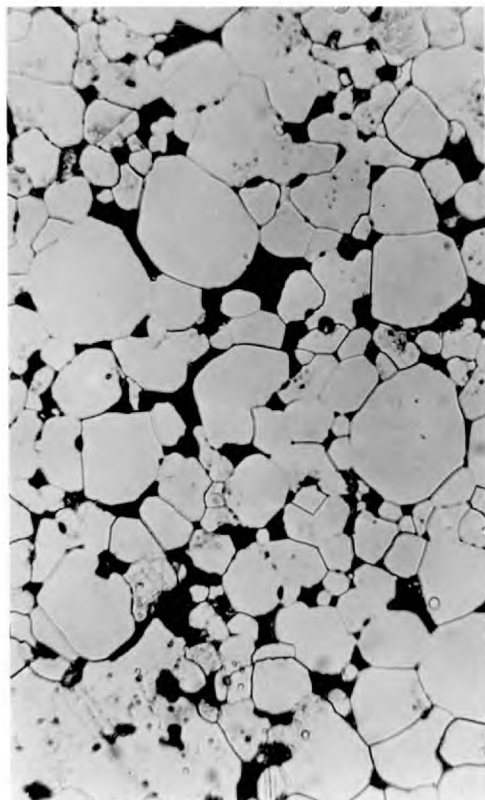
6.9

100 μ



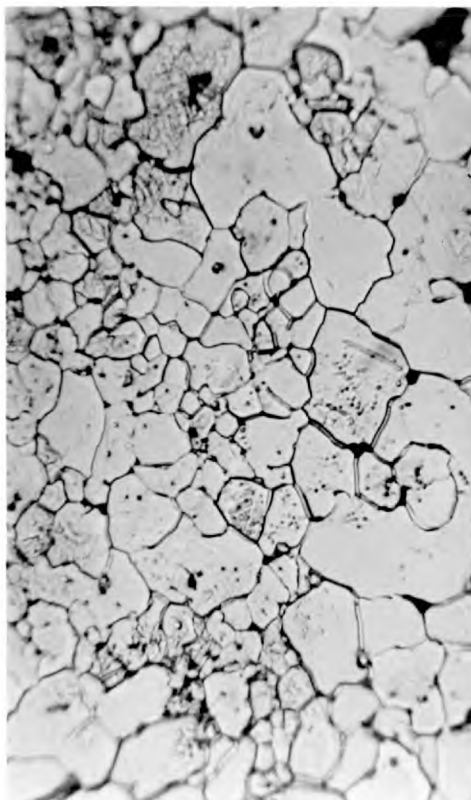
6.10

50 μ



6.11

50 μ



6.12

10 μ

Substantial Recrystallisation

Plates 6.9 and 6.10 Etched microstructure of the sample annealed in experiment SA - 11. for 1 week at 700°C (dry). The abnormally large grains in Plate 6.9 are apparently unmodified by the annealing treatment, and can be identified with grains of similar size, shape and distribution in the starting material. The microstructures illustrated in Plates 6.10 and 6.11 were selected from areas such as that represented by the relatively homogeneous, and fine grained aggregate in Plate 6.9.

Plate 6.11 Etched microstructure of the sample annealed in experiment SA - 07. for 1 week at 700°C (dry). In the samples annealed at 700°C for 1 week, relicts of the primary fabric are retained, and are represented by the considerable grain size variations and by the clustering of grains of similar size. The principal changes in the initial microstructure are due to the development of polygonal grain shapes, dispersal of inclusions, widespread obliteration of the primary growth zone structures, and an increased pore space volume.

Stress-Annealed Specimen

Plate 6.12 Etched microstructure of the sample stress-annealed in experiment CJ - 06. for 1 week at 700°C. This illustration shows the low pore space volume in comparison to that of the starting material. In the fine grained component of the aggregate many of the grain shapes are polygonal. The relict fabric of the initial aggregate is represented by the grain size variations and by the grouped occurrence of small and large grains.

cribed together.

The typical microstructure developed at the stage of substantial recrystallisation is illustrated in Plates 6.9, 6.10, 6.11. Isolated grain boundary voids are extremely rare, though small triangular pores occur at a number of triple-point junctions. Both grain boundary and triple-point pores occur with the highest frequency in the sample annealed for 115 hrs., and are least prevalent in the other three specimens recrystallised for 1 week. In all samples the recrystallised grains, except for the largest, are notably polygonal, and even the grosser irregularities which are characteristic of the initial grain shapes are no longer evident in the annealed fabric. The grain boundaries are invariably plane or gently curved and, in compact parts of the aggregate, there is a marked tendency for grain boundaries to intersect at triple-point junctions and enclose 120° angles. The boundaries of even the largest voids exhibit a strong tendency to be curved, though a number of voids are partly bounded by euhedral grain surfaces. Many small grains which appear to be isolated at voidal interstices exhibit near-spherical shapes (Plate 6.10).

The only part of the recrystallised fabric which retains a direct semblance of the initial aggregate are a few abnormally large grains such as those shown in Plate 6.9. By comparison with the starting material, these grains can be identified with similar large grains which are frequently disseminated through the primary aggregate or clustered in small groups, colloform-like structures or vein aggregates. The intervening and relatively homogeneous aggregate represents the bulk of the recrystallised fabric, and it is from areas of this type that the illustrations of Plates 6.10, and 6.11 were selected.

Although the bulk of the recrystallised fabric

exhibits an overall homogeneity, the detailed microstructure is characterised by a considerable grain size variation, and frequently, by the direct juxtaposition of grains of markedly different size (Plates 6.10, 6.11). These features are comparable with the microstructure of typical examples of the starting material (compare for example Plate 6.2 and 6.11). On this basis, it is concluded that the grain size heterogeneity in the recrystallised fabric is a relict feature, reflecting the influence of the initial microstructure.

Visual photographic comparisons of etched surfaces suggest that the average grain size of the recrystallised specimens is somewhat greater than that of the starting material (compare Plates 6.1 and 6.2 with Plates 6.10, 6.11; in these two groups of illustrations the magnification differs by a factor of 2). If a grain size increase has occurred, the growth process was almost certainly restricted to the fine grain size components of the initial aggregates. The coarse grains, occurring singly or in clusters, have adjusted their shapes, but their size does not appear to be significantly enlarged.

A striking change produced in the samples annealed at 700°C is the homogenisation of the internal structure of the recrystallised grains. This development reaches an extreme in parts of the annealed specimens such as that shown in Plate 6.11. In small and large grains alike, the homogenisation process is at least partly due to the widespread obliteration of the primary growth zone structures. It is estimated that somewhere in the order of 50% of the grains are completely unzoned. Only the largest grains retain complete euhedral zone structures (Plate 6.9), but even here there is no way of being certain that some

of the original zones have not been obliterated. Grains containing even a few of the relatively 'clear', euhedral zones which are a characteristic component of the primary zone structures are extremely rare (see, however, the large grains at the lower left of Plate 6.11). The characteristic zones retained in the recrystallised fabric are the anhedral to subhedral areas which exhibit a brownish colour and a rough surface texture (these zones are conspicuous in Plates 6.9, 6.10 and are faintly evident in some of the grains in Plate 6.11).

Intragranular inclusions are associated with the characteristic zone structures of the recrystallised aggregate (Plate 6.11). One or two inclusions sometimes occur in completely unzoned grains (Plates 6.10, 6.11). The inclusions are invariably characterised by a spherical or near-spherical shape (Plates 6.10, 6.11), and this is a distinguishing feature of the recrystallised aggregate. The inclusion density in by far the major part of all specimens is approximately equal to that shown in Plates 6.10 and 6.11. Since this concentration is considerably higher than in typical examples of the starting material, it is concluded that at least part of the primary inclusion concentration has been dispersed during the annealing treatment. This factor, together with the widespread obliteration of primary zone structures, contributes to the cleared appearance of the recrystallised grains.

Visual comparisons of photographs of unetched polished surfaces indicate that there was a marked decrease in the density of all five samples recrystallised at 700°C. The increased porosity associated with the annealing process was confirmed by direct methods for three of the recrystallised samples.

As a result of annealing, the diameter of the cylindrical specimen in experiment SA - 10 increased from 9.50 cm. to 9.67 cm. By assuming a proportional increase for the height of the cylinder, it was calculated that the size of the specimen had increased by 5.5% of its initial volume. Since the volume increase can only be accomplished by the generation of internal voids, the specimen density must decrease. After the sample was recrystallised, its density was measured, three determinations giving an average value of 4.47 gm./cc. Considering the 5.5% volume increase, the calculated pre-annealing density of the specimen was 4.71 gm./cc. This is a normal value for typical examples of the starting material.

The densities of the specimens in experiments SA - 26 and SA - 27 were measured before and after annealing, and it was also noted that the diameter of the samples had increased at the end of the experiments. These data and the calculated volume increases for the two specimens are listed in the following table.

	<u>SA - 26</u>	<u>SA - 27</u>
Measured initial density gm/cc.	4.61	4.68
Initial cylinder diameter mm.	9.50	9.47
Final cylinder diameter mm.	9.87	9.75
Volume increase as % of initial volume	12.1	9.1
Measured final density gm/cc.	4.15	4.42
Calculated final density gm/cc.	4.12	4.29

The post-annealing density of the specimens can be calculated from the measured initial density and the bulk volume increase of the samples. The densities obtained in this way are recorded in the foregoing table, and show reasonable agreement with the measured final densities.

Experiment No.	Temperature of Experiment °C	Pre-heating time (spec. capsule unsealed) in air at 180°-200°C (hrs.)	Total time to reach temp. from room temp. (hrs.)	Experiment Duration (hrs.)	Cooling time (hrs.)	Strain
CJ-03	400	Nil	16	170	2	0
CJ-05	600	6	26	160	2	0
CJ-07	650	117	118	185	3/4	0
CJ-01	700	Nil	12	24	3	
CJ-06	700	180	181	180	4	ca. 10%

Table 6.2 Details of stress-annealing experiments. Fine grained Rio Tinto pyrite as starting material.

Assuming that 5% of the aggregate is composed of chalcopyrite and sphalerite (an estimate confirmed by later point count determinations), then the proportion of voids in the original samples can be calculated from the measured initial densities. The pore space density in the recrystallised samples can then be obtained by adding the initial pore volume to the bulk volume increase of the specimens. These data are listed in the following table.

	<u>SA - 26</u>	<u>SA - 27</u>
Calculated initial pore vol. as % of initial spec. vol.	8.7	7.3
Bulk vol. increase of spec.	12.1%	9.1%
Calculated final pore vol. as % of final spec. vol.	18.6	15.0
Final pore volume determined from final measured density	17.7%	12.5%

The final pore volumes can also be calculated from the measured final specimen density. These values are recorded in the above table, and show good agreement with the final pore volume obtained by addition of the initial pore space density and the bulk volume increase of the specimens.

6.4.2 Stress - Annealing Experiments

Four experiments were conducted in which cylindrical specimens were stressed near their fracture point and simultaneously heated at temperatures between 400°C and 700°C for approximately 1 week; one other experiment was terminated after approximately 24 hrs. at 700°C (see table 6.2).

In all experiments there is no evidence for mechanical deformation of the samples. This might be expected since, although the experiments were conducted at elevated temperatures, the specimens were stressed below their measured, room temperature fracture point. All samples were whole

and coherent when removed from the sealing capsule and their microstructure showed no evidence for fragmentation. The gross grain shapes are essentially equant and similar to those in the starting material. Primary euhedral growth zone structures retain their strict euhedralism and are not distorted even in the grain boundary region. These features constitute sufficient reason to conclude that the stressed samples did not undergo mechanical plastic deformation (see sect. 8.3.1 (2)). The absence of gross distortion in three of the samples (CJ - 03, CJ - 05 and CJ - 07) is directly indicated by the fact that no differences were recorded in the measured lengths of the cylindrical specimens before and after the stress-annealing treatment. The shortening (approx. 10%) produced in the sample annealed for 1 week at 700°C (CJ - 06) is correlable with the simultaneous increase of the specimen density (see below), but was apparently accomplished by a diffusional mechanism.

On the basis of the different changes effected, it is convenient to describe the results of the stress-annealing experiments in three groups, namely, the experiments at 400°C and 600°C, the experiment at 650°C and the experiments at 700°C.

(1) Experiments CJ - 03 and CJ - 05 at 400°C and 600°C The microstructure of the specimens annealed at 400°C and 600°C for 1 week is indistinguishable from that of the starting material. Even in the experiment at 600°C there is no evidence for the exsolution phenomena (see sect. 6.4.3) which are initiated in chalcopyrite grains at temperatures as low as 400°C in the static annealing experiments.

(2) Experiment CJ - 07 at 650°C Extremely minor alterations were induced in the sample annealed at 650°C for 1 week. Chalcopyrite and sphalerite grains have developed features which are similar to those in the specimens

statically annealed at 400°C and 500°C (see sect. 6.4.3).

The microstructure of the pyritic aggregate is indistinguishable from that of the starting material except that a few lenticular pores have been generated along some of the grain boundaries. This development is equivalent to the incipient stage of recrystallisation (400°C - 600°C) in the static annealing experiments, but the incidence of grain boundary pores is very much less than in any of the statically annealed specimens.

(3) Experiments CJ - 01 and CJ - 06 at 700°C The microstructure of the specimens stressed and heated at 700°C for 24 hrs. for 1 week show noticeable changes compared to the starting material. Chalcopyrite and sphalerite grains exhibit features which are similar to those in the specimens statically annealed at the same temperature. There is a less marked tendency for these same features to develop in the sample stress-annealed for 24 hrs.

The most striking change induced in the pyritic component of the sample annealed for 1 week at 700°C (CJ - 06) is the marked density increase. Density determinations were not carried out before and after the experiment, but visual comparison of the proportion of voids in unetched surfaces of the starting material and the recrystallised aggregate strongly suggest that the bulk specimen density increased during the stress-annealing treatment. The increased specimen density is most apparent from observations of the detailed microstructure. Plate 6.12 shows a typical area in the recrystallised fabric where it is reasonable to assume that the initial microstructure was substantially uniform and equivalent to aggregates of the starting material such as those illustrated in Plates 6.1 and 6.2. The recrystallised aggregate in Plate 6.12 is remarkably compact and the proportion of pore space is noticeably less than in the typical primary aggregates shown in Plates 6.1

and 6.2.

It is evident from the direct juxtaposition of grains of markedly different size and from the general pattern of grain arrangement (Plate 6.12) that the main grain size and shape characteristics of the initial aggregate are retained in the sample stressed and heated at 700°C for 1 week. However, there is a marked tendency for the grain boundaries to assume plane or gently curved shapes, and the medium and fine scale irregularities which typify the grain boundary morphology in the initial aggregate are almost totally absent from the recrystallised fabric (Plate 6.12). The grain boundaries frequently meet at triple-point junctions, enclosing 120° angles, and together with this development, the smaller grains acquire noticeable polygonal and equant shapes. The grain shape modifications in general are best developed in the smaller grains, but the acquisition of curved grain boundaries tending to meet at 120°, triple-point junctions is also extended to the margins of the large grains where the latter are directly in contact with clusters of smaller grains. In some of the fine grained clusters there is a distinct tendency for many of the grains to be slightly elongate, and for the long axes of these grains to be oriented approximately at right angles to the applied compression direction. Many of the grain surfaces facing pore spaces have assumed noticeably curved forms, though euhedral voids are common.

There is some suggestion that the grains in the recrystallised fabric are relatively clearer and less frequently zoned than in the starting material (compare Plate 6.12 with Plates 6.1 and 6.2). However, it is not certain that these differences exist.

The pyritic component of the sample stressed and heated at 700°C for 24 hrs. (CJ - 01) is similar to that in the specimen annealed for 1 week. However, in the

specimen annealed for 24 hrs. all of the changes induced by recrystallisation are distinctly less marked than in the sample annealed for 1 week. The main difference between the two samples is the relatively lower density of the specimen annealed in the short term experiment. The density difference is marked, and in fact it is estimated that in the sample annealed for 24 hrs. the proportion of voids has actually increased in comparison to the pore space density in typical examples of the starting material. This change is the reverse of that observed in the long term experiment. The apparent decrease in the density of the specimen annealed for 24 hrs. is estimated to be roughly the same as that for the specimens statically annealed for 1 week at 700°C.

6.4.3 Static Annealing Changes Induced in Chalcopyrite and Sphalerite

All samples of the starting material contain a few grains of chalcopyrite and sphalerite, most of which occur at strictly euhedral interstices. The chalcopyrite displays a clear, pale yellow colour, but in some samples or in certain grains of the same sample, the colour of the chalcopyrite assumes a distinctly more golden tinge. Almost all the sphalerite grains contain numerous oriented inclusions of chalcopyrite. Chalcopyrite and sphalerite grains may coexist at the same interstice or occur at different sites.

In all samples statically annealed at and above 400°C the chalcopyrite and sphalerite grains have undergone noticeable changes. The annealing effects show a broad correlation with temperature, but are quite independent of the recrystallisation phenomena in the pyritic aggregate.

(1) Changes Occurring at the Chalcopyrite/Pyrite and Sphalerite/Pyrite Phase Boundaries In all the specimens annealed at temperatures up to 650°C and for several of the chalcopyrite and sphalerite grains in the

sample annealed at 700°C for 11 hrs. (SA - 27), pore spaces tend to accumulate at the chalcopryite/pyrite and sphalerite/pyrite phase boundaries. At the margins of chalcopryite grains the voids are relatively large and isolated and occur preferentially at the corners of the original interstices. The pore space at the margins of sphalerite grains is mainly developed as a closed spaced array of small lenticular voids. In the samples recrystallised at temperatures up to 650°C the overall shape of pre-existing euhedral interstices occupied by sphalerite or chalcopryite can generally be easily recognised. However, significant shape changes are associated with the development of the grain boundary voids, and are manifested by a tendency for the free surfaces of both the pyrite and interstitial grains to assume smoothly curved forms.

In the samples of the long term experiments at 700°C , almost all the sphalerite/pyrite boundaries and many of the chalcopryite/pyrite boundaries are ~~coherent~~ and are not associated with preferential concentrations of pores. The coherent phase boundaries tend to assume markedly curved shapes and the pre-existing euhedralism of the interstices can be difficult to recognise.

(2) Changes Occurring at the Chalcopryite/Sphalerite Phase Boundary In recrystallised samples where pore spaces are developed along the chalcopryite/pyrite and sphalerite/pyrite phase boundaries, similar pores nearly always occur at the boundary between coexisting chalcopryite and sphalerite grains.

In the starting material, chalcopryite and sphalerite frequently coexist at the same interstitial site, but always occur in such a way that their separating boundary intersects the pyrite aggregate. This relationship is markedly altered during the annealing treatment. In all of the recrystallised samples there is a distinct tendency for the sphalerite grains to assume curved shapes, and to

become isolated within the chalcopyrite interstices. In samples annealed at and below 600°C the isolation of sphalerite grains may be either complete or incomplete. In the specimens recrystallised at 650°C and 700°C nearly all the sphalerite grains coexisting with chalcopyrite are completely isolated, and occur near the centre of the chalcopyrite interstices.

(3) Dispersal of Chalcopyrite Inclusions in Sphalerite Grains In the specimens annealed at 500°C the density of chalcopyrite inclusions in sphalerite appears to be noticeably less than that in the starting material.

Sphalerite grains in the samples recrystallised at temperatures between 575°C and 700°C are completely homogeneous and free from all types of inclusions. It is noteworthy that the sphalerite grains are homogeneous irrespective of whether the specimen was slowly cooled or quenched to room temperature at the end of the experiment.

(4) Internal Changes Associated With Discrete Chalcopyrite Grains In two experiments at 400°C (SA - 01, a and b), two experiments at 500°C (SA - 02, a and b), two experiments at 600°C (SA - 03, a and b) and two experiments at 700°C (SA - 26 and SA - 27) many discrete chalcopyrite grains developed a coarse or a fine lamellar substructure. In some cases the annealing of the chalcopyrite was also accompanied by the development of a gross zonal structure.

In all of the samples annealed at 700°C many of the chalcopyrite grains developed minute, equant or star-shaped inclusions of sphalerite, which are either disseminated, or occur with a high density in planar or curved rows. The sphalerite inclusions occur both in samples which were slowly cooled and in those which were quenched at the end of the experiment.

In two of the specimens annealed at 700°C (SA - 26 and SA - 11), small sphalerite inclusions in pyrite occupy

a narrow discontinuous rim which occurs immediately adjacent to some of the chalcopyrite interstices.

In the samples of two experiments at 500°C (SA - 02, a and b), the experiment at 650°C, and the experiments at 700°C the colour of the chalcopyrite is noticeably darker than in the starting material. Usually the colour is uniform over the area of single grains, but a number of grains in three experiments at 700°C (SA - 07; slowly cooled, and SA - 10 and SA - 11; quenched) exhibit distinct marginal rims where the colour becomes progressively lighter than in the centre of the grains.

6.5 Discussion

For the purpose of this discussion, the following terms are defined at the outset:

- (1) Grain boundaries whose structure is determined by an atomic fit between the neighbouring lattices (of similar or dissimilar orientation) will be referred to as coherent grain boundaries, or coherent interfaces. These interfaces are distinguished from incoherent grain boundaries where the inter-lattice distance reaches a macroscopic dimension (i.e. a few or more atom diameters wide). In unetched polished surfaces of the starting material and the recrystallised aggregates, there is no direct physical manifestation of the grain boundaries (where grain boundary pores are developed, there is no direct physical manifestation of the segments of the grain boundary between adjacent pores). This suggests that the grain to grain interfaces are essentially coherent.
- (2) Intergranular diffusion is defined as the transport process which occurs when atoms move directly from the surface of one grain to that of the adjacent grain across a coherent interface. This is a solid state diffusion mechanism, and must occur when coherent grain

boundaries migrate. However, intergranular diffusion is distinguished from grain boundary diffusion which does not necessarily imply a transfer of atoms between adjacent grains.

6.5.1 Static Annealing-Incipient Recrystallisation

In all specimens which underwent incipient recrystallisation at temperatures up to 600°C , the grain size, the gross grain shapes and the internal grain structure of the initial aggregate are retained in the microstructure of the annealed sample. The original fabric is not substantially altered by the development of grain boundary pores.

Since the microstructural properties of the primary aggregate are essentially unchanged, it can be assumed that the pyrite grain to grain interfaces did not migrate during the annealing treatment. The retention of the initial grain shape characteristics provides the most direct evidence for this conclusion.

If recrystallisation involves migration of coherent grain to grain interfaces, the diffusion process must occur in the solid state, and the nett effect is for atoms to be released from the surface of one grain and move directly to the surface of the adjacent grain. Thus, the fact that grain boundary migration did not occur in the pyrite samples undergoing incipient recrystallisation can be taken to indicate that the temperatures at which these experiments were conducted - that is, at temperatures up to 600°C - are not sufficiently high to activate intergranular diffusion.

Because the structure of the interfacial region between two grains is generally fairly loose (compared to the interior of the lattice), the energy required to activate intergranular diffusion is probably somewhat similar to the activation energy for diffusion on the free surface of a grain. Thus, it also follows that at temperatures

up to about 600°C, iron and sulphur atoms would not be able to diffuse on the free surfaces of pyrite grains, provided these surfaces were in contact with an inert atmosphere (i.e. provided solvent, interstitial fluids were absent). Therefore, if the initial aggregate contained no interstitial fluids, it seems reasonable to suppose that the free grain surfaces could not undergo shape changes, growth or dissolution at temperatures up to 600°C.

However, the annealed samples are characterised by development of lenticular grain boundary pores, and by a tendency for pre-existing interstices to acquire curved boundary shapes. Both these features imply that the free grain surfaces were unstable and could adjust their shape with reasonable facility. The acquisition of curved surface forms, and the tendency for these shapes to be best developed in the smaller voids (i.e. in the newly developed grain boundary pores and in the smaller pre-existing voids) indicates that the free grain surfaces adjusted their shape in order to reduce their surface energy and reach an equilibrium configuration. The fact that these adjustments occurred under conditions where coherent grain boundary migration is inhibited apparently indicates that the initial aggregate contains interstitial fluids. As explained in the introduction (sect. 6.1), the presence of these fluids increases the facility for atoms to leave the free grain surface (because of the energy of attraction between the atoms of the solid crystal and the atoms of the fluid phase), and hence reduces the temperature level at which the atoms of the solid phase can diffuse between different grains or from one part of a surface to another.

In samples which were annealed under wet conditions (i.e. in the presence of added water), the source of the interstitial fluids is apparently obvious. However, at each of the temperature levels at which the experiments were conducted, one of the samples (i.e. SA - 05, a; SA -

20; SA - 12; SA - 17) was annealed only after pre-heating in air at 180°C - 200°C. The pre-heating treatment was designed to remove all traces of interstitial fluids which may have been contained in the original ore, but all these specimens showed incipient recrystallisation. At the end of three of the experiments (i.e. those at 500°C, 575°C, 600°C) the inside of the specimen capsule was examined and it was noted that in all cases there was no condensed fluid phase. Apparently, in these specimens the interstitial fluids promoting the incipient recrystallisation phenomena are effectively sealed in the crystalline aggregate, and were not removed either during the relatively low temperature pre-heating treatment or during the annealing process itself. Although, at first sight, this may seem to be an unreasonable supposition, there are substantial grounds for believing both that interstitial fluids are contained in the initial aggregate, and that these fluids remain trapped at temperatures as high as 600°C.

The development of intragranular fluid inclusions in the ore minerals is a well known feature of crystal growth under natural hydrothermal conditions. If the ore-bearing fluids can be trapped in the interior of a crystal, it seems perfectly reasonable to suppose that the same phenomenon would occur at the boundaries or interstitial sites between neighbouring grains. Entrapment of intergranular fluids during the final stages of growth would be directly related to the mode of impingement of neighbouring grains or groups of grains. For example, if different parts of the impingement surface (i.e. the grain boundary) between two adjacent grains advances at different rates (due, for example, to uneven diffusion to the growth surface in the confined spatial conditions associated with the final stages of growth), small pockets of interstitial fluids could become isolated at different and perhaps numerous

points in the grain interface. The occurrence of discrete euhedral interstices between groups of pyrite grains in the starting material bears direct witness to the fact that comparatively large, non-crystalline volumes were isolated during the final stages of growth. It seems highly probable that at least some interstitial fluids were trapped in these interstices. Euhedral interstices occupied by chalcopyrite and sphalerite were obviously accessible to later solutions, and therefore not completely sealed. However, interstices which are apparently voidal coexist with those which are occupied, thus indicating that the former interstices were not accessible to the later solutions, and therefore effectively sealed. This implies that if pyritic ore-bearing fluids were trapped in the non-crystalline interstices, they could not escape for the same reason that the copper and zinc bearing solutions could not enter. Where the interstices are sealed, the intersecting grain boundaries are apparently coherent. The manifest entry of later ore solutions into the aggregate implies that, at the completion of the pyrite growth event, there was a considerable proportion of grain boundaries which were sufficiently incoherent to act as effective diffusion channels. However, precipitation would occur in these channels (which need only be a few atom diameters wide) as well as in the larger interstices, and at the completion of mineralisation the total incidence of sealed, coherent grain boundaries could be extremely high.

From the foregoing summary it appears reasonable to assume that primary ore-bearing fluids are trapped at intergranular sites in the starting material used for the recrystallisation experiments. At annealing temperatures up to 600°C , there is no evidence that the grain boundaries migrate, and hence that intergranular diffusion can occur. Under these conditions, coherent grain boundaries could be effectively sealed. Thus during annealing and during pre-

heating, the interstitial fluids would not be expelled from the specimens, but would remain trapped, at essentially the same sites as they occupy in the initial aggregate.

Direct evidence for the presence of interstitial fluids in the natural pyritic aggregates was obtained in experiment SA - O2, a. The specimen used in this experiment was neither pre-heated nor annealed in the presence of added water. The interior of the specimen, at least, should have been representative of the naturally occurring ore. After the annealing treatment (during which the sample underwent incipient recrystallisation) for 1 week at 500°C, it was noted that a few droplets of a fluid phase had condensed on the inside of the specimen capsule. This fluid must have been derived from the interior of the specimen.

The expulsion of interstitial fluids from the sample annealed in experiment SA - O2, a may mean that all samples lose some of their fluids when subjected to pre-heating. In this case, the non-expelled interstitial fluids responsible for the incipient recrystallisation in the pre-heated samples of experiments SA - 20, SA - 12 and SA - 17 might represent only the most thoroughly sealed fluids in the initial aggregates.

The recrystallisation effects associated with interstitial fluids will depend on the temperature of annealing, and on the composition and pore pressure of the fluids. The last two of these factors are unknown, though it seems reasonable to suppose that in the experiments where pre-heated and natural samples were used, the composition of the fluids is fairly uniform, and approximates to that of the primary ore-bearing solutions.

However, the different behaviour of some samples annealed at the same temperature (e.g. in experiments SA-O1; SA - O5; SA - 15) and the similar behaviour of other samples annealed at different temperatures (e.g. in

experiments SA - 01, a; SA - 03, a) suggest that the total amount of fluid present and its pressure at the time of annealing were variable. Even the original samples apparently contain different amounts of interstitial fluids. This is illustrated, for example, by the two specimens which were recrystallised in their natural states in experiments SA - 01, a and SA - 03, a. Both samples showed similar annealing changes, but one was recrystallised at 400°C and one at 600°C. The amount of fluid and its pressure in the sample will also depend on the degree of **sealing** of the grain boundaries. As already indicated above, this is a further variable factor, and could mean that similar pre-heating times do not remove the same amount of fluid from different samples, and that the internal fluid pressure during the annealing treatment changes at different rates for different samples. In experiments where the specimens were recrystallised in the presence of added water, even the bulk composition of the interstitial fluids might be changed, and the amount of water entering the aggregate and its effective pressure will again vary according to the degree of sealing of the grain boundaries. In view of these complications, it is only to be expected that the microstructural changes accompanying incipient recrystallisation show such a poor correlation with the annealing temperature.

Owing to the importance of primary interstitial fluids, it is necessary to re-evaluate the intended role of added water in the experiments deliberately performed under wet conditions. Barnard (1967) has shown that there is no observable solution of pyrite in de-ionised water at 400°C; even at 500°C the solvent capacity of de-ionised water is minimal compared to the solubility of pyrite in chloride-bearing solutions. Their relatively high solvent action suggests that the chloride-bearing solutions are fairly representative of the composition of the natural ore-bearing

solutions. Thus the primary interstitial fluids in the starting material used for the recrystallisation experiments probably have a far greater solvent capacity than de-ionised water. Although pure water was not used in any of the experiments, there would be little complexing associated with the water introduced in the form of pyrophyllite. Water introduced as hydrated ferrous sulphate would be ionised, but there is no basis for estimating its solvent capacity. Thus, at least in the experiments where the hydrous additive was pyrophyllite, it seems reasonable to conclude that the incipient recrystallisation phenomena were effected mainly through the agency of the primary interstitial fluids, and not the added water.

The fact that pyrite is not observably soluble in de-ionised water at 400°C (Barnard, 1967) immediately suggests that the hydrous additives played no part at all in the recrystallisation experiments at 400°C . This conclusion appears to be confirmed by the results of experiment SA - 15 which was performed under wet conditions (water introduced as hydrated ferrous sulphate) at 400°C , but where the annealed specimen showed no microstructural changes. The absence of recrystallisation effects can be taken to indicate that the original sample contained no primary interstitial fluids of the same type as those which were present in the other specimens annealed at the same temperature. Although the bulk of the specimen may have been effectively sealed against the entry of added water, there are no annealing effects even near the margin of the sample. These observations strongly suggest that even the ionised water introduced as hydrated ferrous sulphate is ineffective as a recrystallising agent at 400°C .

The absence of recrystallisation in the specimen annealed under wet conditions at 300°C (SA - 06) is difficult to interpret. As in the specimen of experiment SA - 15, there may have been no primary interstitial fluids in the original sample, and at this temperature it is

virtually certain that water introduced in the form of pyrophyllite would have no solvent capacity. Hence, even if the specimen were permeable, incipient recrystallisation would not be expected to occur. On the other hand, the sample may contain primary interstitial fluids, but at this temperature level the solubility of pyrite, even in the ore-bearing solutions, may be insignificantly small.

Experiment SA - 25 (performed under wet conditions at 400°C for 45 days) was conducted to test whether the microstructural changes produced during the incipient stage of recrystallisation become more extensive with increasing annealing time, or whether the microstructure is stabilised after a relatively short time. Compared to the other samples annealed for 1 week at the same temperature, there is no significant increase in the annealing effects in the specimen recrystallised for 45 days. Although this result suggests that the microstructure is stabilised at an early stage of annealing, it is extremely doubtful that a sound comparison can be made between the long term and short term experiments. As pointed out above, it is almost certain that there are marked variations of annealing behaviour related to the amount, pressure and possibly the composition of interstitial fluids in different samples. Since the importance of these factors in comparison to the length of the annealing time is completely unknown, the results of the long term experiment must remain inconclusive.

6.5.2 Static Annealing - Moderate and Substantial Recrystallisation

Compared to the starting material, the samples undergoing substantial recrystallisation at 700°C are characterised by polygonal grain shapes, a much lower incidence of intra-granular zone structures and inclusions, and probably an increase in the average grain size.

From the grain shape changes it is clear that coherent grain to grain interfaces migrated during the annealing process. Moreover, in view of the reduced grain size variation, the development of plane or smoothly curved boundaries, and the tendency for grain boundaries to meet at 120° , triple-point junctions, it is evident that the grain boundaries adjusted in order to reach equilibrium under the influence of their surface energy.

Although statistical grain size comparisons were not made (for reasons given in sect. 6.2), it appears fairly certain that if the average grain size has increased in the recrystallised samples, then the growth process was restricted to the fine grain size component of the initial aggregate. This is only to be expected since a given volume of small grains is associated with a higher total grain boundary free energy than an equal volume of large grains. Presumably, if the annealing is prolonged, the grain size heterogeneities of the initial aggregate would be completely leveled out, and eventually all grains would grow at approximately the same rate.

Since coherent grain to grain interfaces were able to migrate during the annealing process, it is concluded that intergranular diffusion of both the iron and sulphur lattice components is activated at 700°C . Under these conditions, diffusion could also occur on the free surface of pyrite grains. If interstitial fluids are present, they will have negligible effects on the recrystallisation process, since grain growth and the consequent reduction of surface free energy occurs much more rapidly when atoms move directly across the grain to grain interfaces than when they are transferred via an interstitial fluid. Thus, the experiment performed under wet conditions (SA - 10) has no special significance. Similarly, there is no importance attached to the probability that all samples, including those that were pre-heated, may have contained primary

interstitial fluids.

The partial dispersal of intragranular inclusions and the widespread obliteration of primary growth zone structures indicate that at the temperature of annealing diffusion was also activated in the interior of the pyrite lattice (volume diffusion). Homogenisation of the internal grain structure could occur by diffusion in the grain boundaries as the latter traverse the crystalline aggregate during grain growth (see sect. 7.1.4). However, it can be shown that this mechanism was unimportant in comparison to volume diffusion. As pointed out earlier, although the largest grains (excluding the abnormally large disseminated grains, and those associated with vein structures, etc.) have undergone shape adjustments, their size does not appear to be significantly greater than the size of the equivalent grains in the starting material. Hence grain boundaries have not traversed the bulk of the lattice volume, and certainly not the interior region of these grains. Since compositional zone structures are nevertheless destroyed to the same extent as in the smaller grains, diffusion must have occurred in the interior of the large grains.

Since the destruction of the primary growth zones is not accompanied by the formation of new phases (as discrete grains, or as rims surrounding the pyrite grains), it is evident that the atom species responsible for the compositional variations are uniformly dispersed through the pyrite lattice. A similar conclusion might be applicable to the inclusion particles, though if the latter were actually voids, it seems probable that their dispersal was accomplished by migration of vacancies to the grain boundaries, and finally by incorporation of the free volume in the intergranular pore space.

Although the majority of primary growth zone structures are destroyed during annealing, the characteristic brownish coloured core zones of the initial aggregate are

still evident in the annealed samples and appear to be unmodified by the recrystallisation process. The retention of these zones apparently indicates that at least some of the atom species involved in the compositional changes are either too large or too strongly bonded to undergo volume diffusion at 700°C. It seems much less likely that the primary zoning reflects different types of structural defects in the pyrite lattice. As evidenced by the destruction of other types of zone structures, the temperature of annealing was sufficiently high to activate volume diffusion of at least some of the lattice components, and under these conditions structural defects would almost certainly be unstable.

At least some of the pre-existing inclusions are also retained in the recrystallised grains, but were markedly spherodised, and therefore not inert, during annealing. The fact that these inclusions are not dispersed must indicate either that their atomic components were too large to diffuse or be incorporated in the pyrite lattice, or that the latter was already saturated with respect to these atoms (or vacancies). However, if the inclusions were voidal, there would still be a favourable energy change (i.e. a surface energy reduction) if they migrated to and dispersed at the grain boundaries. Actually there is no evidence suggesting a tendency for the inclusions to disperse at the grain boundaries. On the contrary, a number of relatively large and seemingly voidal inclusions occur very close to the grain boundaries and were apparently quite stable. To account for this observation it seems necessary to assume that the observed inclusions result from coalescence of smaller inclusions. This is a favourable change since it involves a reduction of the total surface energy.

The reduction of the bulk specimen density associated

with annealing is probably due to the growth of pre-existing voids rather than the nucleation and growth of new pore spaces. Coble (1959, p. 157) has shown that when voids are surrounded by more than a critical number of grains, the pore space actually grows during the annealing process. The critical number of surrounding grains depends on the equilibrium angle of the pore wall at the grain boundary intersections. However, even when the equilibrium angle is as high as 150° , pore spaces increase their size if the number of surrounding grains is greater than 12 (in section). In the recrystallised pyrite samples, it is clear that many pores are surrounded by a large number of grains. Thus, it seems likely that the decrease in the specimen density is due to a nett free volume increase resulting from the growth and shrinkage of pores surrounded by a large and a small number of grains, respectively.

Both in the sample showing moderate recrystallisation at 650°C (SA - 21) and in the sample showing substantial recrystallisation after 11 hrs., at 700°C (SA - 27), the annealing process was basically the same as in the specimens recrystallised for 1 week at 700°C .

Since recrystallisation is mainly a temperature activated process, it is only to be expected that the sample annealed for 11 hrs. at 700°C undergoes changes which are similar to those produced in the long term experiments at the same temperature. The differences between the samples annealed in the long term and short term experiments are related only to the degree of development of the same microstructural changes. This observation is consistent with the fact that the sample recrystallised for 11 hrs. had less opportunity to respond to the annealing treatment.

The development of polygonal grain shapes and triple-point grain boundary intersections in the sample annealed

for 1 week at 650°C indicates that coherent grain to grain interfaces were able to migrate under the influence of their surface energy. Thus intergranular diffusion occurs at 650°C, and interstitial fluids would be relatively unimportant at this temperature. Moreover, the reduction in the incidence of primary growth zone structures can be taken to indicate that significant volume diffusion occurs in the pyrite lattice at temperatures as low as 650°C.

6.5.3 Stress-Annealing

In this group of experiments the test samples were simultaneously loaded and annealed with the intention of producing at least small amounts of plastic strain which would tend to facilitate the recrystallisation process. The final objective was to obtain a rough estimate of the reduction of the minimum recrystallisation temperature associated with plastic strain. However, none of the test samples underwent plastic deformation, and the original purpose of the experiments was not achieved. For this reason, the results described in sect. 6.4.2 have not been thoroughly analysed. A brief discussion is presented below but is confined to only the more obvious features of the experiments.

Two specimens were stress-annealed for the same period of time (1 week) and over the same temperature range (400°C - 600°C) as in the static annealing experiments where incipient recrystallisation was produced. In contrast to the statically annealed samples, neither of the stress-annealed specimens responded to the heating treatment. This behaviour might be partly due to escape of primary interstitial fluids. The effect of an applied stress may be important in so far as grain boundaries parallel to the compression axis would tend to become less coherent, thus increasing their permeability and facilitating the escape of interstitial fluids. However, fluids should be sealed

even more thoroughly in grain boundaries oriented at right angles to the compression axis.

In both the experiment at 400°C and in the experiment at 600°C chalcopyrite and sphalerite did not undergo the characteristic internal changes which occur under static annealing conditions at the same temperature (i.e. dispersal of chalcopyrite inclusions in sphalerite grains, and the development of a lamellar substructure in chalcopyrite grains). These changes obviously involve volume diffusion in the chalcopyrite and sphalerite grains, and their absence in the stress-annealed samples is predictable since the effect of the stress field would be to stabilise the crystalline lattice and thus inhibit volume diffusion. However, in pockets of interstitial fluids diffusion can scarcely be inhibited because the interstices are surrounded by rigid grains and only a negligible component of the stress can be transmitted via the interstitial fluids. A proper explanation cannot be offered for the behaviour of the samples stress-annealed at 400°C and 600°C .

In comparison to static annealing at the same temperature, recrystallisation phenomena were again markedly retarded in the specimen that was stress-annealed at 650°C . Sphalerite and chalcopyrite grains undergo internal changes indicating that volume diffusion was operative, but these changes occur during static annealing at much lower temperatures (i.e. 400°C - 500°C). The sparse development of grain boundary pores in the pyrite aggregate suggests that interstitial fluids have been effective as a diffusion medium. Thus the effects of incipient recrystallisation are just being initiated at the same temperature at which moderate recrystallisation is produced under static annealing conditions.

Except in relation to chalcopyrite and sphalerite, the stress-annealing effects induced over a period of 1

week at 700°C are again much less marked than the static annealing phenomena produced at the same temperature. In the pyritic component of the sample, grain shape adjustments are detectable and indicate that coherent grain boundaries were able to migrate, and therefore, that intergranular diffusion was operative. However, in comparison to the specimens that were statically annealed at 700°C , the grain shape changes are much less marked in the stress-annealed sample, thus implying that diffusion was considerably inhibited by the applied stress. There is some suggestion that the internal grain structure was slightly homogenised, but even if these changes were induced, they are much less marked than in the statically annealed samples, and indicate a corresponding inhibition of the volume diffusion process. The tendency for polygonal grain shapes and 120° , triple-point grain boundary intersections to develop in the fine grained clusters suggests that the migration of grain boundaries was strongly influenced by their surface energy. However, the local development of slightly elongate grains with their long axes at right angles to the compression direction probably means that the grain shape adjustments were also influenced by a tendency for atoms to migrate from grain faces in normal compression to grain faces in normal tension.

The reduction of the pore space volume in the sample which was stress-annealed at 700°C for 1 week is quite different from the behaviour of the specimens which were statically annealed at the same temperature, and where the total pore volume actually increased. The contrasting behaviour of these samples testifies to the effectiveness of the stress field in directing the diffusion process. Since mechanical deformation was not produced, pore closure must have been achieved by migration of atoms from the grain boundary region to the free grain surfaces exposed at the interstitial sites.

6.6 Summary and Conclusions

Microstructural changes were produced in samples of the natural, fine grained, Rio Tinto pyrite after static annealing for periods of approximately 1 week at temperatures between 400°C and 700°C. For descriptive purposes it is convenient to divide these changes into three groups, namely, incipient, moderate and substantial recrystallisation. Although the fabric of the recrystallised aggregate is fairly distinctive in each of these stages, an interpretation of the microstructure indicates that there are only two distinguishable ways in which the annealing changes occur, and that there is no physical distinction between the stages of moderate and substantial recrystallisation.

In week-long experiments at temperatures up to 600°C there is no evidence for solid diffusion of the pyrite lattice components, and the microstructural changes are produced via the agency of primary interstitial fluids. Annealing effects are induced in the presence of interstitial fluids at temperatures between 400°C and 600°C. However, the microstructural changes are minimal, and apart from the development of grain boundary voids and modifications to the shape of pre-existing pore spaces, the fabric of the initial aggregate is completely retained. There is no marked correlation between the temperature of annealing and the degree of microstructural alteration, but this discrepancy is almost certainly related to variations in the amount, pressure, and possibly the composition of the interstitial fluids in different test samples. The tendency for grain boundary voids and pre-existing pore spaces to acquire curved boundary shapes indicates that the free grain surfaces adjusted in order to equilibrate under the influence of their surface energy.

The development of annealing phenomena at temperatures as low as 400°C is consistent with the hydrothermal syntheses

reported by Barnard (1967) where significant solubility of pyrite was obtained in chloride-bearing solutions (whose relatively high solvent capacity suggests that they are fairly representative of the primary ore-bearing solutions) at temperatures down to 400°C . There is no evidence for annealing effects below 400°C , but the experimental conditions were not sufficiently well known to be certain of the **potential behaviour of the pyrite ore at these temperatures.**

In week-long experiments at temperatures above 650°C , the pyrite lattice components are sufficiently activated to undergo detectable volume and intergranular diffusion, and the pyrite aggregates recrystallise in the solid state. The facility for volume and intergranular diffusion to occur implies that free surface diffusion is also operative, and can proceed without the aid of interstitial fluids. In fact, at temperatures above 650°C , the role of interstitial fluids will be unimportant because the transport of atoms can be effected more directly by the solid diffusion mechanisms. In the temperature range $650^{\circ}\text{C} - 700^{\circ}\text{C}$, the extent of the microstructural changes induced by recrystallisation increases with increasing temperature, and with increasing annealing time. The natural ore recrystallises under the influence of the free energy associated with the grain boundaries, and the most striking microstructural changes are the development of polygonal grain shapes and the homogenisation of the internal grain structure. After an annealing period of 1 week at 650°C , the main properties of the initial microstructure are easily recognisable. Even after the same annealing time at 700°C , relict features of the primary fabric can still be discerned; however, recrystallisation has led to marked equilibration of the grain boundary configuration, widespread homogenisation of the internal grain structure, a reduction of the bulk specimen density, and probably an increase in the average grain size.

The results of the experiments conducted in the temperature range 400°C - 600°C on the one hand, and in the range 650°C - 700°C on the other, lead to the conclusion that significant solid diffusion of the pyrite lattice components is activated at a minimum temperature somewhere between 600°C and 650°C . This temperature interval must contain the minimum temperature at which the natural pyrite, in week-long experiments, undergoes detectable recrystallisation in the solid state and under the influence of grain boundary free energy.

It is interesting to note that the minimum temperature for solid diffusion as estimated from the annealing experiments shows a good correlation with the measured vapour pressure curve for pyrite (this curve is summarised in the paper by Kullerud, 1959). Near 600°C the vapour pressure of pyrite is negligible, and rapidly increases to 1 atmosphere at 690°C . The negligible vapour pressure near 600°C indicates that the lattice is quite stable at this temperature, and that the number of atoms leaving their sites even at the free surface of the lattice is extremely small. It seems reasonable to infer from this that, although surface diffusion might be activated, significant intergranular diffusion, and certainly volume diffusion, would not occur in short term experiments (for example, week-long tests) at 600°C . This conclusion agrees with the results of the annealing experiments which show that solid state recrystallisation does not occur at or below 600°C . Since the vapour pressure of pyrite reaches a substantial value (approximately 140 mm. Hg) at 650°C , it might be expected that intergranular diffusion becomes a significant factor at this temperature. This prediction is again consistent with the recrystallisation experiments, where coherent grain boundary migration was first observed at 650°C .

Compared to the static annealing experiments, similar

recrystallisation phenomena were induced in the samples that were stress-annealed over the same temperature range. Although the stressed samples were not mechanically deformed, the specimen annealed at 700°C was shortened by approximately 10% as a result of pore space shrinkage. The principal effect of the stress field was to inhibit the diffusion process. The minimum temperature at which the pyrite samples recrystallised in the solid state is raised from 600°C - 650°C , with static annealing conditions, to 650°C - 700°C when the samples are stressed near their fracture point for the same annealing period. In relation to solid diffusion the retarding influence of the stress field is understandable, and is due to the compression and consequent stabilisation of the crystalline lattice. However, a satisfactory explanation cannot be offered for the apparently complete inhibition of diffusion at 400°C and 600°C .

CHAPTER 7RECRYSTALLISATION OF THE MASSIVE ORE

In the ore minerals there are few conclusively established examples of recrystallisation, undoubtedly because of uncertainties about the origin and therefore the primary character of many ore deposits. This is especially true of stratiform, massive sulphide deposits. Unless recrystallisation can be demonstrated by showing that the present fabric of the ore is incompatible with known conditions of primary deposition, adequate criteria must be formulated to enable independent recognition of recrystallisation fabrics. Except in isolated instances (e.g. Stanton, 1964), such criteria do not exist at present, and many interpretations of supposedly recrystallised fabrics are probably open to question.

The object of this chapter is to establish whether the massive ore in the San Dionisio lode has been recrystallised, independently of assumptions regarding the primary origin of the deposit. The problem of recrystallisation is considered from two viewpoints:

- (1) The microstructure of the ore is examined in order to test whether or not the growth history, as recorded by the internal and external structure of pyrite grains, can be interpreted in terms of a recrystallisation process. To analyse the microstructure from this viewpoint, it is obviously necessary to know what are the possible recrystallisation mechanisms that could operate, and what microstructural changes would occur when these mechanisms do operate. The review presented in sect. 7.1 summarises the main phenomena associated with different modes of recrystallisation, and provides a basis for the interpretation of the microstructures which is presented in sect. 7.2.
- (2) The physical conditions under which pyrite can recrystallise.

stalise are partly known from the experimental studies described in Chapter 6. In principle, it should be possible to decide whether the pyritic ore could have been recrystallised by comparing the experimental results with the metamorphic conditions indicated by the mineral assemblages in the country rocks. In sect. 7.3 this comparison is examined together with the implications of the behaviour of the natural microstructure under conditions permitting recrystallisation.

7.1 Possible Recrystallisation Processes and the Accompanying Microstructural Changes.

7.1.1 General Changes Involved

Recrystallisation is generally taken to include all solid state grain adjustments excluding phase transformations and mechanical deformation. Three types of changes can be distinguished:

- (i) Changes driven by surface or interfacial free energy (e.g. gradual grain growth; secondary recrystallisation) (sect. 7.1.3 (1)).
- (ii) Changes directed by an external stress field (e.g. pressure-solution (Riecke growth; Herring-Nabarro creep) (sect. 7.1.3 (2)).
- (iii) Changes driven by stored grain energy (e.g. recovery; primary recrystallisation) (sect. 7.1.3 (3)).

The idea of recrystallisation can be extended to include grain adjustments involving material transfer through the medium of an interstitial fluid. The main characteristic of this type of change is that it proceeds by a solution-precipitation mechanism, and therefore may occur at much lower temperatures than solid state recrystallisation.

When the component grains of an aggregate interlock across the boundaries of atomic or near-atomic fit, interstitial fluids can have no relevance since the structure of

their molecules cannot be maintained in the interface region.

If metamorphic conditions are such that lattice (volume) diffusion is operative, the contribution to material transfer by interstitial fluids depends on the fraction of the total surface area (i.e. at macroscopic pore spaces) accessible to these solutions. However, even if the pore surface area is large, the number of individual transport steps required for diffusion through an interstitial fluid is much greater than that for direct diffusion across a grain boundary. Thus, under conditions where direct intergranular diffusion is operative, the role of interstitial fluids will automatically be unimportant because recrystallisation can be accomplished more rapidly by solid diffusion.

7.1.2 Necessary Environmental Conditions

Recrystallisation is a thermally activated process, and this property is the main factor in controlling whether or not a particular mineral aggregate will respond to a given set of metamorphic conditions. Grain adjustments in the solid state require self-diffusion of all lattice components a process which only becomes possible when the temperature is sufficiently high to activate a significant number of atoms. Owing to the variable structure and bond strength of different minerals, the critical temperature below which diffusion is negligible will vary from one mineral species to another. Some sulphide minerals, for example, may show no response to the same metamorphic conditions under which their country rocks are able to recrystallise.

The effect of pressure on recrystallisation can be directive, and its kinetic influence, although small in principle, is to retard the diffusion process (Shewmon, 1963, p. 81).

Stored **strain** energy lowers the temperature at which

recrystallisation can begin, and increases the rate of the process at a given temperature. The effect of strain energy derives from the presence of lattice imperfections (principally dislocations), which facilitate diffusion and lower the required activation energy. The critical temperature for recrystallisation decreases with increasing strain (Cahn, 1965, p. 344), and when deformation is simultaneously induced (syntectonic recrystallisation), with decreasing strain rate (Carter et al. 1964; Heard, 1963).

Due to the extended periods of time available in the natural environment, the temperature at which recrystallisation would first become noticeable is lower in comparison to that observed under experimental conditions. Individual transport steps which occur slowly and have no observable effect over short periods of time may, under natural conditions, become sufficiently cumulative to produce recognisable changes. The magnitude of this effect is controlled by an exponential relationship between the duration of the process and temperature.

7.1.3 Grain Shape Changes

(1) Recrystallisation Motivated by Surface or Interfacial Energy

There are two quite distinct conditions under which grains can change their shape in response to their boundary free energy. Changes occurring in fully compacted aggregates must be distinguished from those which take place in porous aggregates.

Compact Aggregates Owing to the absence of macroscopic voids, and hence the exclusion of interstitial fluids, diffusion of the lattice components must occur in the solid state. At sufficiently high temperatures, recrystallisation takes place by direct intergranular

diffusion and concomitant grain boundary migration. In aggregates where there is no preferred crystallographic orientation, most grain boundaries have high angle misorientations, and the grain boundary free energy is effectively constant for all boundary orientations. During recrystallisation, grain boundary adjustments occur in such a way as to minimise the boundary free energy, and at the same time to reach an equilibrium configuration of the intersecting grain boundaries. If the growth rate of all grains is approximately uniform, the recrystallised grain size distribution is uni-modal, and the growth process is termed gradual grain growth, (Cahn, 1965, p. 972). If abnormally large grains already exist, or are able to develop, their growth rate is significantly greater than that of the matrix grains, and the grain size distribution in the resulting microstructure becomes increasing bi-modal; this process is termed secondary recrystallisation, or discontinuous grain growth, (Cahn, 1965, p. 977).

The equilibration of constant energy grain boundaries tends to produce a microstructure in which the grain boundaries are smoothly curved and intersect at 120° angles at triple-point junctions. In section, most grains are regular, 6-sided polygons, but the abnormally large grains developed during secondary recrystallisation are many-sided and the grain boundary segments are more strongly curved than the matrix grain boundaries. The grain shapes produced under conditions permitting grain boundary equilibration are virtually unique, and it would only be under extremely fortuitous circumstances that similar shapes could develop ~~during~~ primary growth or during other types of recrystallisation.

In the secondary recrystallisation process referred to above, the shape of the large grains is determined by the uniformity of the matrix. The gross grain shapes can be highly variable, but in detail the grain boundaries are

serrate due to the curvatures introduced at the points of intersection with the matrix grain boundaries. Secondary recrystallisation can also lead to the development of euhedral grain shapes (see for example Kingery, 1960, p. 366). The latter arise under special conditions when an isotropic impurity phase accumulates at the boundaries of the large grains and functions as a diffusion medium. The growth and/or equilibration of the large grains can then be directly controlled by the anisotropy of their lattice structure.

Non-Compact Aggregates: The energy associated with free, or exposed, surfaces of grains can effect adjustments to their shape under a wide range of conditions. The presence of voids means that interstitial fluids can exist and function as a diffusion medium. Hence the temperature range for recrystallisation extends from the field of solid diffusion to a point where the lattice components are still significantly soluble in the interstitial fluid. A distinctive controlling factor in the changes that take place in a porous aggregate is that the surface energy of a free grain surface shows significant variations dependent on lattice orientation, whereas the free energy of the interface between two contacting grains is, except in a few special cases, effectively constant and independent of lattice orientation. It is convenient to discuss the changes which accompany recrystallisation in porous aggregates under two headings, namely, (A) recrystallisation with constant pore volume, and (B) recrystallisation with diminishing pore volume.

(A) Constant pore volume: Because of the time factor involved in the natural environment, it is almost certain that a minimum condition for maintaining a constant pore volume is that solid diffusion is not operative. If this mode of diffusion can operate, then it is always possible

for the pore components to leave the site of the pore, especially if there are intersecting grain boundaries (see below).

The free surface exposed at a pore entirely enclosed within a single grain, if in equilibrium with an atmosphere of the lattice components, will tend to adjust its shape to minimise the total surface free energy. Since different lattice planes have different surface energies, there is an optimum pore shape combining several of these planes, in which the total surface energy is minimised. This shape, known as the equilibrium form, can be euhedral and varies from one mineral species to another. Attainment of the equilibrium form will be distinguished here as habit equilibration, and should not be confused with cumulative growth (or dissolution) processes which may also lead to the development of simple euhedral grain shapes.

Despite the potential capacity for equilibrium crystal habits to develop, the number of instances in which this happens in the natural environment is probably small. When the size of a pore is approximately equal to or less than the average grain size, the area of the pore wall as a whole becomes important, and the resulting shape is governed by a compromise between minimising the total wall area and the energy of the free surface of each grain. At equilibrium the pore wall is curved and meets the intersecting grain boundaries at dihedral angles which depend on the surface tension of the various interfaces involved.

If this type of surface equilibration takes place under conditions such that solid diffusion is not activated, then the inter-grain contacts in coherent parts of an aggregate must remain fixed at least temporarily. However, during equilibrium adjacent pores may impinge, thus regenerating a new disequilibrium structure. Coalescence of pores involves solution at some sites on the pore walls and deposition of this material at other sites. Material

deposited at any one stage may become subject to solution and re-distribution at a later stage. Cyclic adjustments of this type will proceed until the pores reach a size where the driving force for further changes is negligible.

(B) Diminishing pore volume: if the pore components (vacancies, and perhaps interstitial fluids) can diffuse along grain boundaries (or through the crystal lattice), then the pores will decrease in size and eventually disappear. These changes are well exemplified by synthetic sintering processes. The driving force for densification is the reduction in the total pore wall area, which is achieved when the pore components diffuse to an external sink (i.e. the overlying rocks). Emigration of the void components is equivalent to a transfer of the lattice components of the bounding grains into the pore, and hence its closure. In the natural environment, diffusion of vacancies and interstitial fluids to the overlying rocks would be enhanced by the presence of a thermal and hydrostatic pressure gradient.

The facility for diffusion to occur in the grain boundaries means that, contemporaneously with pore closure, the grain boundaries will migrate in response to significant driving forces due to their surface free energy. If pore closure is effected the final fabric will exhibit an equilibrium grain boundary configuration identical to that produced in an aggregate which is initially fully compacted. The transient grain shapes will be similar to the equilibrium fabric of a fully compact, two-phase aggregate.

(2) Stress-Directed Recrystallisation

When an aggregate is subjected to a differential stress there is a thermodynamic potential difference between grain faces normal to the maximum compressive stress and those normal to the minimum compressive stress. The overall effect of this potential is such that it generates a tendency

for material to diffuse from grain faces in maximum normal compression to those in minimum normal compression (Goranson, 1940, p. 327 - 331).

If an aggregate recrystallises under these conditions the resulting grain shapes are elongate. However, especially in the type of structurally anisotropic mineral aggregate encountered in the natural environment, these shapes will not be euhedral (cf. the serrate morphologies of pressure-solution grain boundaries). The principal factor controlling the interface adjustments is the stress field. Along a given grain boundary this will have effective variations due to: (i) the orientation of the grain boundary, (ii) the strength anisotropy of contacting grains, and (iii) the presence of voids or inclusions.

When stress directed diffusion determines the elongate shape of recrystallising grains, one of three mechanisms may be operative.

- (i) If an interstitial fluid is involved (pressure-solution as formulated in the Riecke principle) adjustments can take place at relatively low temperatures, and the potential difference is governed by the supersaturation levels at the stressed faces. This mechanism may have considerable importance in the early stages of compaction when large surface areas are exposed to the interstitial fluids.
- (ii) If direct intergranular diffusion occurs then the potential difference is probably closely related to the vapour pressure at the stressed faces.
- (iii) When diffusion occurs in the lattice volume, the potential difference is provided by the different vacancy concentrations at the stressed faces (Herring-Nabarro creep; see Cahn, 1965, p. 817). This third mechanism is activated at only relatively high temperatures, and for this reason may have little importance under natural conditions.

(3) Recrystallisation Motivated by Stored Strain Energy

Grain shape changes of this type have obvious importance in plastically deformed rocks, where they may take place either subsequent to the relaxation of an external stress (static recrystallisation) or during the actual deformation itself (syntectonic recrystallisation). In metallurgical usage strain energy changes (except recovery) are referred to as primary recrystallisation (Cahn, 1965, p. 944); this terminology will be adopted here.

Primary recrystallisation involves the transformation of strained lattice regions into relatively defect-free equivalents and is motivated by the resultant free energy reduction. If classified according to the origin of the interface separating the strained and newly crystallised lattices, primary recrystallisation processes fall into two categories:

- (i) discrete new grains are nucleated; these nuclei may arise spontaneously, or may develop gradually as a result of a progressive increase in the misorientation of sub-grains.
- (ii) the boundaries between the strained grains themselves migrate and become the interfaces separating strained from recrystallised lattice regions (strain-induced boundary migration).

The configuration of the moving interface, which determines the grain shape, is independent of the origin of the boundary. Growth of the recrystallising region can take place under one of two conditions, and it is these conditions which govern the grain shape. Growth may be controlled by the rate of incorporation of atoms into the new grain lattice (diffusion controlled growth), or by the rate at which atoms cross the recrystallising grain/host grain interface before incorporation (interface controlled growth). Which of these two controls is operative will probably depend mainly on temperature, but also on the

magnitude of the strain energy.

In diffusion controlled growth the shape of ~~new~~ grains is governed by the homogeneity of the diffusion field. Irregular or inequant grain shapes result from non-uniform diffusion, and the latter can arise either because of the symmetry of the lattice structure or through non-uniformity of the strain energy distribution. Since plastic deformation or recovery processes tend to leave a non-uniform distribution of the strain energy (concentrated at slip planes, slip plane intersections, grain boundaries or in a sub-structure), the recrystallising grain shapes will generally be anhedral.

In interface controlled growth the rate controlling step is the diffusivity of atoms across the interface. This factor is influenced by the structure of the interfacial region, which in turn depends both on the misorientation of the grains it separates, and on the orientation of the boundary itself. For certain lattice misorientations and boundary orientations, the grain boundary contains an abnormally high proportion of lattice sites which are coincident or nearly coincident for both grains. If these boundaries move parallel to themselves, the number of atoms that are actually required to diffuse is less than for other types of boundaries. When diffusion is not easily accomplished, these particular boundary orientations maximise the bulk crystal growth rate, and hence ~~delimit~~ the recrystallising grain. Since there can only be a few of the relatively high mobility orientations, the recrystallising grains will tend to develop simple euhedral shapes.

7.1.4 Compositional Changes

Compositional heterogeneities (e.g. growth zoning) or structural defects grown into crystals during their initial precipitation are metastable. Under favourable meta-

morphic conditions these features will be destroyed so that the crystal as a whole attains equilibrium at the prevailing temperature and pressure. Compositional changes are effected by diffusion of the lattice components along concentration gradients between regions of different composition. When volume diffusion is operative, the resulting changes occur readily and involve either homogenisation, or the separation of a new phase as discrete grains (exsolution). Under any conditions permitting grain boundary migration similar changes will tend to occur since the lattice components can always diffuse within and parallel to the grain boundary wherever the latter intersects regions of different composition.

7.1.5 Effect and Behaviour of Impurities

The behaviour of impurity atoms during an annealing process depends on their stability in the host lattice, and this in turn, depends mainly on the recrystallisation temperature. There may be a tendency for the impurities to distribute themselves more uniformly in the host, or to segregate to form discrete particles of a new phase.

When impurity particles occur in the form of discrete grains they are distinguished by the terms, microscopic impurities, or inclusions. The importance of inclusion concentration during recrystallisation derives from the free energy associated with the boundary between the inclusions and the host. A total energy reduction is achieved whenever a migrating grain boundary intersects an inclusion. Thus there is a tendency for the inclusion to remain pinned at the grain boundary. The resulting overall pattern of boundary migration depends on the extent to which the grain boundaries and inclusions remain united.

For recrystallisation processes driven by strain energy, the evolving grain shapes are independent of surface energy changes, and therefore of the boundary free energy associated with inclusion concentrations. The

inclusion array will be effectively inert, and the overall grain boundary configuration unrelated to it. This condition is analogous to entrapment of inclusions during crystal growth from a solution or vapour phase.

Recrystallisation processes driven by interfacial free energy changes are obviously sensitive to the presence of impurities. Incorporation of an inclusion at a grain boundary involves a surface area, and hence an energy decrease which is comparable with that produced by any other boundary adjustment. This means that there is a strong tendency for inclusions to become attached to, and remain at grain boundaries. Any such attraction implies that in the resulting fabric the grain boundaries should be characterised by a **relatively high inclusion density**. This will be especially true where the inclusions are able to migrate readily and accumulate in the boundary, whether the latter is migrating or immobilised.

In the foregoing discussion only rigid inclusions were considered - i.e. those whose shapes remain essentially unchanged during recrystallisation, and in which little or no self-diffusion occurs. If on the other hand, diffusion takes place readily in the impurity particles (which may take the form of either solid particles or pore spaces), there will be a tendency for the inclusions to lower their surface free energy by altering their shapes and by coalescing into increasingly larger particles.

7.2 Significance of the Microstructure of the Massive Ore

There are certain general features of the massive ore which immediately suggest that the primary growth fabric is unrecrystallised. Among these, the following are important: (i) The virtually complete absence of pyrrhotite from the sulphide assemblage suggests that the lode was not subjected to temperature conditions where solid diffusion in the pyrite lattice would be facilitated; (ii) The

widespread preservation of obvious growth structures (i.e. colloform structures and pyrite spheres), and some structures of less certain origin (i.e. the massive-discrete fabrics, and the structures described in sect. 4.5); (iii) The direct juxtaposition of widely different types of monomineralic fabrics (especially of fabrics with extreme grain size differences) is difficult to reconcile with the simultaneity and general uniformity of changes involved in recrystallisation; (iv) The fine grain size of the ore suggests that post-depositional growth processes have not occurred.

The general implications suggested above are fully confirmed by the microstructure of the massive ore, and the purpose of this section is to demonstrate that the observed microstructural properties of the pyrite aggregates cannot be explained in terms of the known changes accompanying recrystallisation (see the preceding section). To simplify the general discussion, the following assumptions are made at the outset, and justified for the reasons appended.

- (1) Intragranular inclusions were present in the original sulphides. This is probably a ubiquitous feature of sulphide deposits in general, especially when the ore minerals have not been subjected to metamorphism. Except through exsolution, solid inclusions cannot be created during recrystallisation. During leaching, voids may be produced and subsequently filled to appear as inclusions, but for obvious reasons, these would nearly always be situated at grain boundaries.
- (2) Metamorphism, if effective, did not involve the breakdown of pyrite to pyrrhotite. A tentative identification suggests that pyrrhotite occasionally occurs as inclusions in pyrite, but the absence of replacement features suggests that these and other types of inclusions are primary in origin. Moreover,

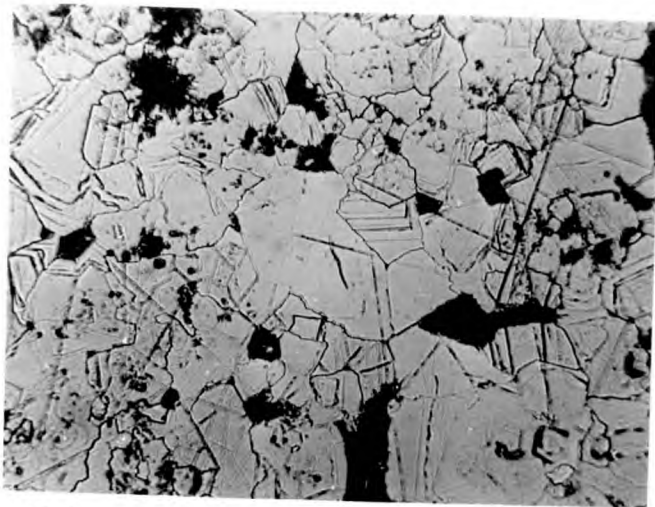
the temperature of the pyrite-pyrrhotite breakdown ($600^{\circ}\text{C} - 700^{\circ}\text{C}$) is far in excess of that represented by the metamorphism of the wall rocks (an upper limit of approximately 350°C).

- (3) If the internal growth zoning of **pyrite** is a primary feature, then its absence from sectional views of some grains is also a primary feature, and due to one of the following causes: (i) the grains in question are unzoned, (ii) the plane of observation does not intersect an existing zone structure, or (iii) the plane of observation corresponds to a lattice orientation for which the dissolution (etching) rate is negligible. Grains in which zone structures are not observed, although frequently grouped together, do not define distinctive structures. In comparison to the surrounding zoned grains, their size distribution is the same and corresponds spatially with that of the zoned grains. These features suggest that both the zoned and apparently unzoned grains belong essentially to the same growth event.

7.2.1 Euhedral Zoning as a Metamorphic Phenomenon

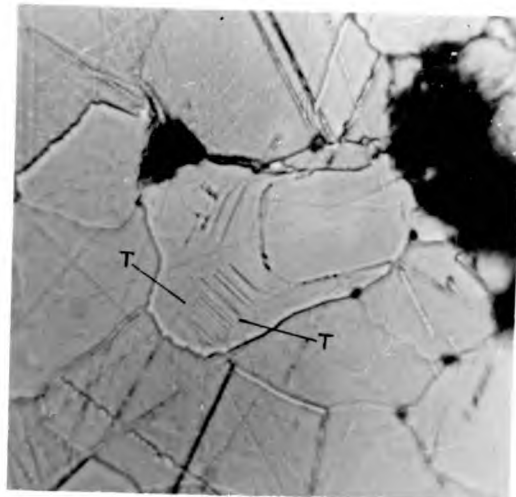
7.2.1 (1) Comparison with Known Examples of Primary Growth Zoning

The intragranular zone structures in the Rio Tinto ore are indistinguishable from those in a number of other deposits for which there can be little doubt that recrystallisation has not occurred. Since comparisons with these deposits are useful both here and in later sections, two examples are briefly described. The Kinousa pyrite deposits of Cyprus (Harris, 1956) are contained in unfolded, though tilted igneous and sedimentary strata which show various types of alteration but which have not been subjected to regional metamorphism. A small pyrite deposit on the island of Hanesavo (British Solomon Islands; see Pudsey-Dawson, 1958) occurs in a tilted succession of unmeta-



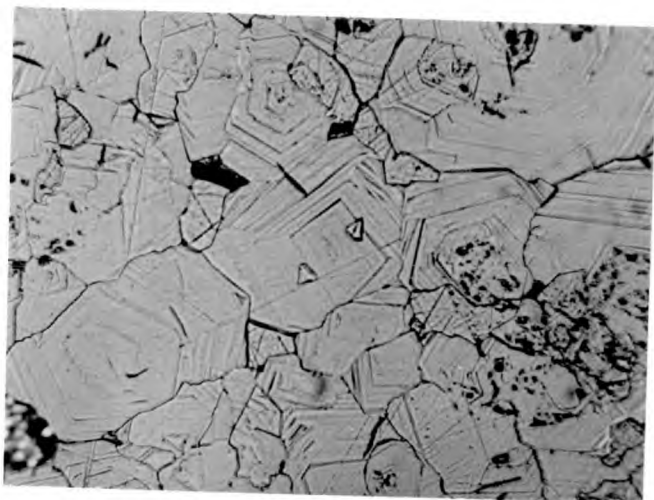
7.1

50 μ



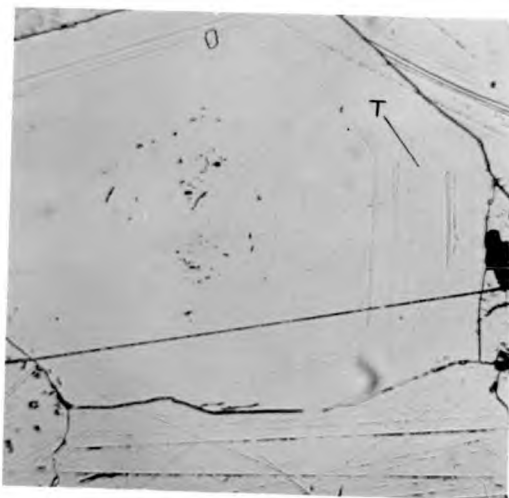
7.2

10 μ



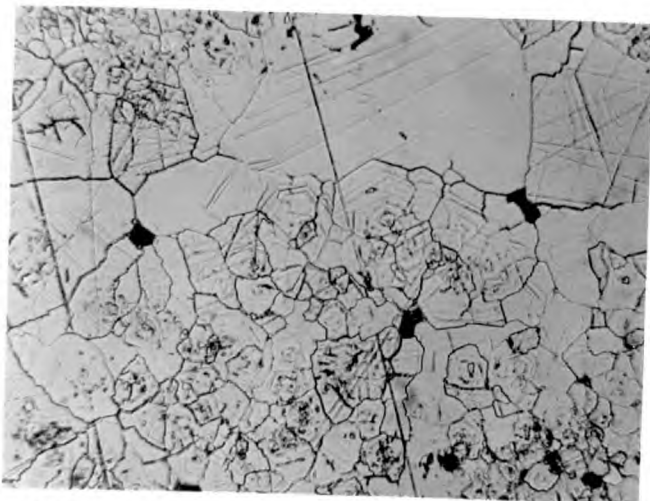
7.3

25 μ



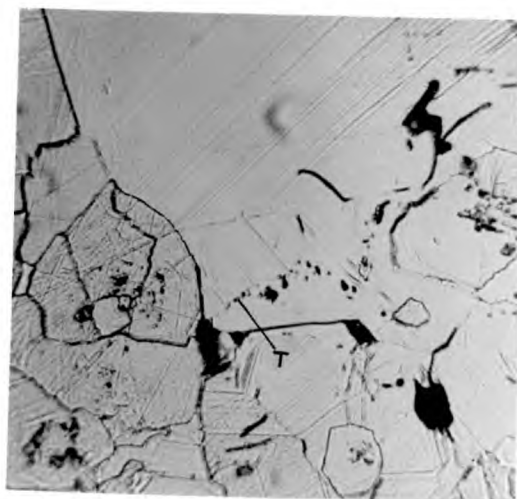
7.4

50 μ



7.5

50 μ



7.6

25 μ

Plates 7.1 and 7.2 Microstructure of pyrite aggregates in a small, near-surface pyritic deposit on the island of Hanesavo (British Solomon Islands).

Most grains exhibit sharply defined compositional zoning, and the predominant structure of the zones is euhedral. In Plate 7.2 the main euhedral zone structure of the central grain is truncated along the surfaces indicated T.

Plates 7.3, 7.4, 7.5 and 7.6 Microstructure of pyrite aggregates in the massive pyritic deposit of Kinousa, Cyprus.

Sharply defined, euhedral zone structures are virtually ubiquitous. In Plates 7.4 and 7.6 the main euhedral zones of the largest grains are truncated along the surfaces indicated T. Inclusions are concentrated at the nucleus regions of many grains and also delineate the truncation surface marked T in Plate 7.6.

morphosed volcanic rocks, under near-surface conditions.

In both of these deposits zoned pyrite grains are commonly observed. Some typical examples are shown in Plates 7.1 - 7.6. These illustrations were selected to show the main features of the zone structures, and could be extended to match practically every type of zone structure observed in the Rio Tinto ores. It seems unlikely that the growth structures produced during the course of a recrystallisation event could duplicate so closely those illustrated in Plates 7.1 - 7.6, which were almost certainly derived during the primary growth history. This suggests that the growth zones in the Rio Tinto ores are not metamorphic features.

7.2.1 (2) Geometrical Implications

Under conditions of metamorphism permitting volume diffusion, the high instability of any form of compositional variations (sect. 7.1.4) makes it unreasonable to suppose that compositionally distinct zones are actually created during recrystallisation.

However, this argument does not apply in the case of low temperature, solid state recrystallisation or in the case of low temperature recrystallisation involving an interstitial fluid. Here, because of the lower temperatures, it is reasonable to suppose that any compositional changes brought about during recrystallisation are imposed on, and retained in the microstructure. The configuration of the resulting compositional zones forms a complex subject, but a brief survey is sufficient to show that the euhedral structure of the observed zones cannot be expected to develop during all but two types of recrystallisation process. Other considerations are required to show that these processes have not been operative.

Assuming the growth zones are metamorphic features, then the obvious explanation for their development is as

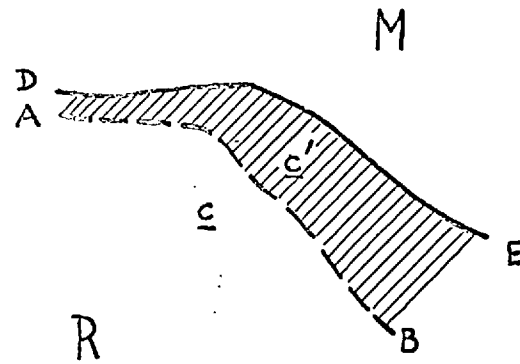


Figure 7.1 Formation of compositional zoning during growth of a recrystallising grain R at the expense of a matrix M. AB and DE are successive positions of the boundary of the recrystallising grain. $\underline{c}$ and $\underline{c}'$ denote the composition of material deposited at different stages of growth.

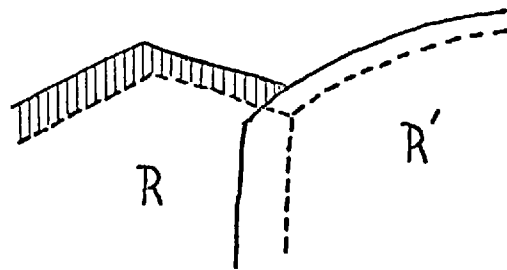


Figure 7.3 Successive stages of growth (denoted by the broken and full line grain boundaries) of the recrystallising grains R and R' under conditions where the interface of each grain migrates under the influence of constant factors and independently of the neighbouring interfaces. The structure of a potential compositional zone in the grain R is indicated by the shaded area.

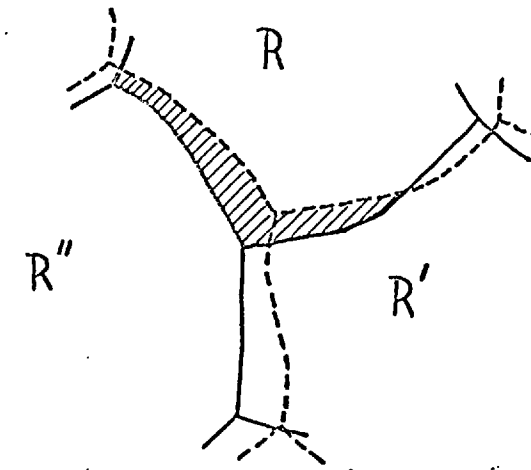


Figure 7.2 Successive stages of growth (denoted by the broken and full line grain boundaries) of the recrystallising grains R, R', and R' under conditions where the migration and configuration of any one grain boundary segment depends on adjustments to neighbouring grain boundaries. The structure of a potential compositional zone in the grain R is indicated by the shaded area.

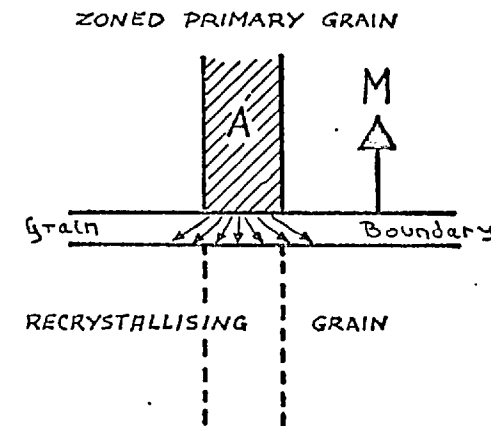


Figure 7.4 Diagrammatic representation of the compositional changes occurring in the interfacial region between a recrystallising grain and a zoned primary grain. The migration direction of the interface is indicated by the arrow M. The shaded area A represents a sharply defined primary zone; the broken lines in the recrystallising grain indicate the diffuse boundaries of re-formed zones. Arrows in the interface region show the general diffusion directions of atoms released from the zone A.

follows. Consider a recrystallising grain R (fig. 7.1) in a primary or recrystallising matrix M. At a particular time its boundary is given by the line AB and material deposited up to this time has composition c . After a further lapse of time, during which material of composition c' is deposited, the matrix/recrystallising grain interface has moved to DE. Successive compositional changes imply successive zones. It is important to note that each zone boundary represents the configuration of an earlier position of the boundary of the recrystallising grain. The final position of the latter is represented by the observed grain boundary.

In discussing the structure of zones resulting from recrystallisation, it is convenient to classify the type of growth involved under two headings, that is, according to whether the growth of single recrystallising grains is dependent or independent of the growth of the neighbouring, matrix grains.

(i) Matrix Dependent Growth

When the migration of the boundary of a recrystallising grain is influenced by, and therefore dependent upon adjustments to the boundaries of neighbouring grains (as in the case of gradual grain growth (sect. 7.1.3)) successive configurations of particular segments of the grain boundaries will generally not be parallel (fig. 7.2). Especially where the grain boundaries do not form an overall orthogonal network, it can only be by chance that a particular boundary migrates parallel to itself.

If successive positions of the grain boundaries are not parallel then the zone boundaries reflecting compositional changes at successive sites will also be non-parallel. This prediction conflicts with the characteristic parallelism of the observed euhedral zone boundaries (see for example Plates 4.37 to 4.40).

(ii) Matrix Independent Growth

When the adjustments to any one grain boundary occur independently of neighbouring boundaries, then, provided the mode of migration is determined by constant factors (i.e. constant mobility and constant driving force), successive positions of the grain boundary will be parallel (fig. 7.3). Under these conditions, parallel zone boundaries are formed, but in order to account for euhedral structures, a special shape for the recrystallising grain must be postulated.

The transitory grain shapes associated with different types of recrystallisation have already been described in section 7.1.3, where it was shown that only in two instances are euhedral forms able to develop (this excludes the local habit equilibration of free grain surfaces, which is irrelevant to the question of bulk recrystallisation):

- (a) During strain energy driven recrystallisation (i.e. primary recrystallisation), when the growth of new grains is controlled by diffusion across the matrix/new grain interface, the shape of the recrystallising grain can be euhedral. If all boundary orientations advance contemporaneously, the resulting growth zones will be essentially continuous. Growth zones produced under these conditions might be structurally identical to the observed euhedral zones. Thus the origin of the latter as metamorphic features remains a possibility, which must be considered at further length.

In comparison to strain energy, surface energy effects are unimportant during primary recrystallisation. The behaviour of inclusion particles is independent of migrating grain boundaries, and hence the euhedral zone structures, and the final positions occupied by the grain

boundaries, will generally transect pre-existing inclusion arrays (sect. 7.1.5). However, these are not the observed relationships. Inclusion concentrations are commonly isolated within single grains and do not transect the grain boundaries (see for example Plates 4.41, 4.57). Moreover, it is frequently observed that inclusions are arranged along discrete euhedral zones (see for example Plate 4.41). This latter relationship is important because it directly implies that euhedral zone boundaries do not represent earlier positions of the boundaries of grains recrystallising under the influence of strain energy.

- (b) When recrystallisation is driven by surface energy, abnormally large grains grow more rapidly than the matrix. This process is known as secondary recrystallisation, and may lead to the development of euhedral grain shapes if an isotropic impurity phase accumulates at the boundaries of the large grains and can function as an effective diffusion medium (sect. 7.1.3).

For two reasons it can be shown that this type of secondary recrystallisation was not operative in determining the transient euhedral grain shapes reflected by the observed zone structures.

Firstly there is no evidence for an isotropic impurity phase. The final site that this phase should occupy is at the grain boundaries resulting from impingement of neighbouring recrystallising grains. In carefully polished, unetched sections there is no direct physical manifestation of the pyrite grain boundaries. Pore spaces are frequently observed at the grain boundaries, but are always disconnected, and cannot therefore, represent the diffusion medium which must be continuous, at least to the extent ind-

cated by the continuity of single growth zones. Grain boundary melting could produce the required boundary phase, but in view of the absence of pyrrhotite this possibility seems exceedingly remote.

Secondly, during the initial stages of recrystallisation, before the boundary phase has accumulated to form a continuous film around the fast growing grains, the boundary free energy of the latter is effectively uniform. The grain shapes developed at this stage are polygonal and include curved grain boundaries, which do not move parallel to themselves, (sect. 7.1.3). The resulting zone structures are not euhedral. The early growth stage thus requires that grains which recrystallise with euhedral shapes in the later stages of growth should exhibit non-euhedral zones in the nucleus region. In fact, this is not observed, and where zones are developed close to the nucleus they are always euhedral and conformable with the surrounding zones.

7.2.2 Significance of Euhedral Zoning as a Primary Growth Feature

7.2.2 (1) Geometrical Implications

It has already been indicated in sect. 4.1.4 (3) that the total pattern delineated by the euhedral growth zones and inclusions arrays enclosed within a single, closed grain boundary is uniquely related to the containing grain. The self distinctive character of discrete sets of internal structures, and evidence suggesting that each of them is associated with a single growth nucleus (sect. 4.1.4 (3) A), indicate that individual sets of structures represent essentially complete and independent regions of growth. These regions, which are recognisable independently of the presence of the grain boundaries, can be regarded as single grains of arbitrary origin.

If euhedral zones are primary growth features, then the limits of individual sets of zones must approximately define the spatial extension of the complete, ~~corresponding~~ primary grains. Moreover, the region between neighbouring sets of zones must contain the primary grain boundary.

If during a metamorphic event, the primary grain boundaries had migrated over distances that were detectable, then in general the resulting grain boundary configurations would transgress the discrete structures defined by zoning. However, the observed grain boundaries do not transect discrete zone structures, but occupy regions which must have contained the primary grain boundaries. This relationship clearly means that post-depositional adjustments in the primary fabric were minimal or non-existent. Moreover, since discrete zone structures, independently of the enclosing grain boundary, define the main limits of extension of ~~individual~~ grains, a minimum conclusion demands that the major aspects of the observed microstructure were established during the primary growth event.

Wherever both sets of zone structures belonging to two neighbouring grains extend to, and intersect the grain boundary, it is directly evident that there has been no migration of this boundary (see for example Plates 4.37, . . . 4.38).

Where euhedral zone structures are truncated short of the grain boundary, the full extension of the primary grains is not directly apparent (see for example Plates 4.46 to 4.56). The region defined independently by the presence of euhedral zones is unrecrystallised, and to this extent, it is certain that the observed aggregates represent the primary growth fabric. However, the region intervening between the grain boundary and the truncation surface (i.e. the anhedral zone, or anhedral region) is usually homogeneous, thus suggesting that this region may have been originally zoned, but subsequently homogenised during migration

of the grain boundary to its present site. This interpretation of the marginal zones can be dismissed for the following reasons:

- (i) Truncation of euhedral zone structures is apparently a common feature in other types of pyrite deposits (e.g. those in Cyprus and on Hanesavo; see Plates 7.2, 7.4, 7.6) where there can virtually be no question of recrystallisation. These occurrences suggest that it is unnecessary to invoke recrystallisation to account for the presence of truncated zones in the Rio Tinto ore.
- (ii) In sect. 4.1.4 (3) A, it was pointed out that the truncation surfaces are frequently characterised by an irregular morphology (see for example Plates 4.46, 4.47, 4.49, 4.50, 4.52), suggesting that the shape of these surfaces was controlled by leaching, which occurred at intermittent periods during the main growth event.
- (iii) According to the recrystallisation hypothesis, a truncation surface represents the foremost point of advance of a migrating grain boundary. Hence, the shape of this surface should reflect the general type of grain boundary morphology which obtained during recrystallisation. In particular, it is reasonable to suppose that the shape of the grain boundary in its final position (i.e. as observed) would correspond in a general way with the shape of the truncation surface. Although this is the most commonly observed relationship, it is noteworthy that there are numerous exceptions. For example, plane truncation surfaces are associated with curved or irregular grain boundaries (see Plates 4.44, 4.54, 4.56), and irregular truncation surfaces are associated with comparatively regular grain boundaries (see the surface marked T_2 in Plate 4.52).
- (iv) In many occurrences euhedral zone structures are truncated on both sides of the grain boundary (see

Plates 4.52, 4.53, 4.56). According to the recrystallisation hypothesis, this implies that boundary migration occurred in two opposite directions, and therefore that at least part of the anhedral zones have been recrystallised twice. In reality, this event is extremely unlikely because there would almost certainly be a greater driving force for boundary migration through the remaining unrecrystallised material (i.e. the regions occupied by euhedral zone structures) than through material that had already been recrystallised once. That is, an anhedral zone could scarcely recrystallise twice whilst contiguous unrecrystallised material remained.

- (v) Along single grain boundary segments euhedral zone structures are frequently terminated only in local regions (see Plate 4.43). On either side of these regions, the zones in both grains extend up to, and intersect the grain boundary, thus indicating that the grain boundary occupies its original position. Over the volume of single grain boundary segments in which truncated and non-truncated zone structures coexist, it is reasonable to assume that the factors influencing recrystallisation would be effectively constant. Hence, if recrystallisation occurred at all, the entire grain boundary segment should have migrated, and the neighbouring zone structures would be truncated at all points along the perimeter. This prediction implies that the observed localised truncation effects are not due to recrystallisation.

It is important to emphasise that where euhedral zone structures do not intersect grain boundaries, it is perfectly reasonable to suppose that this feature developed during the primary growth event. Therefore the necessity to explain the truncation features does not constitute a positive argument for grain boundary migration. Where

truncated zones are present, a difficulty can arise in evaluating the question of grain boundary migration, but the truncation is not significant in the sense that, in order to explain it, grain boundary migration must be invoked. Euhedral zone structures are useful markers delineating, independently of the grain boundary, the extension of discrete primary grains. The problem of grain boundary migration is sometimes difficult to assess simply because these markers are not always present through the entirety of single, adjacent grains. But where the markers are ubiquitous in neighbouring grains, the marker/grain boundary relationship automatically indicates that the grain boundary occupies its original site. The fact that these occurrences are common is taken to indicate that grain boundary migration was not operative in any instance.

7.2.2 (2) The Stability of Growth Zones During Recrystallisation

It is a generally accepted criterion of the metamorphism of silicate rocks that pre-existing compositional variations tend to become diffuse or obliterated. For example, zoned feldspars undergo homogenisation during metamorphism. The reason for these changes can be viewed as the tendency for compositional equilibrium to be restored during the course of the diffusion process which enables recrystallisation to take place.

The general recrystallisation process is adequately described as the growth of new grains at the expense of a diminishing matrix. In the case under discussion, the matrix corresponds to zoned, primary grains. Fig. 7.4 is a diagrammatic representation of the region at a primary/new grain interface; progressive recrystallisation means that the grain boundary moves in the direction of the arrow M. Retention of the primary zones requires that atoms diffuse directly across the primary/new grain interface. However, in the plane of the grain boundary, there is a concentration

gradient to which the diffusing atoms can respond. This situation means that atoms released from the zone marked A, for example, will tend to migrate laterally, as well as directly across the boundary. The resultant effect is that the boundaries of zones re-formed in the new grains are more diffuse in comparison to those in the parent grain. If there is sufficient opportunity for lateral diffusion, then zones will not be re-formed in the new grains (sect. 7.1.4). Except when volume diffusion operates, the new zone boundaries will tend to be most diffuse when diffusion occurs through the medium of an interstitial fluid. In this case, the minimum diffusion path is larger, and therefore associated with a greater opportunity for homogenisation, than when diffusion occurs in the solid state across a coherent grain boundary.

The tendency for compositional zoning to become obliterated by diffusion in the grain boundary region is a minimum consequence of recrystallisation. If recrystallisation is accomplished in the solid state under conditions permitting volume diffusion, then compositional adjustments can occur within the grains, and are not only restricted to the grain boundaries (sect. 7.1.4). Under these conditions, compositional zones are highly unstable and can scarcely be expected to survive at all.

The observed compositional zone boundaries in the pyrite aggregate are sharp to the extent that the etched escarpments defining these boundaries do not exhibit diffuse edges under the optimum conditions of optical observation (see for example Plates 4.37 to 4.56). One specimen was observed using direct electron microscopy, and even at this scale the zones are sharply defined (Plate 4.44). The sharpness of zone boundaries indicated by these observations suggests that inter-zone diffusion has not been operative.

A direct solution to this problem cannot be obtained since there is no independent way of establishing the sharp-

ness of the primary zone boundaries. However, it is instructive to draw a comparison with growth zones in other types of deposits which are almost certainly unrecrystallised (e.g. the Cyprus and Hanesavo deposits; see above). Plates 7.1 to 7.6 illustrate the morphology of typical growth zones from these deposits. In regard to the sharpness of the zone boundaries, the structures illustrated in Plates 7.1 to 7.6 are indistinguishable from the growth zones in the Rio Tinto pyrite (see for example Plates 4.37 to 4.56). This similarity implies that the zone structures in the Rio Tinto pyrite have not been modified by inter-zone diffusion.

The significance of unzoned grains has already been referred to (see (3) in the introduction to sect. 7.2). However, at this point it is important to emphasise again that the absence of manifest zoning may not reflect a real absence of zoning. In any case, the unzoned grains are an integral part of the total fabric, and in view of this relationship it seems entirely reasonable to attribute their growth to the same event during which the zoned grains grew. On this basis, the absence of zoning, if real, cannot be taken to indicate a response to recrystallisation.

7.2.3 Significance of Inclusion Arrays

The distribution of both solid and voidal inclusions must be accounted for in the observed fabrics, and since both these types of inclusions are coextensive it is reasonable to assume that they had a common history. There are two ways in which intragranular inclusions can behave during recrystallisation (sect. 7.1.5); their original sites may remain fixed, or they may undergo re-arrangement whereby the inclusions coalesce or become localised at grain boundaries.

If surface energy effects are unimportant, or the included particles are immobile, the sites of individual

inclusions, and the total inclusion array, will remain unchanged. In relation to the inclusions, however, the associated grain boundaries migrate, and finally occupy new positions. If the inclusions are initially arranged in discrete regions coinciding with single primary grains, then in the recrystallised fabric these arrays will generally be transected by grain boundaries, and their distribution will bear no special relationship to single recrystallised grains.

In the observed fabrics intragranular inclusions frequently occur in discrete concentrations which are essentially coincident with single grains (see for example Plates 4.30, 4.41, 4.57). Assuming these concentrations represent primary inclusion arrays, for which there is good evidence (see below), then the associated grain boundary configuration must be regarded as inconsistent with any recrystallisation process (e.g. primary recrystallisation) where the behaviour of inclusions is independent of the grain boundary adjustments.

There are also many occurrences where the grain boundaries transect concentrations of more or less randomly disseminated inclusions (see for example some parts of the aggregate in Plate 4.11). The relationships observed here are consistent with recrystallisation. However, it is noteworthy that the inclusions themselves frequently occur in sharply defined, regularly shaped areas which are independent of the overall grain structure (see Plates 4.56, 4.58). These special types of distribution cannot be explained in terms of recrystallisation, and strongly suggest that the distribution of the inclusions was derived by pseudomorphism of corresponding structures during the primary growth of the aggregate.

When recrystallisation is motivated by a reduction in the total interfacial free energy of an aggregate, inclusions tend to accumulate at the boundaries of the host grains

(sect. 7.1.5). Thus, since the observed inclusions are not concentrated at grain boundaries, their distribution cannot be attributed to re-arrangement during surface energy driven recrystallisation. Inclusions delineating discrete euhedral zones (see for example Plates 4.41, 4.57) do not represent accumulations at earlier sites of the boundaries of recrystallising grains because, as shown above (sect. 7.2.1 (2)), the euhedral zone structures cannot be interpreted as representing the transient shapes of grains recrystallising under the influence of their surface energy.

7.2.4 Significance of Grain Shapes

Except in the case of gradual grain growth, and in one of the two types of secondary recrystallisation (sect. 7.1.3), criteria relating to grain shape are of little value in distinguishing fabrics which have responded to recrystallisation. Consequently no attempt will be made here to discuss the significance of the observed grain shapes and grain boundary morphologies. However, it is necessary to draw attention to the foliate fabrics.

The elongate grain shapes which are characteristic of these aggregates do not constitute a special occurrence favouring an interpretation in terms of recrystallisation. Although recrystallisation can lead to the development of elongate grains (sect. 7.1.3), this shape is as much subject to ambiguous interpretation as others, and could be produced during primary growth or by mechanical plastic deformation. Indeed, it is important to point out that, because of the orientation of the laminar structure of the foliate fabrics (i.e. parallel to the regional slaty cleavage), their special microstructural properties can be readily interpreted in terms of an anisotropic primary growth mechanism (see sect. 8.3.2 (3)).

Euhedral zoning is the characteristic intragranular growth structure of the foliate fabrics (see Plates 4.65,

4.66). Moreover, although the concentration of inclusions is generally low, single inclusion particles tend to occur in the nucleus region as defined by the zone structures (see Plate 4.66). As indicated in the preceding sections, these properties constitute sufficient evidence to show that recrystallisation has not been operative.

7.3 Comparison of the Wall Rock Metamorphism and the Micro-structure of the Natural Ore, with the Results of the Recrystallisation Experiments

In the immediate and distant wall rocks of the San Dionisio lode the mineral assemblages correspond to the lower greenschist facies (i.e. quartz-chlorite-epidote-albite), and there is no evidence that minerals indicative of higher grades of metamorphism were ever present. It can thus be assumed that the maximum temperature sustained by the wall rocks was somewhere in the region of 350°C (see Hietanen, 1967, fig. 1).

The annealing experiments described in Chapter 6 indicate that in the natural pyrite ore detectable solid state recrystallisation driven by grain boundary energy first occurs at a temperature somewhere between 600°C and 650°C , in week-long experiments. This suggests that the temperatures attained during regional metamorphism may not have been sufficiently high to enable the pyrite ore to recrystallise. However, owing to the long duration of natural metamorphic conditions, the minimum recrystallisation temperature for pyrite as determined in relatively short term experiments cannot be directly compared with the temperature conditions of the regional metamorphism.

Unfortunately there is no basis for extrapolating the experimental results in order to estimate the minimum temperature at which detectable recrystallisation could be induced over long periods of time. This would have been

possible if the activation energy for the recrystallisation process was known, but this is unknown because substantial grain growth was not produced in the experiments. In any case, owing to the initial grain size heterogeneities, the natural ore is not well suited to experiments of this kind where the object is to establish a relationship between the grain size increase produced in a given time (i.e. the rate of grain growth) and the annealing temperature. A reasonable estimate could also be made using the activation energy for self-diffusion in the pyrite lattice, but these data were not available.

The experimental results directly illustrate the instability of the natural microstructure under conditions enabling recrystallisation. The observed grain shape adjustments are relevant only in relation to recrystallisation driven by a grain boundary energy reduction. That is, the production of these changes under experimental conditions indicates that the natural ore has not been recrystallised under the influence of grain boundary energy. However, the destruction of compositional zoning, and probably the dispersal of intragranular inclusions, involve a volume diffusion process, and these changes are therefore independent of the driving force for grain boundary migration. The observed instability of intragranular zoning in particular indicates that the natural ore has not been recrystallised under conditions permitting volume diffusion.

7.4 Summary and Conclusions

In deciding whether or not the pyritic ore has been recrystallised two independent approaches to the problem were considered. Firstly, the microstructure of the ore was examined in relation to known processes of recrystallisation to test whether or not any of these processes could account for the observed microstructural properties of the pyrite. Secondly, experiments were conducted (Chapter 6) to test

whether or not the pyritic ore could recrystallise at the temperature level of the regional metamorphism, and to examine the stability of the microstructure under conditions permitting recrystallisation.

Both the interpretation of the natural microstructure and the comparison between the natural and experimentally recrystallised microstructures lead to the same conclusion, that is, that the massive ore is unrecrystallised. It should be emphasised again that this conclusion refers only to the pyritic component of the ore, and does not include the accessory sulphide and gangue minerals. The latter have not been studied, but their strictly isolated and minor occurrence means that, even if these minerals were recrystallised, there are still no significant metamorphic effects in the primary growth fabrics. For example, since euhedral interstices are defined by unrecrystallised pyrite grains, single crystals of accessory sulphides which occur at these sites could only be internally recrystallised, and the observed shape of the interstitial grains must be the same as at the time of their original deposition.

The conclusions derived from the interpretation of the natural microstructure and of the recrystallisation experiments are summarised below:

- (1) Intragranular growth zone structures occur in other types of pyrite deposits for which there can be little doubt that recrystallisation was not operative. The similarity between the zone structures in these deposits and in the Rio Tinto pyrite suggests that in the latter case also the growth zones are primary in origin.
- (2) If the growth zoning were a metamorphic phenomenon, then the configuration of the zones indicates that the transient recrystallised grain shapes were almost invariably euhedral. From the summary presented in sect. 7.1.3, it is apparent that these grain shapes

could only be explained if special types of primary, or secondary recrystallisation had operated. However, primary recrystallisation is inconsistent with the observed coincidence between zone structures and discrete inclusion arrays. Secondary recrystallisation must be rejected because there is no evidence at the grain boundaries for the diffusion medium which would be required to ensure that the recrystallising grains could develop crystallographic boundaries; moreover, the initial grain shapes produced during secondary recrystallisation should be non-euhedral, and this is again inconsistent with the observed microstructures.

- (3) From (1) and (2) it is concluded that the development of the euhedral zone structures cannot be attributed to recrystallisation, and must be connected with the initial growth of the sulphide aggregate.
- (4) The absence of inclusion concentrations at grain boundaries, and the common tendency for inclusion particles to be concentrated in discrete groups which are coincident with single grains indicate that the observed inclusion arrays were not established during migration of grain boundaries under the influence of their surface energy. If the inclusions were inert during recrystallisation, then the observed coincidence of single grains and discrete inclusion concentrations still implies that recrystallisation has not been operative.
- (5) Assuming that the intragranular zone structures are primary in origin, then their preservation and sharp definition, comparable to that observed in other pyrite deposits which are almost certainly unmetamorphosed, are inconsistent with recrystallisation.
- (6) Since discrete euhedral zone structures, independently of the enclosing grain boundary, define the principal

limits of extension of individual grains, the development of the observed overall grain size and shape characteristics of the pyrite aggregates cannot be attributed to recrystallisation. A minimum conclusion demands that the major aspects of the observed microstructure were established during the primary growth event.

- (7) Because of the virtually ubiquitous occurrence of euhedral zone structures the conclusions summarised above are directly applicable to almost every type of microstructure in the massive ore. There are only two occurrences where the significance of the microstructure is not definitive. Firstly, the ultra-homogeneous fabrics described in sect. 4.5 cannot be interpreted, because the external and internal structure of the component grains is unknown. Secondly, since unzoned grains provide no independent markers of the extension of the primary grains, there is no direct way of establishing whether ~~their~~ original shapes have been modified. However, the integral relationship of unzoned grains to the overall granular assemblage in which they occur strongly suggests that the absence of zoning is not indicative of recrystallisation. Moreover, there may be many instances where the absence of zoning is spurious, and due to a sectioning effect or to a negligible response to etching. The two occurrences of pyrite referred to above are extremely minor constituents of the total ore. This fact is significant to the extent that the demonstrable absence of recrystallisation in the bulk of the ore suggests that, in general, the requisite conditions for recrystallisation did not exist.
- (8) Although the minimum recrystallisation temperature (approximately 600°C, for detectable solid state changes driven by grain boundary free energy) for the

natural pyrite as determined in week-long experiments is much higher than that indicated by the wall rock metamorphism (i.e. a maximum of approximately 350°C), a meaningful comparison cannot be made because there is at present no basis for extrapolating the experimental results to periods of time comparable with a natural metamorphic event.

- (9) The instability of the intragranular zoning observed in the annealing experiments directly indicates that the natural ore was not recrystallised under conditions permitting volume diffusion in the pyrite lattice.

In relation to the time of emplacement of the lode, the final conclusions of this chapter are:

- (i) ~~the~~ lode was emplaced prior to the regional metamorphic /tectonic event, but ~~the~~ temperatures attained during metamorphism were not sufficiently high to induce detectable alterations in the primary microstructure, or
- (ii) the lode was emplaced subsequent to the regional metamorphic/tectonic event.

CHAPTER 8

DEFORMATION OF THE MASSIVE ORE & FOLDING OF THE SAN DIONISIO LODE

For secondary minerals or rocks the possibility arises, at all scales of replacement, that structures indicative of distortion may be inherited from the parent host rock. The facility for structural pseudomorphism to accompany replacement is amply demonstrated in nature. In particular, there are several examples where the deposition of massive and disseminated pyrite and other iron sulphides is known to duplicate the structure of volcanic host rocks (see for example Tan, 1959; Mukaiyama, 1959). Thus, although current views (Williams, 1962; Kinkel, 1962) regard the Rio Tinto deposits as exhalative-sedimentary in origin and therefore imply that the San Dionisio lode was initially flat-lying, in principle there seems to be good reason to investigate the possibility that the observed shape and internal structure of the lode was inherited by replacement of pre-existing tectonic and primary structures.

It is proposed to consider two modes of origin for the San Dionisio ore body, namely: (1) syngenetic or epigenetic deposition in a flat-lying sedimentary/volcanic basin, and (2) epigenetic replacement of an already folded favourable horizon. Following from these hypotheses, there are two alternative interpretations of the present shape of the lode. Corresponding to (1) and (2) above, these are: (i) the shape was derived by folding during the first regional deformation event, and (ii) the shape is an inherited feature. The object of this chapter is to establish which of the latter interpretations is correct.

In attempting to evaluate the significance of the shape of the lode, the approach adopted here is to clarify whether or not the structure of the massive ore reveals direct evidence for deformation.

The first necessity is to explain the broad implications of

the gross structure of the lode in relation to the general features of the deformation required to account for the observed shape. This discussion forms the subject of sect. 8.1 where the main conclusions are that folding of the lode must produce internal deformation of the ore and that the distribution of the fold-producing displacements must be penetrative.

In sects. 8.2 and 8.3 the microstructure of the ore is examined with the object of determining whether or not recognisable primary structures have been modified by later deformation. The results obtained in both these sections, and especially in sect. 8.3, depend on the conclusion reached in Chapter 7, namely, that the massive ore is unrecrystallised. In sect. 8.2 the gross shape and/or internal features of multi-granular primary growth structures are considered from a geometrical viewpoint, independently of any specified deformation mechanism. In all cases the external and/or internal configuration of the structures indicates that the massive ore is undeformed. In Sect. 8.3 the microstructure of each of the fabric types described in Chapter 4 is examined in relation to the three deformation mechanisms, mechanical and diffusional plastic flow, and cataclastic flow. The effects produced when each of these mechanisms operates are predicted, and comparisons are made with the observed microstructure. Again it is found that the recognisable primary component of the microstructures (i.e. the shape, arrangement, spacing and continuity of euhedral zone structures) does not exhibit modifications consistent with the changes predicted for plastic or cataclastic deformation. Unless stated otherwise, the discussion of the microstructure in sects. 8.2 and 8.3 refers only to the pyritic component of the ore.

In sect. 8.4 the course of the previous arguments is summarised and the significance of the slickensides and leaching zones described in Chapter 3 is re-examined. The conclusion is reached that the San Dionisio lode has not been folded, and direct evidence of post-folding mineralisation is presented.

8.1 Significance of the Shape of the Lode & of the Morphology of Primary Depositional Marker Surfaces

In a certain sense the problem of deciding whether or not uniformly dipping, tabular ore bodies have been folded together with the enclosing stratigraphic sequence is more difficult than the equivalent problem as posed by the San Dionisio ore body. An initial flat-lying lode of simple lenticular shape may assume a tilted orientation (conformable with bedding, or perhaps conformable with cleavage) in one of two ways.

If the lode behaves as an integral part of the total deforming rock mass, then it must undergo shape changes and suffer internal displacements. Provided there has been no subsequent re-constitution, evidence for these displacements should be recognisable.

Tilted orientations might also be achieved by simple bodily rotation. This involves no shape change for the ore body, and the deformation is accommodated by non-uniform distortion in the surrounding rocks. Since the lode remains undistorted, there will be no internal evidence for its participation in the folding event.

The second of these tilting mechanisms is likely to be specially important in the case of many pyritic ore bodies in pelitic or pelitic/volcanic country rocks, where the relatively high competency of the sulphide deposits favours a response to deformation as rigid bodies.

Where the ore horizon has a folded shape, the problem of determining the origin of the structure is considerably more tractable. In order to assume any type of non-planar configuration and remain physically continuous, an initially flat-lying horizon must alter its shape. A change in shape, known as pure strain, is needed to account for fold structures since bodily displacements, regardless of the manner in which they are arranged, cannot be used to reconstruct simple tabular forms. Shape changes necessi-

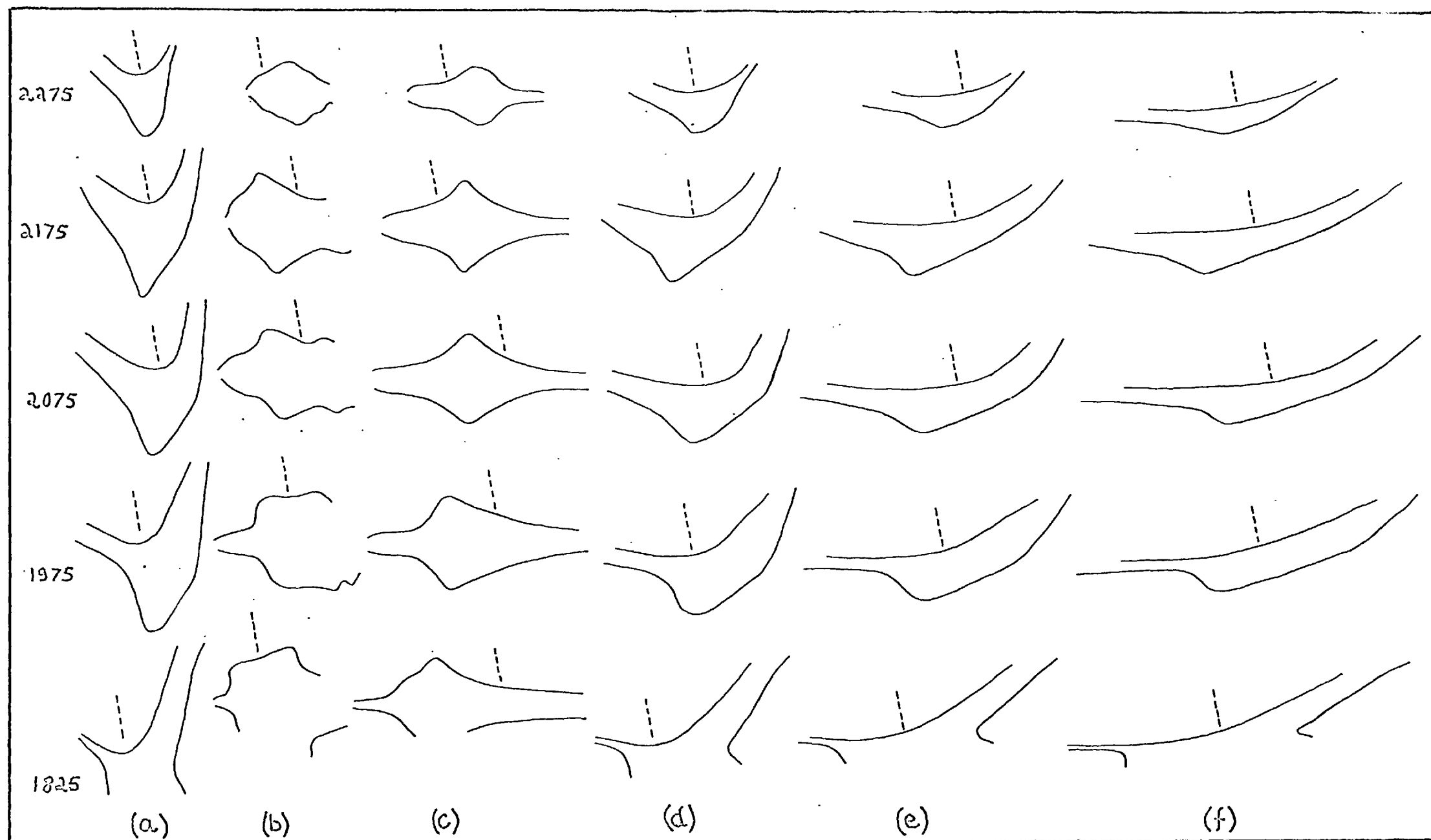


Figure 8.1 Configuration of the San Dionisio lode in sections sub-normal to the plunge of the main synclinal structure. Orientation of the regional slaty cleavage is indicated by the broken lines.

Column (a) simplified forms of the sections shown in fig. 2.9.

Other columns show the initial shape of the lode assuming the observed shape was produced by:

Column (b) similar-folding of a flat-lying horizon.

Column (c) concentric-folding of a flat-lying horizon.

Column (d) 30% compression normal to the regional slaty cleavage.

Column (e) 50% compression normal to the regional slaty cleavage.

Column (f) 60% compression normal to the regional slaty cleavage.

tate differential displacements of points within the body concerned. Recognition of these displacements constitutes the most direct evidence for deformation.

Particular geometric systems of displacements which account for simple fold styles are specified by the similar - or shear-fold, and concentric-fold models. However, the actual geometry of the displacement field is not specially relevant to the question of whether or not a particular structure has a tectonic origin. Nevertheless, even a broad knowledge of the displacement field will be useful, especially in indicating where and along which directions the major effects of the deformation are likely to be found.

Some idea of the type and amount of displacement necessary to account for the shape of the San Dionisio ore body can be obtained through a simple analysis of sections sub-normal to the plunge of the lode. Although the detailed configuration of the ore body is complex (figs. 2.8 and 2.9), its overall synclinal form is simple and well defined. The re-drawn profiles in fig. 8.1 (a) were constructed from the five structurally representative sections shown in fig. 2.9, and were selected at approximately equal intervals along the central half of the lode where the complete synclinal form is well developed.

Owing to the difficulty in interpreting the crenulations and other irregularities of the lode contact, the simplified profiles of fig. 8.1 (a) were constructed by taking an average boundary line between the crests and troughs of the crenulations, and by adjusting this line to join smoothly with the regular orientation of the northern limb and the apex of the lower contact. All five profiles have two main characteristics in common: (i) both fold limbs become thicker in the axial region, and (ii) the orientation of both limbs changes rather sharply along the lower boundary at approximately equal distances from the

apex.

The profiles of fig. 8.1 (a) bear considerable resemblance to similar-folds, and if unrolled according to the conventional mechanism of formation, the reconstructed sections of the flat-lying ore body acquire the shapes shown in fig. 8.1 (b). If the profiles are unrolled assuming initial concentric folding, the shape of the lode is represented by the sections shown in fig. 8.1 (c). Sulphide ore bodies of replacement origin in flat-lying sedimentary strata are known to show considerable thickness variations (see for example Mukaiyama, 1959, pp. 33, 45, 49, 51, 73). However, it seems unlikely that the shapes shown in figs. 8.1 (b) and (c) represent feasible sedimentary forms, and there appears to be some indication that flattening has been important during the deformation.

The effects of flattening were briefly studied by using a simple rectilinear grid system which enabled the profiles of fig. 8.1 (a) to be reconstructed at selected magnitudes of strain. The axial plane of the synclinal structure defined by the ore body corresponds to the regional slaty cleavage, and was assumed to be normal to the maximum shortening direction.

At 50% compression normal to the axial plane cleavage, the shape of the lode at the five selected profiles is shown in fig. 8.1 (e). The average ratio of the maximum and minimum thicknesses of the ore body is approximately 2.8:1. For the similar and concentric models (figs. 8.1 (b), (c)) the average thickness ratio is approximately 5:1. Thus the shape of the lode becomes far more reasonable in terms of a sedimentary deposit when the deformation involves considerable flattening, rather than simple concentric or shear folding.

At 60% compression (fig. 8.1 (f)), the width of the lode is perhaps unreasonable, and at 30% compression (fig. 8.1 (d)), the thickness variation corresponds to an average

ratio of 3.5:1.

The above results suggest that if the lode has been deformed during the main regional folding event then somewhere in the region of 50% flattening has been involved. This figure is indicative of the minimum magnitude of displacements that should be observable in the internal structure of the ore body. The actual displacement directions are not specified, but if flattening has been important, they must occur with two or more orientations, at least one of which is oblique to the axial plane cleavage.

Some knowledge of the spatial distribution of the fold-producing displacements is necessary in order to assess the significance of samples selected to test the occurrence of deformation features. For a simple analysis, it is sufficient to consider only two folding mechanisms: (i) deformation involving displacements along one or more sets of shear planes of constant or variable orientation, and (ii) deformation involving bodily rotation and displacement of rigid blocks in a relatively incompetent and yielding matrix. The separation of the displacement planes in case (i), and the size of the rigid blocks in case (ii), can be estimated by examining the configuration of marker structures involved in the deformation. Two such markers are available: (1) the upper and lower boundaries of the lode, and (2) the boundaries of primary, depositional structures within the massive ore.

Except where the massive ore is gradational to the underlying stockwork zone, the morphology of both the upper and lower contacts of the lode is characteristically smooth and shows no fault-like offsets, small scale projections or embayments. In the massive ore itself, grain size differentiation and other fabric variations define a whole range of macroscopic and microscopic structures whose general shape characteristics almost certainly indicate a primary depositional origin (see for example Plates 4.1, 4.2 and 4.20 to

4.24). The boundaries of these structures are continuous and do not exhibit step-like features or other irregularities which could reasonably be described in terms of truncation phenomena.

The significance of the general morphology, and especially the continuity, of the marker boundaries provided by the lode contacts and internal structures can be explained as follows. If the San Dionisio fold was produced by a deformation involving approximately 50% compression, then the relative displacements occurring along planes at right angles to the maximum compression direction must be of a similar magnitude to the spacing between the displacement planes. Hence, if the movement planes were spaced at megascopic intervals, the marker boundaries should be offset at step-like features with similar dimensions. The megascopic continuity of the marker boundaries thus implies that the fold-producing displacements could not have been confined to a relatively small number of widely spaced movement zones. In fact, the continuity of the marker boundaries, as registered in the microstructure, indicates that the deformation must have been penetrative to the extent that the displacement planes were spaced at distances in the order of a few grain diameters or less.

A similar conclusion applies in the case where the deformation is accomplished by rotation of rigid blocks in a yielding matrix. These blocks must have dimensions not greater than a few grain diameters, otherwise their identity would be reflected by observable discontinuities in the marker boundaries.

The penetrative quality of the deformation is directly implied by the presence of microscopic folds in the massive ore (sect. 3.2.2). The orientation of at least some of these folds (and their axial plan cleavage) corresponds to the orientation of the regional first generation fold system. On the basis of this relationship it is reasonable

to suppose that, if the folds in the ore are tectonic, their development was contemporaneous with the main deformation of the lode. Since the pyrite layers defining the fold structures are continuous and show no significant offsets at the scale of the microstructure (see Plates 3.16 to 3.20) the fold-producing displacements must be spaced at extremely small intervals. Where the folded layers are composed of grains whose diameters approach the layer thickness, a smooth morphology of the boundary of the layer can only mean that at least part of deformation occurred by intragranular distortion. The occurrence of fold structures also implies that the displacement directions were systematically arrayed, and that the deformation was probably not produced by a mechanism involving rotation of rigid blocks in a yielding matrix.

The direct juxtaposition of massive ore and incompetent pelitic rocks at the upper contact of the lode has further implications supporting the conclusions reached above.

From field observations it appears that the massive ore maintains its normal density and composition up to distances of a few millimetres or less from the sharply defined contact with the overlying sediments. At one representative locality, a suite of samples was collected at approximately 10 cm. intervals along a traverse extending from the upper contact into the massive ore. Microscopic examination of these samples reveals that the normal density of the ore is retained up to a distance of less than 10 cm. from the margin of the lode. In the two samples collected in the upper 10 cm. layer the porosity increases considerably (from the normal average of 5% - 10% to an estimated 20%), but the pyrite aggregate is physically continuous. On the basis of the equivalent or near-equivalent composition of the ore at the upper contact and in the interior of the lode, it seems reasonable to conclude that the response to

deformation would be essentially the same at both localities. However, the overlying pelitic rocks are much less competent than the ore, and their facility to accommodate inhomogeneous deformation would be correspondingly pronounced. Thus if the fold-producing displacements were confined to widely spaced movement zones, the evidence for these zones, their spacing and their general configuration should be especially apparent along the upper contact of the lode.

7 The smooth morphology of the upper lode contact cannot be explained by assuming that pre-existing irregularities were smoothed out by intensive shearing in the pelitic rocks overlying the ore body. In the immediate vicinity of the hanging-wall, the slaty cleavage is undistorted and retains its normal, steep dipping orientation independently of the local attitude of the lode contact. Fault-gouge material is apparently rare, and even where it appears the morphology of the hanging-wall is the same as it is elsewhere. If pre-existing irregularities were smoothed out by shearing in the overlying rocks, small or large fragments of ore would be detached from the margin of the lode. ~~Since~~ the overlying rocks are comparatively incompetent, many of these fragments are likely to become completely isolated, and would appear as tectonic inclusions. In fact, there are no isolated lenses or other deposits of massive ore above the upper lode contact.

The main conclusions reached in this section are.

- (1) If the San Dionisio lode has been folded, there should be direct evidence for the deformation in the structure of the ore.
- (2) An estimate of the magnitude of the deformation indicates that the folding would have involved substantial displacements, and therefore that the structural manifestations of the deformation should be readily apparent.
- (3) The morphology of primary depositional marker surfaces

(i.e. the lode contacts and the boundaries of primary structures within the massive ore) implies that the deformation must have been penetrative to the extent that the displacement zones are separated by distances in the order of a few grain diameters or less. It is also reasonable to assume that, at least within regions where the orientation of the marker surfaces is uniform, the magnitude of the displacements is approximately constant.

The importance of the first part of conclusion (3) should be emphasised. The penetrative spacing of the displacement zones implies that, irrespective of where the massive ore is sampled, there should be evidence for the deformation. That is, if there is no evidence for deformation, this result must be directly significant, and cannot be attributed to samples being selected from undeformed regions between zones of active movement. Since the area of conventional polished sections encompasses several hundreds to several thousands of grain diameters, even samples of this size are sufficiently large to incorporate large numbers of movement zones, and should be more or less representative of the deformation at larger scales. It is also significant that the composition of the lode is virtually monomineralic, since this implies a corresponding uniformity for the mechanical properties of the ore, and hence confirms the general validity of the procedure of examining small specimens for evidence of deformation.

In the following two sections the microstructure of the ore is examined on the basis of the conclusions obtained above. Approximately 70 polished sections were studied and the locations of these are shown in fig. 3.1. The samples were collected in the western two thirds of the lode at localities near the upper and lower contacts, near major crenulations in the upper contact, in the axial region of the syncline and in the lower parts of the fold limbs.

Thus, although the sampling is limited, the locations are fairly representative of the main parts of the fold structure. In addition to the polished sections, flat-ground surfaces were examined on 15 other samples (see fig. 3.1 for localities); although it is difficult to interpret these observations directly, there are no obvious differences between samples which were sectioned and polished and those on which only ground surfaces were prepared.

8.2 Implications from the Shape and Internal Features of Primary Growth Structures

In monomineralic aggregates the preservation of the original shapes of primary growth structures is inconsistent with deformation, and cannot be attributed to preferential yielding of a surrounding matrix. In the massive sulphide ore there are four types of growth structures whose original shapes are either partly or completely known. Since these structures have widespread occurrence, their implications provide an important contribution towards assessing the evidence for deformation of the lode.

8.2.1 Multi-granular Aggregates of Spherical and Sub-Spherical Shape

The occurrence of spherically shaped grain aggregates has a unique significance. If the aggregates were initially spherical, an assumption which does not conflict with their interpretation as growth structures, then they are clearly undeformed.

If the aggregates were initially non-spherical, then a special strain (or strains) must be postulated to account for their present shape. Since the deformation is mainly controlled by the external stress-field, shape changes from non-spherical to spherical can only be regarded as fortuitous. Even in the most favourable case, when the initial aggregates

are elliptical and have a preferred dimensional orientation, it can only be fortuitous that the maximum compression axis remains parallel to the long axis of the ellipses, and that the resulting deformation just compensates for the initial shape factor. It is therefore concluded that the existence of spherical grain aggregates implies the absence of deformation, and furthermore, that these aggregates are indeed original growth structures.

Apart from the fine grained pyrite spheres and ellipses whose evolution has already been discussed (Chapter 5), other types of close-packed and disseminated spherical and sub-spherical grain aggregates are also found in the massive ore (see sect. 4.1.1 (3); Plates 4.3, 4.5, 4.7).

- (i) In close-packed aggregates, the tendency towards sphericity and relatively equant shapes is obvious. Where there are departures from sphericity, these can be shown to have a primary origin, for the following reasons:
 - (a) Elliptical and otherwise elongate shapes exhibit no preferred dimensional orientation (see Plate 4.7).
 - (b) Since the external boundaries of non-spherical structures are continuous and not step-like, distortion of these structures could only have taken place by intragranular deformation. The shape and internal structure of the component grains of an aggregate should therefore reflect whether or not deformation has been effective.

Owing to the random grain arrangement within individual structures deformation would produce a fabric in which some grains have their long axes parallel to the axis of maximum compression while others have their long axes perpendicular to the maximum compression axis. If the initial grains are assumed to have had similar

axial ratios, then in distorted structures, grains initially aligned parallel to the compression axis should be more equant in comparison to those initially aligned normal to this axis. Since the shortest dimension of elliptical aggregates is parallel to the compression axis, relatively equant grains should occur along this axis, and elongate grains should lie along the axis connecting the apices of the ellipse.

In the observed elliptical structures, however, there are no obvious grain shape variations of the type predicted above. In the majority of structures, the axial ratios of the component grains are approximately uniform throughout the ellipse (see Plate 4.8), but there are some instances where extreme developments of inequant-irregular grain shapes make it difficult to estimate the axial ratios of many grains.

- (ii) Disseminated aggregates frequently exhibit spherical or near-spherical shapes (see Plate 4.3), but where there are marked departures from sphericity, the aggregates almost invariably occur with well developed elliptical shapes (see Plate 4.4). Although at first sight the latter appear to be deformed, it can be shown that their internal grain structure is explicable only when the overall elliptical shape is regarded as a primary growth feature.

Assuming the elliptical shapes were initially spheres, then as already pointed out in (b) above, the axial ratios of the component grains would be approximately uniform. Since the grain arrangement is radial, subsequent distortions means that grains aligned parallel to the shortest dimension of the ellipse would be more equant than those aligned parallel to the longest dimension. This configuration is frequently observed, but the change in axial ratio is invariably accompanied by a change in grain size (see Plate 4.4).

If the initial structures are assumed to be spherical, it is reasonable to suppose that, because of the radially uniform growth of the sphere, the size of the component grains was approximately uniform. Thus the grain size variation observed in the elliptical structures cannot be explained in terms of deformation, and must be regarded as a primary growth feature. Even if there was a grain size variation in the initial sphere, then the observed symmetrical distribution of the coarse and the fine grains in the ellipses ~~implies~~ that there was always a corresponding symmetrical relationship between the external stress-field and the internal structure of the spheres. However, as pointed out in the introduction, this can only be a fortuitous occurrence. In summary, the internal and external structure of the elliptical aggregates cannot be attributed to distortion of pre-existing spheres, and was apparently derived by anisotropic accretion during the primary growth event.

8.2.2 Colloform Structures

Although the exact shape of these structures in their primitive state cannot be independently established in most specific examples, their general shape characteristics can be estimated. Colloform structures have been described and illustrated from flat-lying, undisturbed sulphide deposits (e.g. the Kinousa deposits, Cyprus; Harris, 1956). These structures, which presumably represent the primitive depositional form, are multi-layered and are characterised by a botryoidal appearance of the three dimensional surface topography of individual colloform bands.

In the Rio Tinto ore it is convenient to consider the colloform structures in two categories (sect. 4.4): (i) open structures (see Plate 4.69), and (ii) closed structures (see Plate 4.68).

Implications from the shape of open structures are

inconclusive. If they are deformed, then the curvature of the boundary and the angle of intersection between adjacent botryoids should be significantly different from the curvatures and angles of intersection in equivalent, undistorted structures. Such differences will be most apparent where the trend of the colloform band is parallel or at right angles to the maximum compression direction. Although there is no record of the shape parameters of undistorted colloform structures, there certainly appears to be no obvious disparity in the shape exhibited by these structures in the Rio Tinto ore and those in undeformed deposits. This suggests that the colloform structures are undistorted.

The shape of closed structures substantiates this conclusion. Although many of these structures are complex in detail, in nearly every instance either single structures or parts of composite structures exhibit a spherical form (see Plate 4.68). As pointed out in the introduction, the ~~existence~~ of spherical shapes can be taken to indicate that the original growth structures are undeformed. Non-spherical structures are also compatible with known growth forms and, especially where they are in direct juxtaposition with spherical structures, the departures from sphericity are difficult to attribute to deformation.

8.2.3 Abnormally Large Single Grains

In some fabrics with a strongly bi-modal grain size distribution, the coarse component is represented by grains with diameters up to approximately 50 times greater than the average matrix grain size. Euhedral arsenopyrite grains with diameters in the order of one or two millimetres have been reported from the massive ore (A.P. Millman, pers. com.). With respect to penetrative deformation in the matrix, many of these large crystals are useful marker objects.

The shape of abnormally large grains is frequently anhedral and therefore of doubtful significance in attempting

to distinguish the possible effects of deformation. In many instances, however, the grain shape is characterised by complete or partial euhedralism (see Plate 4.25). Because of their size and euhedralism, there is little doubt that the deposition of the large grains ~~pre-dates that of~~ the sulphide matrix. Therefore, if the latter is deformed, there should be manifestations of ~~the displacements~~ in the boundary morphology of the large grains.

7 In fact, the preservation of euhedral grain shapes is basically inconsistent with deformation. Planar grain boundaries could be explained if intragranular displacements were affine, but this condition can scarcely be justified in the case of a polycrystalline matrix.

The existence of substantially complete growth zone structures implies that the coarse euhedral grains are not fragments derived from larger grains, and the preservation of sharp grain edges indicates that the large grains were not bodily rotated as rigid units in the surrounding matrix. Where planar grain boundaries degenerate to irregular shapes, the boundary morphology can probably be explained in terms of leaching (see sect. 4.1.4 (1)).

8.2.4 Interstitial Sites

Interstitial sites between the component grains of essentially monomineralic pyrite aggregates fall into two categories, namely, euhedral and leached interstices (sect. 4.6). Although the marginal grains of leached interstices usually exhibit delicate shapes (Plates 4.81 to 4.84) which are unlikely to be retained during a deformation event, the significance of these features is doubtful because of the difficulty in establishing whether the leaching occurred before or after the regional folding.

On the other hand, euhedral interstices can be interpreted as primary growth structures. Moreover, it can be shown that the microstructure of their marginal grains is incompatible with deformation of the primary fabric, irrespec-

tive of the presence ~~or~~ absence of infilling minerals. The importance of these structures in evaluating the general incidence of deformation phenomena lies in their ubiquitous occurrence throughout the lode, and in their small distance of separation (a few to a few tens of grain diameters).

Euhedral interstices show the following important properties:

- (1) the boundary surface is composed of plane grain faces corresponding to euhedral growth forms of the marginal pyrite grains (Plates 4.78, 4.79, 4.80),
- (2) the marginal grains frequently exhibit (a) an increase in size compared to the average grain size of the surrounding aggregate, and (b) a sub-radial elongation (Plate 4.79).
- (3) nearly all interstices are characterised by physical continuity of equivalent growth zones between at least some of the marginal grains (Plates 4.78, 4.79, 4.80),
- (4) a high proportion of interstices are approximately equal or greater in size than the average surrounding grain size (see for example Plates 4.10, 4.79, 4.80).

The first two of the properties listed above suggest that euhedral interstices must be explained essentially in terms of the primary depositional history. In brief, interstitial regions represent sites in the local fabric where, when the surrounding aggregate was fully replaced, grains at these centres had not yet fully impinged, and hence retained their transitory growth habits. Continued growth at the interstitial site is likely to occur on all unimpinged surfaces contemporaneously, and must proceed towards the centre. The continuity of zoning between adjacent marginal grains, the elongation of the grains, and their radial growth directions can be explained on this basis.

For a number of reasons it can be shown that the primary fabric immediately surrounding the interstitial region has not been distorted.

- (1) The presence of plane faces on the marginal pyrite grains is incompatible with deformation. Plastic grain boundary sliding or internal deformation of individual grains would produce at least local distortion of euhedral faces both at voidal and filled interstices. Euhedral forms incorporating sharp grain edges and corners cannot be expected to persist during cataclastic displacements.

Although the total sequence of internal growth zones in the marginal grains frequently incorporates changes of growth habit, there is no record of disturbance or extensive corrosion effects at any stage of the growth history. Because of their essential continuity and identity with grains of the surrounding fabric, the marginal grains cannot be regarded as belonging to a separate or later period of deposition, which might be argued to post-date a later deformation event. Even if this were so, then the interstitial region must have been occupied by other material during the deformation if stability were to be retained. There is no evidence for this material, or for its subsequent removal.

- (2) The physical continuity of equivalent growth zones between adjacent marginal grains indicates that intergrain displacements have not occurred since the primary depositional event.
- (3) A large proportion of voidal interstices must be regarded as unstable during a compressional deformation event. This is especially true of abnormally large pore spaces whose dimensions exceed the average grain size of the surrounding aggregate. Since compression would tend to minimise the total volume, pore spaces whose size approaches the average surrounding grain size are unlikely to be retained. If the infilling sulphide and gangue minerals were introduced

later than the deformation, then the vast majority of interstices must be considered unstable.

8.3 Implications of the Microstructure in Relation to Mechanical and Diffusional Plastic Deformation and Cataclastic Deformation

In a wide variety of materials the structural manifestations of deformation at the granular level are known, and there is sufficient knowledge of the basic principles of shape-changing mechanisms to be able to predict the structural changes accompanying the deformation of crystalline materials in general. By using this knowledge it is possible to test whether or not the grain structure of particular mineral aggregates is consistent with the changes required by deformation.

A body subjected to strain may behave either as a brittle material or as a viscous/plastic material. Since the manifestations of the response to deformation under these two conditions are different, they need to be distinguished.

Stress-strain relationships can be used to distinguish brittle and plastic types of deformation. However, a distinction on this basis serves little useful purpose because the actual displacement mechanisms are not referred to directly.

Strain accomplished by brittle fracture and accompanying displacements is referred to geologically as cataclastic deformation. This process is characterised by discontinuous adjustments and involves extended repetition of the following sequence of events: failure at the limit of the elastic region; displacement accompanied by firstly, stress relief, and secondly, stress increase; failure at the limit of the elastic region, etc. Failure occurs by loss of cohesion between discrete surfaces which are referred to as fracture planes.

Plastic deformation strictly refers to the mechanical

distortion produced in solids in their ductile region, above the yield point. Although this definition excludes shape changes produced by diffusional mechanisms, it is convenient to group non-brittle mechanisms and diffusional changes under the one heading, namely, plastic deformation. This term, unless qualified, will be used to encompass all types of deformation outside the realm of cataclasis. The distinction between diffusional and mechanical plastic deformation is outlined below.

The cold-working process undergone by metals involves mechanical plasticity. Distortion is achieved by intragranular displacements and by grain boundary sliding. Deformation of the lattice structure of single grains occurs by translation and twin gliding, and the actual atomic rearrangements are produced by dislocation movement.

When the deformation is not controlled by dislocation glide, material reorganisation must occur by diffusion. These changes are grouped under the heading diffusional plastic deformation. They are exemplified in the hot-pressing process used for fabricating metallic compounds and ceramics, and probably in the hot-working of metals.

In almost every type of pyrite aggregate in the massive ore the component grains exhibit euhedral zone structures. Since it can be shown that the zoning was not induced by a recrystallisation process (Chapter 7), its origin must be connected with the initial growth of the sulphide aggregate. The importance of euhedral zone structures derives from the fact that they record not only the internal structure of single grains, but also, and **independently of the grain boundaries**, the main grain size and shape characteristics of the primary sulphide aggregate. The object of this section is to test whether the recognisable primary component of the microstructure (i.e. the shape, arrangement, spacing and continuity of euhedral zone structures) is modified by

features which could be interpreted in terms of the deformation mechanisms referred to above. This has been done by predicting the microstructural changes which should occur when the ore is plastically and cataclastically deformed, and then by comparing these changes with the observed microstructure. Each of the microstructures described in Chapter 4 are treated separately, but the main emphasis is placed on the massive and foliate fabrics which are the dominant components of the ore. In fact, the basic problem is presented by the massive and foliate fabrics, and the criteria developed there can be readily applied to the other types of microstructure.

Since the bulk shape of the lode requires that displacement domains be spaced at distances in the order of a few grain diameters or less (sect. 8.1), the influence of deformation on the grain structure must be recorded at an equivalent scale. It is therefore meaningful to test for these effects by examining small specimens, which was the procedure adopted in obtaining the following results.

8.3.1 Massive Fabrics

8.3.1 (1) Cataclastic Deformation

Two repetitive events are involved in cataclastic deformation. In the first place, discrete units in the initial aggregate must become effectively isolated by the development of a sufficiently large number of fracture planes, so that secondly, relative displacements can be initiated between the resulting units. In principle, the first stage is a pre-requisite for the actual deformation, which is produced in the second stage.

Unless the shape of the granular units undergoing displacement is extremely regular, their final packing arrangement must incorporate voids. Neighbouring units will generally impinge at points, along lines, and rarely across extensive surfaces. The voidal regions will therefore be

almost continuous. Thus, since the observed sulphide fabrics are essentially compact, the initial voids resulting from a hypothetical cataclastic deformation event must have been largely infilled at a later stage.

It is reasonable to expect that in some form (if other the infilling material (derived from attrition of the fragments, subsequent introduction of material or both these sources) differs from that comprising the fragments themselves. Hence, in the absence of recrystallisation, the identity of the units of fragmentation and of the cementing material should be recognisable in the form of: (i) some sort of fabric discontinuity at the fragment/cement interface, and (ii) a morphology of the fragments consistent with their evolution. The bulk structure is likely to exhibit close-packed, equant or elongate fragments, separated by cementing material which occupies a semi-continuous interstitial structure.

A. Size of the Units of Fragmentation

In predicting the effects of cataclasis it is advantageous to consider at first the possible dimensions of the units of fragmentation. It has already been shown in sect. 8.1 that, in order to account for the morphology of the lode contacts and of primary depositional marker surfaces within the lode, the displacement domains must have dimensions in the order of a few grain diameters or less. This condition means that discrete units of fragmentation could be either single grains or polygranular aggregates. Direct juxtaposition of polygranular aggregates of sharply different grain size is a common feature in the massive fabrics, and indicates the necessity to establish whether or not the different grain size components can be correlated with the fragment and matrix components of a cataclastically deformed aggregate. This question is examined under (1) and (2) below. The significance of interstitial sites, which might be argued as representing relicts of the initial voids derived

during cataclasis, is discussed under (3). The general conclusion, that the units of fragmentation must be either single grains, or perhaps small groups of grains, is derived in (4).

(1) In the massive ore there are numerous fabrics composed of a fine grained matrix enclosing either discrete coarse grained aggregates (massive-composite fabrics, sect. 4.1.3; see for example Plates 4.17, 4.18) or singly occurring, abnormally large grains (sects. 4.1.2, 4.1.4 (1); see Plates 4.25 to 4.29). In principle it seems possible to interpret the overall structure of these fabrics in terms of brecciation; the coarse grains or aggregates of these grains would represent the main units of fragmentation, and the fine grained component would represent an attrition derived matrix. However, this interpretation must be discounted for the following reasons:

- (i) Coarse grained components cannot be identified with the main units of fragmentation because:
 - (a) the fabrics containing discrete coarse grained clusters or singly occurring, abnormally large grains are not ubiquitous in the lode, and therefore, if considered alone, cannot account for the required penetrative character of the deformation.
 - (b) the boundary morphology of discrete coarse grained aggregates nearly always shows detailed irregularities which are correlable either with the microstructure of the matrix or with the microstructure of the coarse grained aggregate itself (see for example Plates 4.17, 4.18); this relationship implies that the boundary configuration was derived during growth and not by the development of fractures, and subsequent displacements along

the margins of the coarse grained aggregates.

- (c) singly occurring, abnormally large grains exhibit euhedral shapes which usually incorporate, or may be entirely replaced by embayments or irregular projections (Plates 4.25 to 4.29); these features almost certainly mean that the entire grain shape was derived during growth and/or leaching. Both the development and preservation of euhedral shapes and embayed or projecting forms is difficult to reconcile with the displacements involved in cataclasis.
- (ii) Since singly occurring coarse grains or clusters of these grains are usually well separated, the intervening matrix must have been present at the time of the hypothetical deformation event in order to support the main fragmentation units. Thus, the fine grained component of these fabrics can only be interpreted as an attrition derived matrix, and not as cementing material which was subsequently introduced. On this view single or small groups of matrix grains must be regarded as discrete units of fragmentation. The general question of cataclasis which is penetrative at the scale of single grains is discussed under B, below. The arguments presented there are fully applicable to the relatively fine grained matrix components of the fabrics under consideration at present. Under B, below it is shown that single grains or small groups of grains cannot be interpreted as units of fragmentation. Hence, fine grained components do not represent attrition derived matrices.
- (2) In massive fabrics where the different grain size components are strongly differentiated and occupy sharply defined aggregates, the shape of these aggregates must

satisfy certain conditions if the different grain size components are to be identified with a matrix and fragments derived during cataclasis. The units of fragmentation will be essentially isolated, and probably fairly equant. Elongate fragments could develop, and these would tend to assume a preferred orientation during the movement episode. The matrix would tend to occupy a continuous interstitial volume.

In the majority of massive fabrics these conditions are not met. The closest approach to gross structures resembling a breccia aggregate are the fabrics composed of singly occurring, or small groups of abnormally coarse grains contained in a fine grained matrix. These fabrics have been discussed in (1) above, where it was shown that the detailed microstructure cannot be explained in terms of cataclasis. In the massive-composite fabrics coexisting aggregates of different grain size usually exhibit irregular shapes (see Plate 4.17). Grain size differentiation in the massive-discrete (sect. 4.1.1) and massive-composite fabrics also produces aggregates with angular shapes (see Plates 4.2, 4.23, 4.24), but these forms are difficult to reconcile with the effects of attrition at the corners and edges of fragments. In bi-modal massive-homogeneous fabrics (sect. 4.1.2), neither of the grain size components occupies regularly shaped or equant clusters which could reasonably be identified with units of fragmentation (see Plates 4.13, 4.14, 4.15).

- (3) Occupied or voidal interstitial sites cannot represent the voids produced during cataclasis. The following arguments apply to (a) leached interstices (sect. 4.6.2) and (b) euhedral interstices (sect. 4.6.1).

(a) The sporadic distribution of leached interstices is inconsistent with the required penetrative character of the deformation. Moreover, in the

context of a cataclastic genesis, leached interstices must be regarded as embayed modifications of the initial voidal regions. Since the latter must already be almost continuous, isolated leached interstices cannot be interpreted as voids which originated during cataclasis. Continuous leached pore spaces are characteristic of the leaching zones, but as already shown (sect. 3.2.5), these structures are not associated with mechanical displacements.

- (b) The size of euhedral interstices implies that the size of the units of fragmentation approximates the inter-interstice distance or more. The disconnection of interstices means that much of the original voidal space has been subsequently infilled. Since the size of the postulated relict voids (i.e. the observed interstices) generally approaches the average surrounding grain diameter, the infilled regions should be conspicuous. Moreover, these regions should exhibit a microstructure resembling that at the margins of the present interstices. In fact none of these features is present in the observed fabrics. The grain structure along lines linking nearest-neighbour interstices is identical with that found elsewhere in the compact aggregate. In particular, the grain shapes and arrangements characteristic of additional-growth interstices are entirely restricted to the sites of these interstices, and do not extend into the surrounding region to connect with adjacent interstices. It is also important to point out that there is no evidence for mechanical disruption in the internal structure of the marginal grains at the observed interstices (see sect. 8.2.4).

- (4) From the foregoing discussion it is evident that the

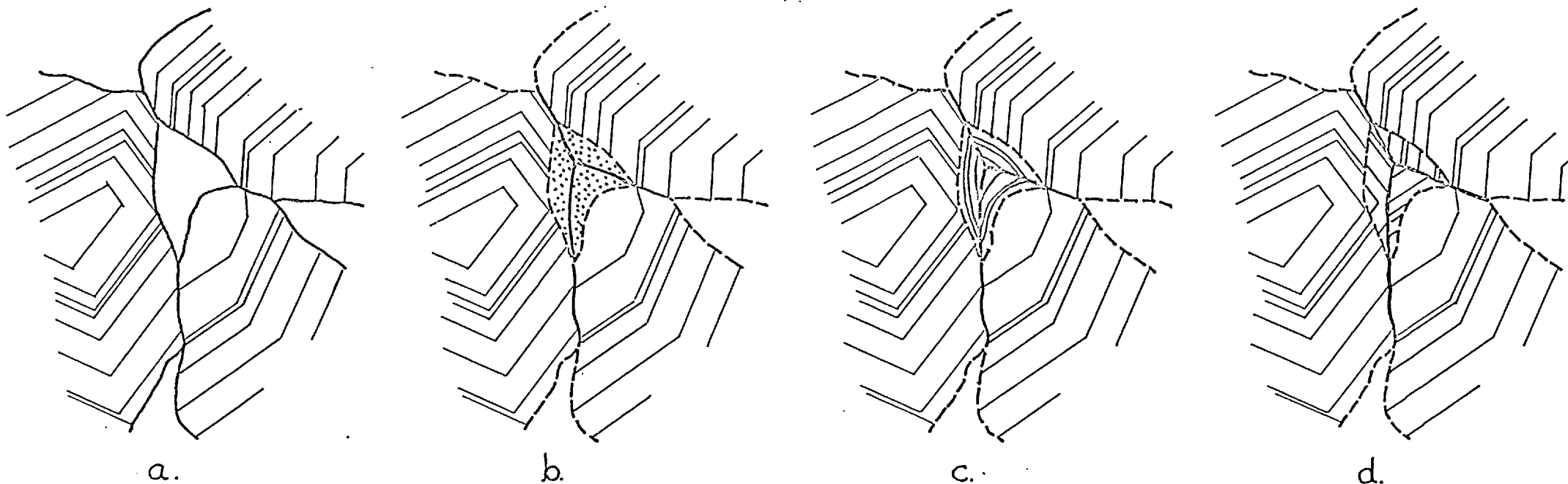
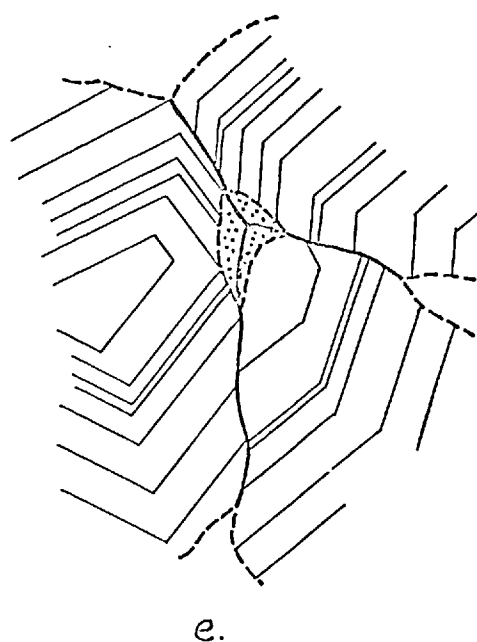


Figure 8.2 Diagrammatic illustration of the microstructure resulting from cataclastic deformation of an aggregate of zoned grains.

- (a) Compacted fragment units immediately following the deformation and prior to cementation. Blank areas represent interstitial voids.
- (b) Fragment units cemented by overgrowths of uniform composition.
- (c) Fragment units cemented by overgrowths showing compositional zoning controlled by the shape of the fragment surfaces.
- (d) Fragment units cemented by overgrowths showing compositional zoning controlled by the lattice structure of the overgrown grains.
- (e) Compaction of fragment units by pressure-solution of material at the original fragment contacts and re-deposition of this material in the initial voids.



various structural relationships between groups of grains characterised by different grain sizes cannot be interpreted in terms of a fragment/cement structure. If the units of fragmentation are multigranular, then their boundaries must in general transect the boundaries separating aggregates characterised by different grain sizes or different fabrics. With subsequent displacements, the latter boundaries must lose their continuity, and the growth fabric will appear fragmented. However, since the fabric and grain size variations which define the growth structures are continuous and show no evidence for multi-grain diameter offsets, the postulated units of fragmentation must be single grains, or perhaps in some instances, small groups of grains.

B. Single Grains or Small Groups of Grains as the Units of Fragmentation

Four main arguments are relevant in showing that single grains or small groups of grains have not undergone cataclastic displacements.

- (1) Since the present sulphide aggregates are almost fully compacted, most of the initial voids resulting from cataclasis must have been infilled. Apart from the contribution due to attrition derived fragments (where it is largely speculative to estimate the quantity of these fragments that would be produced), there are two possible mechanisms by which the infilling might be accomplished, namely, (i) simple overgrowth, and (ii) pressure-solution and overgrowth combined.

The microstructural changes produced by the operation of these mechanisms are illustrated diagrammatically in fig. 8.2. The microstructure at an initial void can generally be represented as in fig. 8.2 (a). At most voids at least part of the enclosing surface will be defined by the truncation of primary growth zones at the margins of the contacting fragments.

If the void is infilled by simple overgrowth at the free surfaces of the fragments, then the resulting microstructure must be represented by one of the three alternatives shown in figs. 8.2 (b), (c), (d). When the overgrowth deposition is not accompanied by compositional changes (which is likely for small volume overgrowths), the voids will be replaced by homogeneous extensions of the original grains (fig. 8.2 (b)). These extensions will be obvious where they are superimposed on free surfaces which are intersected by growth zones belonging to the primary grains (upper fragments in fig. 8.2 (b)). Even where they are superimposed on free surfaces which are not intersected by growth zones (lower fragment in fig. 8.2 (b)), homogeneous overgrowths are likely to differ in composition from the adjacent primary grain. The identity of the overgrowth will then be reflected by the compositional change across the overgrowth/primary grain interface.

If compositional changes occur during overgrowth, the resulting zonation may be controlled by the configuration of the initial free surface or by the lattice structure of the overgrown grains. Where the zonation is controlled by the shape of the initial free surface, the overgrowth will be easily distinguished by the zonal unconformity at the overgrowth/primary grain interface (fig. 8.2 (c)). Overgrowths whose composition is crystallographically controlled (fig. 8.2 (d)) will also be recognisable, though perhaps less readily than other types. Changes in composition during overgrowth cannot be expected to correspond with the changes which occurred during precipitation of the primary grains. Hence the individual zones in a crystallographically controlled overgrowth will not, in general, be continuous with the zones in the contiguous primary grain (fig. 8.2 (d)).

When void filling is accomplished by a simple overgrowth process, the identity of attrition derived fragments must be preserved.

Compaction of the fragmental aggregate could also be effected without the introduction of additional material. When interstitial fluids are present, and when the aggregate is subjected to a load, solution will be promoted at points, lines and surfaces of contact between adjacent fragments. The material removed at these sites can then be re-deposited at the free surfaces of the voids. During pressure-solution the area over which the original fragments are in contact becomes enlarged (fig. 8.2 (e)). The grain structure across these boundaries could be indistinguishable from that across the initial grain boundaries. However, at the sites of re-deposition, the identity of the original voids would be preserved in the form of overgrowths with distinctive internal features corresponding to the three possible types described above. Interstitial fragments of attrition would be subjected to similar solution and re-deposition adjustments, but the additional number of growth nuclei provided by these fragments should be reflected by the presence of a multi-granular, fine grained aggregate occupying part of the overgrowth region.

Previously existing voids may also be defined by solid inclusions or other defects which could accumulate on the fragment surfaces and become entrapped during the subsequent overgrowth.

In massive fabrics, there is no evidence for the previous existence of voids in the vicinity of grain boundaries or grain boundary intersections. The conformability of the euhedral growth zone structure in single grains indicates that each grain grew during essentially a single continuous time interval.

Microstructures corresponding to overgrowths of the types shown in fig. 8.2 are not present. Adjacent grains meet across simple interfaces and are not separated by fine grained interstitial deposits which could be identified with attrition derived material. However, the structure of growth zones in the grain boundary region is frequently complicated by truncation effects (sect. 4.1.4 (3) A), and the full significance of the zoning in relation to the possible existence of overgrowths connected with cataclastic phenomena needs to be considered at further length. For this purpose it is convenient to divide the discussion into four parts.

- (i) Groups of grains in which the internal zone structures extend to and intersect the grain boundaries (see for example Plates 4.37, 4.38, 4.39). These occurrences are common in all types of massive fabrics and the microstructural relationships provide definitive evidence that cataclasis has not been operative. The continuity of primary growth zones to the grain boundaries means that the entire volume of these aggregates is occupied by material which was deposited during the initial growth event. Overgrowths are absent and the grain to grain contacts are those established during primary growth.
- (ii) Groups of grains in which the internal zone structures do not extend to the grain boundaries (see for example Plates 4.46 to 4.56). These occurrences are also common, and in some aggregates are probably more prevalent than those discussed under (i). Although the anhedral zones intervening between the truncation surfaces and the grain boundaries appear as overgrowths, there is no evidence to suggest that the deposition of

these overgrowths followed a period of cataclasis and re-packing of the fragmented grains. As shown in fig. 8.2, the voids in a fragmented aggregate should be largely confined to the immediate vicinity of triple- or multi-grain boundary intersections since it is at these sites that the least close packing of the fragments will be achieved during cataclasis. Thus the later deposited overgrowths should occur as more or less discontinuous and roughly triangular zones centred at the grain boundary intersections. The observed anhedral marginal zones do not exhibit this configuration.

In a few instances anhedral zones occur as major discordant features (Plate 4.46) which appear in only a few grains in aggregates containing in the order of hundreds of grains. The gross size and sporadic distribution of these zones shows no similarity to the predicted form of the overgrowths developed in a cataclastically deformed aggregate (fig. 8.2).

More commonly anhedral zones occupy wide or narrow marginal rims which are more or less conformable with the grain boundary (Plates 4.47 to 4.56). Again, these rims are not confined to the grain boundary intersections. Indeed, where the marginal zones are discontinuous (see for example Plates 4.52 to 4.55), they are more frequently situated between the grain boundary intersections. However, there are many instances where the anhedral zones tend to be continuous around the entire perimeter of a grain. Where the marginal zones show maximum continuity (Plate 4.47), the truncated euhedral zone structures are completely or almost completely isolated, and similarly unsupported

through contacts with neighbouring euhedral zone structures. Since this condition would obviously be unstable during cataclasis, the discrete euhedral zone structures cannot be interpreted as fragments, and the marginal rims cannot represent material deposited in cataclastically developed voids.

The morphology of many truncation surfaces almost certainly indicates that these surfaces are not fracture planes, and hence that the superimposed anhedral zones do not represent overgrowths deposited on cataclastically derived fragments. Euhedral zone structures are frequently terminated along surfaces which exhibit gently curved, embayed and projecting forms (see for example Plates 4.46, 4.47, 4.49, 4.50, 4.52). These features are difficult to reconcile with mechanical phenomena occurring at the fragment surfaces. Externally projecting shapes would be especially unstable when fragments undergo rotation and relative displacements. Pre-existing embayments could be preserved, but are extremely unlikely to be generated during cataclasis. Marginal attrition could lead to the development of grossly rounded fragments, but is scarcely consistent with the smooth boundary morphology which frequently persists at least to the limit of optical resolution.

In many instances, euhedral zone structures are truncated along planar surfaces (Plates 4.44, 4.54, 4.56). The absence of a well developed cleavage in pyrite suggests that plane fracture surfaces are unlikely to develop, and especially when the effects of attrition are taken into account, the maintenance of a smooth fracture plane morphology is difficult to explain.

It is noteworthy that in the case of truncation surfaces with anhedral configurations, there is considerable evidence to suggest that the surface morphology was derived through leaching which occurred at intermittent periods, as an integral part of the main growth event (sect. 4.1.4 (3) A). Even if the leaching was initiated on fracture surfaces developed during cataclasis, then the observed infilling of the voids implies that a second and substantial mineralising event followed the deformation. There is no independent evidence for this.

In conclusion it is important to point out that the truncation of the main euhedral zone structures is not a special feature for which it is necessary to invoke an origin outside the primary or secondary depositional history of the lode. Identical features occur in the microstructure of other types of pyrite deposits for which there can virtually be no question of metamorphic or tectonic adjustments. For example, in the massive pyrite deposit of Kinousa (Cyprus) and Hanesavo (British Solomon Islands) referred to in sect. 7.2.1 (1), intragranular euhedral zone structures are common, but are frequently truncated short of the grain boundary along both plane and irregular surfaces (see Plates 7.2, 7.4, 7.6).

- (iii) Groups of grains in which zoning is absent (Plate 4.36). These occurrences are comparatively rare, and moreover it should be emphasised that the absence of zoning may frequently be an apparent effect (sect. 4.1.4 (3) A). In principle, it could be impossible to establish whether or not overgrowths are incorporated in unzoned grains.

Since their initial growth did not involve compositional changes, there are no independent markers of the extension of the primary grains.

If cataclasis occurred, the resulting voids might be infilled by material derived from the fragmented grains themselves. The final compact aggregate could be composed of internally homogeneous grains. This mode of overgrowth in the voids would imply that pressure-solution was operative; hence at least some parts of the grain boundaries could be expected to exhibit a serrate morphology. This prediction is not borne out by observations, and in fact, unzoned grains are normally characterised by an unusually strong development of plane or smoothly curved grain boundaries (sect. 4.1.4 (2); Plate 4.36).

In view of the absence of direct evidence for secondary overgrowths or grain boundary adjustments, it is concluded that unzoned grains grew entirely during the primary growth event. This conclusion is directly substantiated by the genetic correlation between the compositional homogeneity of unzoned grains and their plane or smoothly curved grain boundary configuration (see sect. 4.1.4 (2)).

- (iv) Some parts of the massive fabrics are characterised by an abnormally large, intergranular pore space volume. In these aggregates it is extremely difficult to evaluate the possible effects of cataclasis. In terms of brecciation, at least part of the pore space could be interpreted as the excess volume due to the initial packing limitations. Complexly shaped grain boundaries could be attributed to pressure-solution; the material derived through the activity of this process must be deposited elsewhere, as overgrowths or new grains.

Although there is no evidence for re-distributed material, this might partly be expected since the thickness of overgrowths would be small where large pore wall areas are available for deposition.

Where pore space has developed during the course of leaching, which is frequently the case, the important, marginal regions of the grains have been destroyed. Pre-existing overgrowths may have been completely obliterated at these sites, or only minor relicts may remain and these might not be easily recognisable.

Comparatively porous aggregates are strictly isolated and are always (except in the leaching zones described in sect. 3.2.5) confined to volumes containing in the order of a few tens to several hundreds of grains. In the surrounding compact fabric all evidence indicates that the primary microstructure is undistorted. Hence, even if brecciation is admitted in the relatively porous aggregates, the deformation must be entirely confined to small isolated regions which could not function as effective movement zones allowing continuous propagation of displacements.

- (2) It has already been shown that because of the special relationships of euhedral growth zone structures (and in many instances, discrete inclusion arrays) to the enclosing grain boundaries each grain has only one growth nucleus (sect. 4.1.4 (3)A). There is no evidence to indicate that growth nuclei are absent from some grains, which might therefore be interpreted as parts of larger grains. Since recrystallisation has not occurred (Chapter 7), and since each grain possesses a single growth nucleus, the main grain size and shape characteristics of any given aggregate must be those of the primary depositional fabric. This means

that, if cataclasis has been effective, the fracture planes must coincide at least approximately with the initial grain boundaries. As there is no evidence for interstitial fragments of attrition, the coincidence of fracture planes and the primary grain boundaries must be virtually complete. This conclusion is difficult to accept.

Intergranular fracture is, in principle, more favourable than trans-crystalline fracture since the cohesion across a grain boundary is less than in the interior of the lattice. However, where equant grain shapes are involved, and when deformation occurs under a considerable confining pressure, it is exceedingly unlikely that all fractures and their associated displacements would be intergranular.

- (3) There is no positive evidence to indicate that pressure-solution has been effective in allowing grains to extend their areas of coherent grain to grain contact. Serrate grain boundaries (Plate 4.35), which are characteristic of known examples of pressure-solution, have limited occurrence, but the relationship of these and other types of grain boundaries to the internal growth zone structures implies that boundary migration was not effective in a fully compacted aggregate (sect. 7.2.2 (1)). This means that the activity of pressure-solution in a breccia aggregate must have been terminated when compaction was complete. At this time, even in a hydrostatic pressure environment, significant stress concentrations are still likely to exist. Thus it is not easy to explain why pressure-solution, if previously operative, suddenly ceased when compaction was achieved. The operation of a pressure-solution mechanism appears even more doubtful because of the widespread occurrence of plane and smoothly curved grain boundaries. These shapes probably imply that

the stresses at the grain boundaries were uniform. This condition is almost certainly not fulfilled, especially in a breccia aggregate whose structure automatically means that the stress distribution at fragment contacts will be complex.

- (4) In all types of massive fabrics there is abundant evidence to demonstrate the absence of intergranular displacements. In small volumes, which may encompass between a few to a few tens of grains, many grains frequently exhibit similar or identical zonal patterns. Where similar zonal patterns in adjacent grains intersect a common grain boundary, equivalent zones invariably meet at this boundary (see Plate 4.37). The intersection of equivalent zones at the grain boundary is obviously a feature developed during the growth process, and the preservation of this relationship implies the absence of intergranular displacements.

The continuity of distinctive zonal patterns between neighbouring grains has already been mentioned in connection with the marginal grains of interstitial sites. It is a common feature in a wide variety of multi-granular growth structures, where the continuity of zoning may even extend over several to several tens of grain diameters (e.g. in the massive-discrete and massive-composite fabrics). In the massive-homogeneous fabrics similar zone patterns can usually only be correlated over small groups of less than about ten grains. If these fabrics are considered together with their interstitial sites, then the spacing between groups of grains in which the zone patterns are contiguous is frequently in the order of ten grain diameters or less.

8.3.1 (2) Mechanical Plastic Deformation

When a polycrystalline aggregate undergoes mechanical plastic flow, single grains are internally distorted and the deform-

ation may be accompanied by intergranular displacements. There are five properties of the deformation which are important here. Each of these is discussed below, and it is found that the predicted modifications to the primary aggregates are inconsistent with the observed microstructure of the massive fabrics.

- (1) During translation gliding individual grains increase their dimensions parallel to the minimum principal stress axis at the expense of a decrease in the dimension normal to this axis. If the grains are initially equant, in the deformed state they will assume elongate shapes parallel to the minimum principal stress axis.

The vast majority of grains in the massive ore are equant. This shape could develop in response to intragranular deformation, but it implies that the initial grains had axial ratios which bore a definite relationship to the ratios of the principal strain axes. The full implications of this requirement need not be elaborated, and it will be clear that even under the most favourable circumstances (i.e. where the initial grains had similar axial ratios and a preferred dimensional orientation) the conditions required to account for a majority of equant grain shapes are too special to be credible.

- (2) In cold-worked polycrystalline aggregates restrictions are imposed on the deformation of any one grain by the presence of surrounding grains. Though the bulk strain for different grains tends to be uniform, the intragranular displacements in single grains are not homogeneous. The constraining effects due to the presence of surrounding grains are especially important in the vicinity of the grain boundaries.

When intragranular displacements are inhomogeneous, the internal strain will be expressed in the form of a non-affine deformation - i.e. features which are

initially linear or planar will acquire curved shapes in response to the deformation. Since euhedral growth zone structures are initially composed of planar zone segments, the configuration of the latter should directly reflect the detailed strain pattern in single grains.

Distorted euhedral zone structures do not occur in the observed fabrics. Each zone segment is planar, and maintains this configuration both in the interior and marginal regions of the grains (see for example Plates 4.37, 4.38, 4.39). These observations imply that the primary growth zones have not been deformed inhomogeneously, and hence that the microstructure of single grains is inconsistent with the predicted effects of deformation in a polycrystalline aggregate.

- (3) Twin gliding involves reorientation of discrete lattice domains. The deformation is inhomogeneous. Thus, as pointed out in (2) above, the regions of differential displacement should be recognisable from the configuration of the primary growth zones.

In the observed aggregates there is no evidence for reorientation of the zone structures in domains which can reasonably be identified with twin lamellae. Discrete zone segments have different orientations in different zone sectors, but this is undoubtedly an integral part of the initial growth structure (which represents the three-dimensional, crystalline morphology at earlier stages of growth) and cannot be reasonably interpreted in terms of deformation.

- (4) During translation gliding the initial lattice structure of a crystal, though undergoing bodily rotation, is not otherwise distorted or transformed. However, material crystal structures are internally rotated and assume new orientations, both in relation to external co-ordinates and in relation to each other. In general,

material structures which initially have rational crystallographic orientations (e.g. euhedral growth zones) will have irrational orientations in the deformed state. Moreover, the characteristic interfacial angles between material structures parallel to rational lattice planes will generally not be retained after the deformation.

Two lines of evidence suggest that in the observed fabrics euhedral growth zones and the free grain faces exposed at euhedral interstices have rational lattice orientations. This implies that the primary structure of the grains is undistorted.

- (i) The interfacial angles between growth zones are difficult to determine directly. However, a serial-sectioning technique (which involves two stages of polishing, etching, photographing and a final graphic solution) was employed to measure two interfacial angles (50° , 50°) between three segments of a typical euhedral zone structure. Within the limits of error of the measurements involved, these segments correspond to the cube and octahedral planes of the pyrite lattice.
 - (ii) Three dimensional observations at voidal interstitial sites suggest that there is a high frequency of crystal faces intersecting at 90° . It seems highly probable that these faces are rational cube planes. The conformability of the free grain faces exposed at these sites with the euhedral zone structures in the corresponding grains suggests that the growth zones have rational crystallographic orientations.
- (5) Except when the component grains have special and highly preferred dimensional orientations, intergranular plastic displacements must be accompanied by intragranular flow if the aggregate is to remain co-

herent. If the bulk strain was accomplished mainly by intergranular displacements then, for the equant and irregular grain shapes in the observed fabrics, the amount of intragranular deformation must be substantial, at least locally (i.e. in the vicinity of the grain boundaries). Thus, since there is no independent evidence for intragranular distortion (see (1) to (4) above), the observed microstructures cannot be accounted for in terms of intergranular plastic displacements.

In addition to this, there is considerable direct evidence to show that adjacent grains occupy the same relative positions that were established at the time of their original deposition (see sect. 8.3.1 (1) B (5); Plate 4.37).

8.3.1 (3) Diffusional Plastic Deformation

When a diffusional mechanism operates to produce bulk distortion of a polycrystalline aggregate, the shape and the lattice structure of single grains are modified by a recrystallisation process. Thus, the problem of evaluating whether diffusional plastic deformation has been operative is reduced to the question of deciding whether or not the ore is recrystallised. This question forms the subject of Chapter 7. By comparing the predicted microstructural changes produced by recrystallisation with the observed transient grain shapes and inclusion arrays, and from other lines of evidence including experimental observations, it was shown that the massive ore is not recrystallised. From this conclusion it follows that diffusional plastic deformation has not been operative. The main steps in the arguments presented in Chapter 7 and based on the comparison of the observed and predicted microstructures can be summarised as follows.

When recrystallisation occurs in a stressed environment single grains adjust their shape, depending mainly on the prevailing temperature conditions, either by volume or grain boundary diffusion; the latter process may or may not take place in the presence of an interstitial fluid. Because of the preferential redistribution of material, the transient and impinged grain shapes are elongate, but not euhedral (sect. 7.1.3). The absence of recrystallisation is inferred from the fact that, in the observed fabrics, the predominant grain shapes are equant and the most conspicuous zone structures (i.e. transient grain shapes) are euhedral. It should be emphasised that this conclusion also applies to the foliate fabrics where, although the impinged grain shapes are elongate, the transient grain shapes are strictly euhedral.

If deformation occurs by a hot-working process (i.e. cyclic repetition of mechanical plastic deformation and primary recrystallisation), the transient grain shapes could be euhedral. Although this prediction agrees with the euhedral structure of the observed zones, it can be shown by a second argument that primary recrystallisation has not occurred - i.e. the observed spatial coincidence between discrete zone structures and discrete inclusion arrays could not be maintained when grain boundary migration is driven by strain energy.

Although reference to diffusional plastic deformation has been included in the discussion of the massive fabrics alone, the conclusions summarised above apply to almost every type of microstructure. That is, except for the ultra-homogeneous fabrics described in sect. 4.5 (where the fine grain size imposes a practical limitation), all other pyrite aggregates are characterised by intragranular, euhedral zone structures which

are frequently associated with discrete inclusion arrays. As shown in Chapter 7, these properties are sufficient criteria to establish the primary origin of the observed microstructures.

8.3.2 Foliate Fabrics

The microstructure of the foliate fabrics is characterised by a preferred dimensional arrangement of elongate grains. Both the elongation of the grains and their preferred orientation are special properties of the foliate fabrics, and in examining the question of deformation the principal emphasis automatically centres on establishing the significance of these features.

In the following three sections the microstructure of the foliate fabrics is examined in relation to plastic and cataclastic deformation. The main objective in the first two sections is to clarify the significance of the grain shape. The third section is an account of the genesis of the foliate fabrics.

8.3.2 (1) Cataclastic Deformation

The occurrence of elongate grains in the foliate fabrics suggests that these aggregates may have originated from pre-existing massive fabrics by: (i) initial development of elongate fragments, and (ii) rotation of these fragments to assume a preferred orientation during the movement episode. Single grains in the observed fabrics should then be identifiable with the initial fragments, and these would be parts of larger grains which originally composed the parent aggregate. If single elongate grains are fragments of larger grains their internal zone structures would generally not show any special relationship to the grain shape. This prediction can be readily tested.

In the foliate fabrics the incidence of zoning is

distinctly less than in the massive fabrics. This is partly accounted for by the small average grain size of the foliate fabrics, which means that, in comparison to the massive aggregates, there is generally a smaller chance that compositional changes will occur during the period required for complete growth of single grains.

Despite the relatively high incidence of compositionally homogeneous grains, zoned elongate grains are frequently observed in the foliate fabrics (see for example Plates 4.65, 4.66). The compositional variations are manifested by closed or open euhedral zone structures which tend to be symmetrically oriented either about the grain centre or about the major or minor axes of the grains. As already pointed out in sect. 4.1.4 (3) A, these properties of the internal structure imply that each zoned grain possesses a single growth nucleus, and is therefore not part of a larger pre-existing grain. Hence, it is evident that the development of elongate grain shapes was not achieved through a process of fragmentation.

In the internal grain structure there is no evidence to indicate that single elongate grains grew during more than one main growth event. For example, there is no evidence suggesting that initially equant grains were subsequently enlarged and acquired elongate shapes by preferential accretion at diametrically opposite sides. Compositional changes occurred during the growth of zoned grains, but, as in the massive fabrics, it is perfectly reasonable to suppose that these changes were an integral part of an essentially single and continuous growth event. Unzoned grains are entirely homogeneous and imply continuous growth under uniform conditions. From the general integrity of single grains it is concluded that their elongate

shapes and their observed sizes were acquired directly during the primary growth event.

Since the main grain size and shape characteristics of the foliate fabrics were established during the primary depositional history, the problem of evaluating whether other aspects of the microstructure (e.g. the grain orientation) are related to cataclasis becomes virtually identical to the corresponding problem in the massive fabrics. In the case of massive aggregates it was shown that, if cataclasis had been operative, the units of fragmentation must be single grains or small groups of grains (sect. 8.3.1 (1) A). To provide a measure of continuity in the deformation of contiguous massive and foliate fabrics it is necessary to assume that similar, single or small, multi-granular grain groups constitute the supposed fragmentation units in the foliate fabrics. From this point, the arguments presented under (1) to (4) in sect. 8.3.1 (1) B are fully applicable in showing that single grains or small groups of grains have not undergone relative displacements and subsequent cementation since the growth of the initial aggregates.

8.3.2 (2) Mechanical Plastic Deformation

The occurrence of elongate grain shapes and their preferred orientation immediately suggests that the foliate fabrics were derived by plastic deformation of pre-existing massive aggregates. However, there are two important properties of the microstructure which are inconsistent with this interpretation.

- (1) If the grain shapes in the primary, undeformed aggregate were equant, then the intragranular zone structures are also likely to have been correspondingly equidimensional. Since distortion of the internal structure must accompany deformation of

the overall grain shape, the deformed grains should exhibit inequant zone structures whose long axes are parallel to the grain elongation. However, in the observed aggregates many elongate grains contain euhedral zone structures whose gross form is equant (see Plates 4.65, 4.66). Inequant zone structures also occur, and their longest dimension is almost invariably parallel to the grain elongation (see Plate 4.66). Although this relationship is consistent with the required equality of internal and external deformation, it does not provide definitive evidence that plastic deformation occurred. In fact, the interpretation of inequant zone structures is ambiguous, and the significance of the shape of both the zone structures and the grains themselves must also be considered in terms of anisotropic growth. These points are clarified in the next sub-section.

- (2) For polycrystalline aggregates in which there is more than one crystallographic orientation of the component grains, plastic deformation occurs by glide on slip systems which are differently oriented in different grains. This means that the deformation of neighbouring grains will generally not be mutually accommodating, and hence, if the aggregate is to remain coherent, that single grains must deform inhomogeneously especially in the grain boundary region. The foliate fabrics are both coherent and, as indicated by the variable orientation of euhedral zone structures, composed of grains with different crystallographic orientations. Plastic deformation of these aggregates should therefore involve heterogeneous distortion of single grains.

It has already been indicated (sect. 8.3.1

(2), (2)) that, during inhomogeneous deformation, intragranular material structures which are initially planar must be distorted, and assume non-planar forms. In particular, the plane segments of euhedral zone structures should acquire curved shapes in response to the deformation. In the observed fabrics, however, the planarity of zone segments is retained ubiquitously, and even in the immediate vicinity of grain boundaries distorted shapes are conspicuously absent (see Plates 4.65, 4.66).

In addition to the evidence discussed in (1) and (2) above, the arguments presented under (2) and (4) in sect. 8.3.1 (2) are also applicable in rejecting the interpretation of the foliate fabrics in terms of plastic deformation.

8.3.2 (3) Origin of the Foliate Fabrics

The evidence presented above leads to the conclusion that the foliate fabrics cannot be interpreted in terms of either cataclastic or plastic deformation. Since it has already been shown (Chapter 7) that recrystallisation was not responsible for the observed microstructure, the development of these fabrics must be attributed to the primary growth process. Assuming the sulphide ore was deposited by replacement of a pre-existing host rock, then the evolution of the foliate fabrics can be explained as follows.

If the host rock was substantially isotropic the ore-bearing solutions would tend to diffuse with equal velocities in all directions. Under these circumstances (and neglecting the inherent growth anisotropy of different crystallographic planes) the rate of accretion would be approximately equal for all growth surfaces, and both the transient and impinged shapes of

the sulphide grains would tend to be equant.

On the other hand, if the host matrix was anisotropic and contained a sufficiently penetrative layering structure, then it is probable that the diffusion of the ore-bearing solutions would be correspondingly anisotropic. Maximum transport would occur in directions containing the highest density of effective diffusion channels (i.e. grain boundaries). If a bedding or cleavage lamination defined the anisotropic structure of the matrix, diffusional transport would reach a maximum parallel to the plane of the lamination, and a minimum at right angles to this direction. For sulphide grains growing in this environment, accretion would be most rapid at growth surfaces oriented at high angles to the laminar structure in the matrix. Under these conditions, where material accretes preferentially at equivalent points on different grains, both the transient and impinged grain shapes would be elongate. Moreover, in the final fabric, both inequant zone structures and elongate grains would exhibit a preferred dimensional orientation parallel to the laminar structure of the original matrix.

8.3.3 Vein Aggregates and Colloform Structures

Both in vein aggregates and in colloform layers composed of zoned grains the microstructural properties which are relevant in evaluating the evidence for deformation are essentially the same as in the massive and foliate fabrics. That is, veins and certain layers in colloform structures are composed of compact aggregates of elongate or equant grains which exhibit euhedral growth zone structures. Because of their basic microstructural similarities, the analysis of vein and colloform aggregates follows the same lines as already discussed for the massive and foliate fabrics (sect. 8.3.1, 8.3.2). It is not proposed to reiterate the various

arguments presented in the preceding sections, but it is worthwhile to emphasise the implications of the two main features which prohibit an interpretation of the microstructure in terms of deformation.

- (1) In sects. 8.3.1 and 8.3.2 it was shown that the presence of euhedral zone structures is inconsistent with the effects of mechanical plastic deformation in a polycrystalline aggregate containing grains with different crystallographic orientations. Although the configuration of zone structures indicates a high degree of preferred crystallographic orientation in vein aggregates, there are numerous instances where neighbouring grains have significantly different orientations (see Plate 4.67). Even here, however, euhedral zone structures are preserved without modification to the plane configuration of the zone segments, thus indicating that groups of variously oriented grains have not been plastically deformed.

Compared to vein aggregates, the degree of preferred crystallographic orientation in colloform layers is considerably higher (see Plate 4.70). However, stress concentrations could be expected to develop in conjunction with deformation of the surrounding, less homogeneous aggregate. Thus, in spite of the crystallographic uniformity of the colloform layers, at least some grains should deform inhomogeneously. This prediction cannot be reconciled with the ubiquitous presence of undistorted euhedral zones.

- (2) In groups of grains which are equidistant from the centre of a vein, or which occur in the same colloform layer, the internal zone patterns (defined by the spacing, thickness and relief of discrete euhedral zones) in different grains are generally either identical or closely similar, and at least some of the equivalent zones in adjacent grains intersect at the grain

boundaries (see Plates 4.67, 4.70). This property is a characteristic feature, and persists along the entire length of a vein or colloform layer even though the gross pattern defined by single zone structures may show gradual changes over several or several tens of grain diameters.

Equivalent zones in neighbouring grains represent the same stage in the initial growth history, and the zone continuity can be simply explained in terms of the particular geometrical conditions which obtain when the growth of adjacent grains is initiated from a single nucleation surface. Thus, the preservation of the zone continuity indicates that inter-grain displacements have not occurred since the original growth event.

8.3.4 Fold Structures

Fold structures in the massive ore are defined by narrow, coarse grained bands in which the grain shapes are usually elongate with their long axes showing a radial arrangement about the fold structure. Apart from these general properties, the coarse grained bands exhibit two fairly distinct types of microstructure.

- (1) In some bands the principal microstructural features are effectively the same as in the vein aggregates. That is, the component grains are euhedrally zoned, and different grains exhibit similar or identical zone patterns which are directly continuous across the boundaries between neighbouring grains (see Plate 3.19). The implications of these properties have already been discussed in the preceding section, where it was shown that the effects of both plastic and cataclastic deformation are inconsistent with the presence of euhedral zones and their continuity between adjacent grains.
- (2) In certain folded bands many of the component grains

are unzoned, though a few singly occurring grains or small groups of grains contain euhedral zone structures (see Plate 3.18). In effect, these aggregates are equivalent to massive-homogeneous or foliate fabrics. Thus, their microstructure can be analysed in the same way as discussed in sect. 8.3.1 and 8.3.2. The main arguments presented in these sections are fully applicable in demonstrating the absence of deformation effects in the banded aggregates defining fold structures. It is not proposed to reiterate these arguments in detail, but the following points are worthy of special emphasis.

- (i) In zoned grains the presence of euhedral zone structures is inconsistent with the required inhomogeneity of plastic deformation in single grains belonging to a polycrystalline aggregate.
- (ii) Where single zoned or unzoned grains are equidimensional their shape indicates that mechanical plastic deformation was not operative.
- (iii) Since elongate grains tend to be arranged radially rather than parallel to the axial plane of the fold structures, it is difficult to reconcile the development of the grain elongation with the likely orientations of the fold-producing stresses. At the limbs of a fold the grains are elongate at high angles to the axial plane, thus implying that the maximum compressive stress was approximately parallel to the axial plane. In contrast to this, a conventional interpretation of fold structures requires that the maximum compressive stress is oriented approximately at right angles to the axial plane (cleavage).
- (iv) Both in groups of zoned and unzoned grains there is no evidence for single or multi-grain overgrowths which could be identified with the infilled voids produced during cataclasis.

8.3.5 Other Special Microstructures

- (1) Owing to their fine grain size no attempt has been made to evaluate the evidence for deformation in the ultra-homogeneous pyrite aggregates described in sect. 4.5.1 (see Plates 4.71, 4.72).
- (2) The spherical and elliptical structures described in sect. 4.5.3 (see Plates 4.73, 4.74) are defined by multiple concentric layers composed of abnormally fine grained pyrite. The shape of spherical and near-spherical structures implies that their microstructure is undeformed (see sect. 8.2.1). In both spherical and elliptical structures certain layers are composed of identical, compact aggregates of euhedrally zoned grains. The identity of the microstructure of these layers in the two types of structures strongly suggests that the elliptical aggregates were not developed by distortion of pre-existing spheres.
- (3) The sub-angular and apparently contorted structures described in sects. 4.5.4, 4.5.5 (see Plates 4.75, 4.77) are composed of internally banded aggregates of substantially equant grains. The presence of equant grain shapes implies that these aggregates have not been subjected to plastic deformation. The continuity of the internal banding and of the external boundary of the bulk aggregate suggests that cataclastic displacements have not occurred.

8.3.6 Accessory Sulphide Minerals

The accessory sulphide minerals (sect. 4.7) occur predominantly at euhedral interstitial sites in the massive (pyrite) fabrics, but also occupy leached interstices, and especially in the case of chalcopyrite, discontinuous polycrystalline veins. Where the accessory minerals occur at euhedral interstitial their deposition must post-date the growth of the surrounding pyrite aggregate. Since it can be shown

that the surrounding aggregate is undeformed, the accessory minerals occurring at these interstices must be similarly undistorted. This conclusion can be extended to apply to all occurrences of the accessory minerals if, as seems likely (see sect. 4.7), the general deposition of the non-pyritic ore minerals post-dates the main, pyrite mineralisation.

Unlike the pyrite aggregates of the massive ore, the accessory minerals do not exhibit internal structures whose development can definitely be attributed to the primary growth event. Thus, it is much more difficult to obtain an independent interpretation of the microstructure of the accessory minerals. This statement applies with equal significance both in relation to the question of deformation and in relation to recrystallisation. Although the microstructure of the accessory minerals has not been examined in detail, it is worthwhile drawing attention to the following points.

- (1) Where accessory minerals occur at, and fully occupy euhedral interstices, the interpretation of the microstructure is unambiguous. The structure of the marginal pyrite grains implies, independently of the presence of the accessory mineral, that euhedral interstices are undistorted (sect. 8.2.4). Hence, even if the accessory minerals were internally recrystallised, the shape of the interstitial grains, or grain aggregates must have remained the same since the completion of the primary growth event.
- (2) Twinned sphalerite grains are rare. Each grain contains only a few lamellae, and these show no obvious relationship to the grain boundary configuration, thus suggesting that the origin of the twinning is non-mechanical.
- (3) Chalcopyrite inclusions in sphalerite grains frequently define two or three differently oriented laminar arrays.

Since the lammellar structure almost certainly reflects a crystallographic control, its plane configuration implies that single grains are not inhomogeneously distorted.

- (4) Chalcopyrite grains are frequently twinned but each grain generally contains only a few lamellae. In some aggregates twinning is extensively developed, but even where the incidence of twinned grains is high, the lamellae in different grains show no preferred orientation, thus suggesting that the origin of the twinning is non-mechanical.

8.4 Summary and Conclusions

The purpose of this chapter has been to establish whether or not the San Duenisio lode was folded during the tectonic activity which affected the country rocks. If the original configuration of the lode was horizontal then its present shape implies that the ore body has been internally deformed. This premise constituted the starting point of the investigation. That is, the basic objective has been to clarify whether or not the structure of the massive ore reveals direct evidence for internal deformation. The success achieved in approaching the problem from this viewpoint depends on the assumption that the composition and structure of the ore have not been subjected to other major changes subsequent to the regional folding events. In this respect, the conclusion established in Chapter 7 is of prime importance - i.e. recrystallisation has not occurred since the time at which the massive ore was first composed of crystalline pyrite.

In the absence of recrystallisation the structural changes produced by deformation must be preserved, and would either obliterate or be superimposed upon the primary growth fabric of the ore. Thus by assuming an initially crystalline, massive ore body it should be possible to test for the

effects of a hypothetical deformation event. If the lode has been folded during the first deformation phase in the country rocks, the shape distortion must occur by significant displacements within the ore body. In examining the ore for evidence of these displacements it is important to distinguish between two different aspects of the lode structure:

- (1) On the basis of the morphology of the lode contacts, and the equivalence or near-equivalence of the composition of the ore at the contacts and in the interior of the lode, it has been argued that the spacing of the fold-producing displacement must be fairly uniform, and with sub-megascopic dimensions. That is, the observed shape distortion of the lode could only be produced by penetrative displacements, and not by movements which were localised in widely spaced or discontinuous zones. A similar argument can be extended to the microstructure where the continuity of the margins of structures defined by grain size and fabric changes implies that the displacement domains must be single grains or small groups of grains.

At this point it is pertinent to refer back to the slickensides and leaching zones described in sects. 3.2.4 and 3.2.5. In many respects these structures have a general appearance which suggests that they might represent important movement zones. The leaching zones are megascopic, discontinuous features which are mainly confined to the axial region of the lode. In some parts of the ore slickenside planes are densely spaced, but generally they occur at wide and uneven intervals, and are invariably discontinuous. Hence, both the slickensides and the leaching zones are strictly non-penetrative structures, and for this reason cannot be interpreted as representing the zones of movement which are required to account for the folded

structure of the lode. This conclusion is confirmed by independent evidence indicating that bulk displacements are not associated with either the slickensides or the leaching zones (see sects. 3.2.4 and 3.2.5).

At this point it is also important to draw attention to a second implication of the required distribution of the movement zones. Although the sampling conducted for this study is limited, there is little doubt that the foliate and especially the massive fabrics are the dominant components of the massive ore. Thus, even if it was subsequently found that there are other types of fabrics which display evidence of deformation, the movement zones represented by these fabrics must be non-penetrative features. For the reasons given above non-penetrative displacements cannot account for the folding of the lode, though they could represent late-stage fault movements. Deformed fabrics could also represent sulphide aggregates deposited before the folding event, and therefore substantially earlier than the main period of mineralisation.

- (2) Having established that the fold-producing displacements must be penetrative, it then becomes a valid procedure to examine the microstructure of the ore for evidence of the deformation.

It should be emphasised here that even though the ore body is large, there should be no major limitations involved either in collecting a comparatively small number of specimens, or in examining the microstructure over continuous areas as small as those of conventional polished sections. The required penetrative character of the deformation means that there should be evidence for displacements wherever the ore body is sampled. Continuous fields of observation contain several hundreds or several thousands of grains, and encompass the most pronounced fabric variations. Hence, if the

microstructural properties influenced the response to deformation, or if they were determined by the deformation, the resulting effects should be directly observable. It is also of considerable significance that the composition of the ore body is virtually monomineralic, since this implies a corresponding uniformity for the mechanical properties of the lode. Furthermore, the minor ore components (i.e. the accessory sulphides, gangue minerals and voids) are distributed both sporadically and at strictly isolated sites in a physically continuous pyrite aggregate. Both these features indicate that the homogeneity of the deformation could not be seriously influenced by the presence of the non-pyritic components. Moreover, since the accessory sulphide and gangue minerals occur at strictly isolated sites, it will be obvious that deformation could not be accomplished by distortion of these minerals alone.

The examination of the microstructure of the ore has been conducted along two lines:

(i) (sect. 8.2) Certain microscopic structures are defined by special types of grain arrangement whose development can only be attributed to the primary growth event. These structures are effectively objects of known initial shape and can be treated on geometrical grounds independently of any specified deformation mechanism. The preservation of their primitive forms means that deformation has not occurred. Moreover, since the surrounding aggregate is composed of similarly compact pyrite, it seems entirely reasonable to suppose that the manifest absence of deformation at the sites where recognisable growth structures exist is actually representative of the ore mass as a whole.

(ii) (sect. 8.3) The second approach to analysing the microstructure of the ore has general application to every type of pyrite aggregate (except the special

elliptical and spherical structures described in Chapter 5 and the ultra-homogeneous aggregates described in sect. 4.5). The results obtained here are important because of their general applicability, because they require minimal assumptions regarding the initial structure of the ore, and because the criteria developed can be readily applied as the sampling is extended to other parts of the lode.

In almost every type of pyrite aggregate the component grains exhibit euhedral zone structures. It can be shown that the development of the zoning was not induced by a recrystallisation process (Chapter 7), and must therefore be connected with the initial growth of the sulphide aggregate. The importance of euhedral zone structures derives from the fact that they record not only the internal structure of single grains, but also, and independently of the grain boundaries, the main grain size and shape characteristics of the primary sulphide aggregates.

Three deformation mechanisms could be effective in producing distortion of the lode, namely, mechanical and diffusional plastic deformation and cataclastic deformation. When these mechanisms operate there are certain basic modifications which must be produced in the primary microstructure. By predicting these modifications it is possible to make direct comparisons between the total observed microstructure and that part of the fabric which must represent the features derived during the initial growth event (i.e. the shape, arrangement, spacing and continuity of euhedral zone structures). In sects. 8.3.1 to 8.3.3 it has been shown that the predicted effects of both plastic and cataclastic deformation are inconsistent with the observed microstructure of the massive and foliate fabrics, vein aggregates and colloform structures.

The only fabrics in which there is definitive evidence for deformation are the pyrite ellipses described in Chapter 5. However, these fabrics occupy a negligible volume of the total ore. Moreover, they are essentially unrepresentative of the normal massive ore since their deposition involved a special mode of growth (i.e. a colloid - crystalline transformation), and the deformation occurred under special conditions (i.e. when the ellipses were composed of a viscous, non-crystalline precipitate).

On the basis of the results summarised in (1) and (2) above it is concluded that the massive ore is undeformed, and exhibits megascopic and microscopic structures which were already established during the primary growth event. In relation to the regional tectonic activity, this conclusion means that:

- (a) the original lode was not flat-lying,
- (b) the observed shape of the lode was not produced by folding during the first phase of deformation in the country rocks, and
- (c) the lode was directly emplaced in a pre-existing fold structure.

Two occurrences in the microstructure provide direct evidence for the deposition of sulphides later than the regional first phase folding event:

- (i) From oriented specimens it is known that at least some of the fold structures in the massive ore are geometrically equivalent to the first generation fold system in the country rocks - i.e. their axes trend EW and a steep dipping axial plane cleavage is defined by elongate features in the microstructure. On the basis of their similar orientation it is reasonable to suppose that the folds in the ore were developed at the same time as the first generation folds in the country rocks. Thus,

since the folds in the ore are composed of pyrite aggregates which are undeformed (with the exception of layers composed of pyrite ellipses), the deposition of the sulphides must post-date the folding.

In support of this conclusion it is significant that the long axes of elongate grains (in the foliate fabrics) and elongate interstitial sites show noticeable departures from the axial plane orientation near the margins of, or within, certain bands defining the fold structures (see Plate 3.20). These departures are analogous to the configuration of the axial plane cleavage frequently observed in silicate rocks composed of intercalated competent and incompetent bands.

Competency variations reflect differences in mechanical behaviour, and are almost certainly caused by bulk mineralogical or density changes. It seems reasonable to suppose that different layers composed of substantially compact, monomineralic pyrite aggregates would not exhibit significantly different mechanical properties, even if the initial microstructure was dissimilar in different layers.

These remarks suggest that the observed configuration of the axial plane lamination was not developed, as a result of folding, at a time when all layers were composed of pyrite. However, it is reasonable to suppose that the composition of layers, now occupied by different microstructural assemblages, was initially different. Under these conditions, folding could lead to the development of the observed cleavage patterns. With subsequent mineralisation, the mechanical distinction between different layers would be preserved by pseudomorphism of the cleavage structure, but at the same time, the compositional differences, which determine the mechanical properties, would be obliterated,

though indirectly preserved in the form of sulphide aggregates with different microstructural properties.

- (ii) From oriented samples in which the foliate fabrics occur it is known that the orientation of the laminar structure defined by elongate grains is equivalent to the orientation of the slaty cleavage in the country rocks (i.e. the axial plane cleavage of first generation folds). However, the foliate fabrics are undeformed, and it is necessary to invoke an anisotropic growth mechanism to account for their special microstructural properties. For this mechanism to be effective, sulphide deposition must occur by replacement of a pre-existing matrix which contains a penetrative laminar structure corresponding to the layering in the foliate fabrics.

When the country rocks were flat-lying the only penetrative structural anisotropy which could exist would be the horizontal bedding planes. However, the orientation of the laminar structure in the foliate fabrics is sub-vertical, and therefore cannot be explained in terms of replacement of flat-lying rocks.

In fact, the absence deformation in the foliate fabrics and the orientation of the layering structure can only be reconciled in terms of a pseudomorphic replacement process in which the pre-existing anisotropy corresponds to the slaty cleavage in the country rocks. This interpretation implies that sulphide deposition post-dates the development of slaty cleavage, and hence the development of the regional first generation fold system.

In the country rocks the deformation effects (i.e. the development of folds and a fracture cleavage) associated with the second generation fold system are entirely confined

to the less competent rock types. This relationship suggests that, even if the lode was emplaced prior to the second phase of deformation the subsequent effects are unlikely to be imposed on the massive ore which is an extremely competent material. Actually there is evidence that the lode was emplaced later than the second phase of folding. In some parts of the ore elongate interstices and leaching zones occur in undeformed pyrite aggregates, and are parallel to the fracture cleavage (i.e. the axial plane cleavage of second generation folds) in the country rocks (sect. 3.2.2). The orientation and the general laminar character of the structures observed here strongly suggest that sulphide deposition was controlled by, and therefore post-dates the axial plane cleavage of second generation folds.

CHAPTER 9

CONCLUDING REMARKS

In Chapters 7 and 8 it has been shown that the San Dionisio ore body was not subjected to the Hercynian metamorphism and folding which affected the Paleozoic country rocks. Thus, the deposition of the pyritic ore is epigenetic, and is not related to the volcanism associated with the underlying host rocks in the way that is specified by the exhalative-sedimentary theory of ore genesis (Ofstedahl, 1958). Although the country rock volcanism and the deposition of the ore were not synchronous, there may be a distant connection between these phenomena in so far as the magma source from which the volcanics were derived may have also contributed at a later stage to the pyritic mineralisation. The presence of a joint system in the massive ore and its symmetrical relationship to the trend of the main fold system in the country rocks suggest that the lode was emplaced at depth and subsequently uplifted. In view of this it seems reasonable to consider the possibility that the mineralisation occurred in relatively close proximity to a magma source, and perhaps at a time when the Hercynian folding had produced maximum down-warping of the Paleozoic geosyncline.

Epigenetic deposition of the lode can be envisaged in two ways: (i) a replacement process involving concomitant dissolution of the host rocks and precipitation of pyrite from hydrothermal solutions, or (ii) intrusion of a sulphide magma and subsequent crystallisation of pyrite. The latter mode of origin implies that the internal structure of the lode should resemble that of igneous intrusions. That is, a sub-horizontal layering might develop and substantial grain size variations could be related to the proximity of the lode contacts, but the microstructure of the ore should be essentially isotropic. These features are not observed, and in fact the ore body is character-

ised by variously oriented layering structures, an extremely uniform grain size and by a heterogeneous structure both at the megascopic and microscopic scale. Furthermore, deposition of the ore from a sulphide magma is scarcely compatible with the occurrence of primary growth structures such as those described in the accounts of the massive-discrete and massive-composite fabrics, the foliate fabrics, and in sects. 3.2.5 and 4.5. The external form and internal fabric of these structures is extremely difficult to explain except in terms of pseudomorphic replacement of equivalent structures in a pre-existing host rock. Pseudomorphism of tectonic features resulting in the preservation of small scale folds and the development of the foliate fabrics has already been discussed in Chapter 8. The general importance of pseudomorphic replacement is supported by the resemblance between many of the pyrite microstructures and features which might reasonably be expected to have existed in the earlier host rocks. For example, spherical structures such as those illustrated in Plates 4.3, 4.7 and 4.73 can probably be identified with primary volcanic spherules; grain aggregates showing angular shapes or sharp definition against the surrounding matrix could represent pre-existing rock fragments (see for example Plates 3.15, 4.2), phenocrysts or euhedral crystals (see for example Plates 4.22, 4.23, 4.24); the structures illustrated in Plate 4.77 bear a marked resemblance to volcanic shards. These observations strongly suggest that the deposition of the pyritic ore involved replacement of a pre-existing host rock and therefore occurred by precipitation from hydrothermal solutions.

It is not proposed to discuss the course of the mineralisation history, but in connection with this there are two points which need to be clarified because of their possible implications concerning the validity of the conclusions reached in Chapter 8.

- (i) In principle, the deposition of the lode could have occurred during two separate periods of mineralisation. In the first period isolated sulphide aggregates could

develop by replacement of a pre-existing host rock. If the ore-bearing horizon was subsequently folded, the sulphide aggregates could escape internal deformation and behave as rigid bodies, rotating in a less competent matrix. If the remaining host rock was replaced during a second period of mineralisation, there would be no direct evidence (except possibly at the margins of the aggregates produced during the first period of mineralisation) for the deformation event in the structure of the massive ore.

Apart from one minor exception (i.e. the early deposition of pyrite spheres distorted during the first phase of folding), there is no independent evidence to suggest that the deposition of the lode occurred during more than one period of mineralisation.

The massive fabrics are the dominant components of the massive ore. The different grain size components of these fabrics are frequently related by continuous grain size variations, and there is an overwhelming predominance of non-euhedral grain boundaries. These features leave little doubt that the different grain size components grew contemporaneously. Moreover, since grain size differentiation defines continuous structures at a megascopic scale, it seems reasonable to conclude that contemporaneous growth is a general feature and applies with equal significance to both small and large volumes of the massive fabrics. Similar considerations apply to the foliate fabrics. Furthermore, the massive aggregates frequently show gradational transitions to the foliate fabrics, a relationship which suggests that the deposition of the two main groups of fabrics in the massive ore was essentially contemporaneous.

It has been estimated that the massive and foliate fabrics, taken together, occupy more than about 80 per cent of the total ore. Because of their dominant volume contribution it is virtually certain that the massive and

foliate fabrics occur with complete physical continuity throughout the lode. In this case there could be no isolated aggregates, and folding could not be accomplished by independent displacements between blocks of ore which were surrounded by a continuous matrix. Thus the manifest absence of deformation in these fabrics is significant, and a minimum conclusion requires that the bulk of the massive ore was deposited later than the regional folding.

The depositional age of vein aggregates and colloform structures is difficult to establish directly because of their general tendency to appear as structurally distinctive components of the ore. However, the shape of the gross structures defined by vein aggregates and colloform layers strongly suggests that these structures would be unstable during deformation, even if they were surrounded by a less competent matrix. For this reason it seems most likely that the vein and colloform aggregates do not represent an early period of sulphide deposition, but are directly connected with the main mineralisation event.

Pre-folding mineralisation is certainly represented by at least some of the pyrite spheres and ellipses. There appears to be only one other instance where a similar period of deposition could be involved. The abnormally large, euhedral or embayed grains described in sects. 4.1.2 and 4.1.4 (1) frequently appear to be quite unrelated to the immediately surrounding or neighbouring fabrics. This suggests that the large grains represent a separate period of growth which, as implied by the size and shape of the grains, must pre-date the deposition of the enclosing aggregate. However, this is a simplified time relationship, and there appears to be no way of establishing whether the early period of growth is essentially connected with the main mineralisation event, or distinctly earlier than it, and therefore possibly pre-folding.

(ii) Ramdohr and Amstutz (1964) have suggested that the deform-

ation of the Mount Isa lead-zinc ores occurred at a time when the sulphide deposit existed as a viscous, non-crystalline material. It is not proposed to discuss the arguments which led to this conclusions, mainly because they are not particularly relevant to the simple monomineralic ores at Rio Tinto. However, the importance of the suggestion made by Ramdohr and Amstutz derives from the fact that if an ore body is deformed whilst the sulphide deposit is still in a non-crystalline state, then there would be no evidence for the deformation in the crystalline microstructure which developed after the folding event.

For the Rio Tinto deposits the only realistic non-crystalline state would be some form of colloidal iron sulphide. In fact, there is positive evidence from the shape and internal structure of pyrite spheres and ellipses (Chapter 5) that the pyrite now composing these aggregates was initially deposited in an amorphous state. However, there is no basis for extending a similar conclusion to the normal crystalline ore. The pyrite spheres and ellipses provide a direct record of the microstructure **resulting** from the crystallisation of an amorphous substance under conditions of the natural environment. This microstructure is characterised by three important properties: (a) an abnormally fine grain size, (b) uniformity of grain size, and (c) ordered crystallographic and packing arrangements in the polycrystalline aggregate. None of these properties are found in the normal crystalline ore. In comparison to the pyrite spheres and ellipses, the microstructure of the normal ore is much coarser grained, and even in small volumes, is heterogeneous with respect to grain size, grain arrangement and crystallographic orientation.

There are two other serious difficulties in attempting to interpret the microstructure of the crystalline ore in terms of a colloid-crystalline transformation.

Firstly, the colloidal state is essentially metastable

and once nucleation has occurred the subsequent crystallisation rapidly proceeds to completion. The short duration of the growth interval means that during this time there is a correspondingly small chance that changes will occur in the external environment. Since the bulk composition of the colloidal deposit is already determined at the precipitation stage, only external changes can influence the instantaneous composition of the crystallising material. The component grains of the crystalline aggregate should therefore record relatively few compositional changes (i.e. zones), and to this extent it is difficult to explain the high frequency of zoning in many of the observed microstructures.

Secondly, if a colloidal substance remains stable during the time interval between its initial deposition and the completion of folding, there would be ample opportunity for compositional and structural homogenisation. Hence, even if the original colloid deposition was accompanied by pseudomorphism of structures belonging to a pre-existing rock mass, which seems doubtful in the first place, these structures could scarcely be expected to persist in the final crystalline microstructure. In view of these remarks, it is difficult to account for the sharp definition of the apparently pseudomorphic structures referred to above.

In contrast to the difficulties arising from a colloidal origin, the main features of the structure of the ore can be readily explained in terms of direct hydrothermal crystallisation. For example: (1) a prolonged growth history incorporating intermittent periods of leaching accounts for both the internal structure and the compositional variations recorded in single grains, and (2) pseudomorphic structures can be explained as reflecting a direct relationship between the composition and/or structure of the host rock and the nucleation and growth of pyrite as determined by the accessibility of ore solutions.

It should be stressed here that the deformation of the lode cannot be accounted for by assuming that the fold-producing displacements were localised within the previously colloidal deposits now represented by aggregates of pyrite spheres and ellipses. Several arguments are relevant here: (1) since pyrite spheres and ellipses occur in strictly discontinuous aggregates, the deformation would be similarly confined, and could not lead to bulk distortion of megascopic volumes of ore, (2) even if displacements were propagated between different isolated aggregates, the movement zones would be widely spaced and the deformation insufficiently penetrative to account for the continuity of the internal and external structure of the lode, (3) many aggregates are composed entirely of pyrite spheres, and are therefore obviously undeformed, (4) if the fold-producing displacements were confined to the colloidal deposits, the deformation in these zones would be extreme, and recognisable ellipses could scarcely be expected to remain. In reality, the elliptical shape of distorted spheres is usually recognisable and indicates a comparatively moderate deformation.

In discussing the deformation of the massive ore the basic assumptions have been that: (1) from the time of its original deposition the lode was composed of compact, crystalline pyrite, which, (2) has not been significantly re-constituted since the formation of the lode. As already indicated, the second assumption was justified in Chapter 7 where it was shown that the massive ore is unrecrystallised. The first assumption is justified in (i) and (ii) above, where it is argued that the bulk of the massive ore was deposited by direct precipitation of crystalline pyrite during a single period of mineralisation.

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