A STUDY OF MINERALIZATION IN THE PYRITIC DEPOSITS OF SOUTHERN SPAIN AND PORTUGAL.

by

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ABSTRACT.

A brief description of the geology of the Iberian pyritic belt is followed by more detailed accounts of the general geology of three of the principal mines of the belt, namely, San Domingos, Rio Tinto and La Zarza. Attention is drawn to certain features of the igenous rocks of the district which resemble those described from pyritic districts in other parts of the world, and evidence is presented to show that the similarities may be due to a high alkali and volatile content in the igneous magmas associated with the pyritic deposits. Metasomatic growth forms such as spherulites, metacrysts and 'pressure shadows' are described, an account is given of the experimental synthesis of spherulites, and theories are advanced concerning the origin of the various growth forms. Wall rock alteration associated with the ores is detailed, and some new concepts offered on the nature of sericitization and the relative stabilities of K and Na during metasomatism. A brief 'resume of the mineralogy of the ores is supplemented by more detailed accounts of the ore textures. Evidence is advanced, based on the results of electrolytic etching, which strongly indicates the hydrothermal origin of the pyritic ores and throws new light on the formation of colloform textures and the mechanism of emplacement of the orebodies. The pyrite geo-thermometer is critically discussed and results obtained from its application are

statistically correlated with the distribution of values in the ores. Details are given of the various controls of mineral localization at individual mines in the Iberian belt. Finally, all the data is summarized, the problems of genesis are discussed, and a tentative theory on the origin of the orebodies is advanced. Suggestions for future exploration, based on the results of this research and the writer's field experience, are given in an appendix.

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INTRODUCTION.

The pyritic deposits of Spain and Portugal include the largest known orebodies of their kind, and during the last 80 years have yielded over 200 million tons of ore. Much has been written about them and although their origin is now largely accepted as being hydrothermal, the nature of the ore-forming solutions, the controls of mineralization, the distribution of metal values and other problems are still the subject of strong debate. It has been the aim of the writer to seek new evidence which, together with existing work, will provide a better understanding of the fundamental issues concerning the geology of the deposits.

During the course of the work, generous field accommodation was provided at the Rio Tinto, San Domingos and La Zarza mines by the Rio Tinto Company Ltd., Mason and Barry Ltd., and the Tharsis Sulphur and Copper Company Ltd., respectively, to whom the writer is greatly indebted. In particular, he is grateful to the Rio Tinto Company for their principal share in sponsoring the research. It is a pleasure to record sincere thanks to Professor D. Williams, who supervised the work, and to Dr. J.S.Webb for their continual help and encouragement.

CHAPTER 1.

GENERAL GEOLOGY OF THE MINERAL PROVINCE. (1-6).

Position and Topography. The orefield is situated in a belt of country which stretches eastwards from Alentajo in Portugal to Seville in Spain, a distance of about 120 miles. The land falls gradually from the Sierra Morena Mountains in the north, at the southern edge of the Spanish Plateau, to the coastal plain. Several large rivers flow southwards to the coast across the pyritic belt and the prevailing strike of the rocks, and have cut deep gorges where they intersect the harder, more resistant rocks. The tributaries which follow the softer beds produce a trellis pattern drainage, and the whole area shows evidence of the dissection of an earlier peneplain whose level lay approximately at the uniform elevations shared by many of the present hilltops. Occasional ridges of hard igneous or quartzitic rocks stand out as monadnocks, and are typified by the great dyke ridges of Salomon and the Smelter Porphyry at Rio Tinto, the igneous rock - jasper complex of Alconocoso at La Zarza, and the quartzite ridge of Bairro Alta at San Domingos.

Soil covering is mostly poor and surface erosion has been severe due to past and present agricultural methods, timber stripping, severe climatic conditions and other causes. The soil types often reflect very closely the underlying rocks and thus facilitate mapping, but much caution

has to be observed owing to the close interdigitation which commonly occurs between slate and intermediate or basic rocks, and the liability of soil derived from chloritized porphyry resembling in colour that produced from intermediate and basic rocks.

Structure and Rock Types. The central Spanish plateau is a Hercynian fragment or block bounded by structures referable to Alpine orogeny. The belt containing pyritic mineralization lies close to the southern margin of the block and is composed of Palaezoic formations which have been folded along east-west axes by Hercyian earth movements and intruded by a series of igneous rocks. Hercynian pressures have impressed a steeply dipping slaty cleavage on the more argillaceous sediments, and various lesser degrees of secondary foliation on the more competent rocks. The east-west trend of the rocks has controlled the form of dyke intrusions, and since earth pressures were maintained or renewed after intrusive activity there is a marked parallelism in strike throughout the belt, of a.b. tectonics such as axial fold-planes, primary and secondary foliation, lineation, and release joints.

Faulting has been recognized in most of the areas examined, and in some cases it may be closely connected with mineralization. Most of the faulting appears to consist of north-westerly shears, but thrust faulting is almost certainly present. To the south-east the pyrite field is terminated by the Guadalquivir fault, a major movement of north-easterly strike associated with the Alpine orogeny.

The sedimentary rock types include slates, shales, phylitic rocks, grits and quartzites, and occasional but significant developments of black shales, hematite shales, greywackes, radiolarian cherts and sedimentary jaspers. Pyroclastic rocks, interbedded with the sediments, include lithic and vitric tuffs, sometimes containing radiolaria, and volcanic agglomerates. Collins[2] reported the existence of contemporaneous lavas among the sediments, and the general rock assemblage points clearly to depositional conditions of geosynclinal character.

Among the acid igneous rocks of the belt include are biotite granites[2], quartz monzonites, quartz porphyries, and quartz keratophyres. In the intermediate class there are porphyritic andesites, trachy-andesites, micro-syenites, monzonites (mapped as porphyry, as opposed to quartz-porphyry, by G.Williams[5] at La Zarza), quartz-porphyrites and augite porphyrites (pyroxene micro-diorites). Basic types are represented by basaltic and doleritic rocks which, because of intense alteration, may be classed as diabases. It should be noted that the term 'diabase' is considered by many petrologists to signify altered doleritic rocks, though in mining parlance it is sometimes applied to a wide range of melanocratic rocks. Many of the darker rocks of intermediate composition are currently being called diabase by students of the pyrite belt, and since the genetic relationship between the true diabase and the dark intermediate rocks seems very close there is ample justification for this

broad use of the inclusive term for purposes of mapping and mining reports.

There is a widespread development of chlorite, epidote and carbonate in many of the intermediate and basic dykes, and the association of these minerals with alunite and the occasional development of adinoles in adjoining sediments seems to indicate a spilitic assemblage. Frequently the acid igneous rocks accompanying the more basic rocks which have been altered in this way, are strongly sodic and of quartz keratophyric type, and it is claimed that some intrusions in the area can be regarded as spilite-keratophyre complexes. Sodic metasomatism (for discussion of this problem, see Turner[7], pp.120-124), constantly occurs in regions of mesothermal pyrite mineralization, a significant fact which is discussed elsewhere in this thesis.

Hydrothermal jaspers are widely developed in association with intermediate and basic rocks[8] and in addition they are often closely connected with pyritic and manganese mineralization.

Ore Deposits. The pyrite masses most frequently occur on the margins of igneous intrusions as lenticular bodies containing subordinate amounts of chalcopyrite, sphalerite other sulphides and a small amount of gangue. Interesting exceptions are those orebodies which occur isolated within sedimentary rocks and others which are alleged to occur isolated within igneous rocks (Edge[3]). The longitudinal

axes of the lenticular bodies generally lie in the direction of the regional trend and the orebodies vary in size from a few thousand tons up to quantities in excess of 100 million tons. Stockworks and disseminated ores frequently adjoin the massive deposits and are sometimes worked for the copper values they contain.

Pyritic mineralization took place towards the close of igneous activity, and was roughly contemporaneous with the lead and silver mineralization of the Linares region at the south eastern margin of the Iberian Hercynian block, and the mercury mineralization of Almaden in the interior of the block. The prolonged erosion which followed metallization has in many cases exposed the pyritic deposits to oxidation. Extensive gossans have been formed above the ore, and some of the ferruginous material carried away has been deposited as bog-iron ore, as at Rio Tinto where Miocene plant remains have been found in them[9], and at La Zarza. It is sometimes difficult to differentiate between gossans which have resulted from the prolonged erosion of a disseminated sulphide zone and are more or less in situ, and those which have been transported. The true gossans sometimes contain gold values, especially near their bases[6], and the secondary copper enrichment in the ore beneath them has, in the past, been a principle source of wealth from mining operations

Summary of the Geological History of the Area.

Sedimentation under geosynclinal conditions took place during much of the Palaezoic era, and was accompanied by some volcanic activity. This phase was succeeded in Permo-Carboniferous times by orogenic folding and uplift accompanied by the intrusion of a series of rocks varying from granitic to doleritic in composition. Mineralization and widespread soda metasomatism of the igneous rocks occurred towards the end of intrusive activity.

A long period of erosion and peneplanation followed, extending from Triassic to late Cretaceous times, equivalent to about 50 million years (A.Holmes[10]), after which a fresh uplift of the Iberian block during the Alpine orogeny led to the dissection of the peneplain by a rejuvenated drainage. Thus the Iberian block, which includes the pyrite belt, has undergone erosion since its formation during Permo-Carboniferous times, for a period of at least 220 million years.

CHAPTER II.

OBSERVATIONS ON THE GENERAL GEOLOGY OF SOME OF THE MAJOR DEPOSITS.

MINA de SAN DOMINGOS, PORTUGAL.

Acknowledgments. The writer has carried out a considerable amount of field work at this mine in connection with an exploration programme arranged by Dr.J.S.Webb for the operating company, Mason and Barry Ltd. Full acknowledgment is made to Dr. Webb for his supervision and invaluable guidance, and thanks are also due to the Chairman of Mason and Barry Ltd., Colonel Cross Brown, and the Board of the Company for permission to include this section in the thesis.

General. The mine is situated in Portugal about 2 miles from the Spanish frontier and about 50 miles from the south coast. The geology of the area around the mine is depicted on the accompanying 1/1000 scale map, which is divided into lettered squares for convenience in discussion. A number of igneous dykes varying from basic to acid in composition are intruded along the regional strike of the Palaezoic sediments, which include slates, quartzites and interbedded tuffs.

Broadly speaking, the orebody lies between quartz-porphyry on the north wall and intermediate rocks on the south wall (Edge[3]), and is largely due to the replacement of a slate tongue, as originally suggested by Webb.

The topography of the area shows the typical features of an eroded and dissected peneplain, the hilltops

rising to a more or less uniform level, with the igneous rocks and quartzites often forming conspicuous resistant ridges. Apparently the River Chanca has reached about middle maturity having carved a deep valley for itself, the flanks of which are deeply dissected by many small tributary streams.

Sedimentary Rocks. These include slates, phyllites, shales, grits, greywackes, quartzites and radiolarian schists. Owing to the dearth of fossils some controversy exists concerning the age of the sediments. Nereites, which are supposed to be fossils of Silurian age, are reported to have been found in the San Domingos slates, and on this basis Gonzalo[11] mapped the area as Silurian. According to later work, however, the nereites are much more probably worm trails or shell-fish burrows, and Delgardo[12] subsequently mapped the area as Devonian. Finlayson[1] pointed out the total absence in these slates of the graptolites which occur in Silurian rocks in the extreme north, and considered the rocks to be either Lower Carboniferous or possibly Devono-Carboniferous in age.

Hercynian pressures impressed a strong flow cleavage on the more incompetent rocks, the strike of which lies between 110° and 125° (true), and the dip mostly between 70° N and 70°S. Bedding is generally parallel to the cleavage in strike but frequently differs in dip, since the strata have been intensely folded.

The slates vary from pure fissile mudstones consisting of a featureless matt of clay minerals, to argillaceous shales which contain varying amounts of quartz grains set in a clay matrix. Quartz grains are often aligned as gritty bands along the bedding planes and sometimes the rock is intersected by fine quartz veins of post-consolidation age. Various forms of alteration affect the slates, including chloritization, sericitization, carbonatization, pyritization, kaolinization and alkali metasomatism, the alteration being mostly developed in the immediate vicinity of igneous intrusions or the orebody. A study of the results of metasomatism on the sedimentary rocks, together with etch pattern studies of the massive ore, has produced what the writer considers to be the most direct evidence to date on the mechanism of ore formation a subject discussed elsewhere in the thesis.

Quartzites are extensively developed at San Domingos and owing to their resistance to erosion they form some of the principal high points of the region. Quartzitic nodules generally merge into grits, and the slates which surround them tend to develop a cleavage which is moulded around the nodules. The quartzites occur as highly competent rocks amongst plastic slates, and form structural discontinuities which have provided channelways for manganese mineralization and jasperization.

Jaspers. Although the jaspers are not extensively developed at San Domingos, their ubiquitous distribution throughout the pyrite belt and their frequent association with ore has made their study of particular interest. There are at least three modes of origin of reddened siliceous rocks in the San Domingos area, as listed below, and the fourth type enumerated probably exists also.

1. Jaspers of hydrothermal origin.
2. Quartzites containing hydrothermal hematite.
3. Ferruginous cherts of sedimentary origin (i.e. sedimentary jaspers).
4. Quartzites with authigenic hematite.

The iron-stained quartzites can be readily distinguished in the field from the hydrothermal and sedimentary jaspers by their quartzitic texture, though it may be difficult to differentiate between the two types of jasper owing to their similarity both in hand specimens and thin sections. The existence of radiolaria, however, provides a positive identification of sedimentary origin. At Pinheiros for example (Square B), radiolaria are well developed in a sedimentary jasper which is intimately associated with a hydrothermal jasper.

A study of thin sections from all the principal jasper croppings at San Domingos shows that sedimentary and hydrothermal types nearly all contain spherulitic textures, even though they may not be extensively developed. These spherulites, exemplified by figures 1 and 2 , consist of

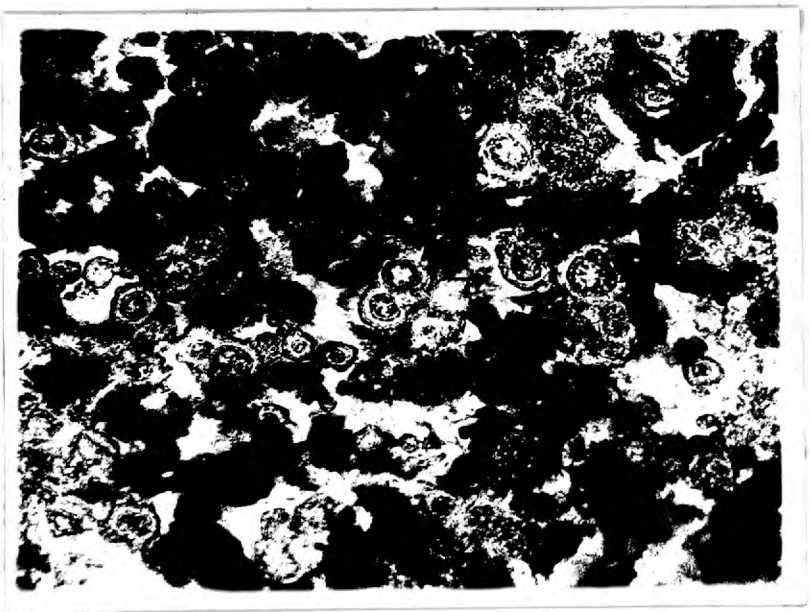


Fig. 1. x60.

Spherulites in jasper showing concentric Liesegang rings.

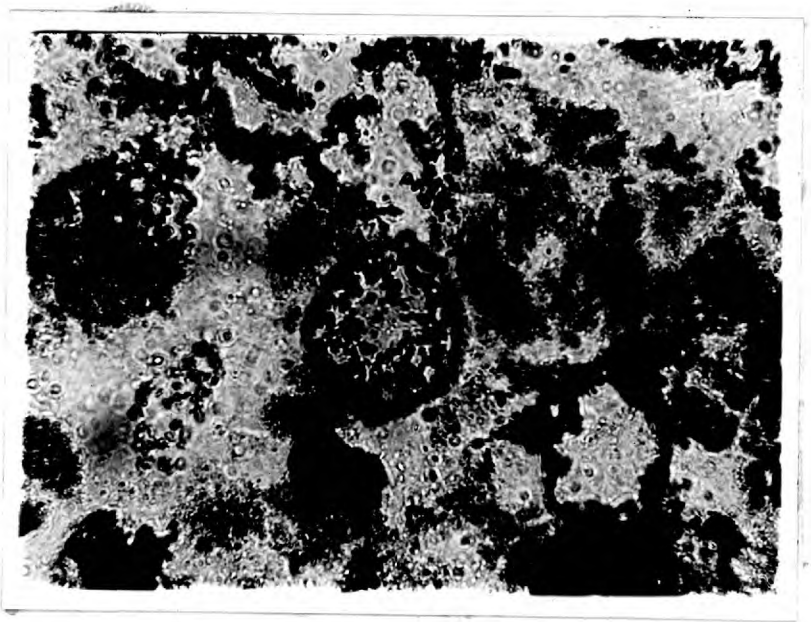


Fig. 2. x1000

Jasper Spherulites.

minute particles of hydrated iron oxides clustered as imperfect spheres within a silica matrix. Sometimes two or more spheres are arranged concentrically and clusters of spheres may coalesce, whilst the spherulites are frequently associated with delicate colloform bands of hydrated iron oxide.

Spheres of the type described were first formed synthetically by Hatschek [13] in 1911. He allowed solutions of hydrofluosilicic acid, sodium sulphate, sodium carbonate, potassium iodide, and ammonium bichromate to penetrate gelatin and agar gels of various concentrations containing either calcium chloride, barium chloride, lead nitrate or silver nitrate. These solutions were chosen so that insoluble precipitates would be formed within the gels during diffusion, and Hatschek noted that a tendency to form spherical aggregates and banded structures recurred with notable persistence throughout the whole series of experiments. Practically every precipitate could be obtained as spherulites by choosing suitable concentrations of gel, whilst the concentrations of the solutions only affected the length of time taken for spherulites to appear. These experiments emphasize the importance of the physical state of the media in which growth appears, and help to explain the sporadic nature of spherulitic growth in nature, not only in the case of jaspers but also in other cases discussed later in this thesis.

Since the work of Hatschek, synthetic spherulites have been prepared by many others, notably Morse, Warren, and Donnay[14], who formed them from over a hundred slightly soluble substances by slow diffusion in jellies. The compounds formed of direct geological interest included hydroxides, sulphides and carbonates. They concluded that spherulites can be formed from many substances if the reacting solutions are allowed to mix by diffusion, avoiding all convection. In some cases spherulites can be formed by controlled precipitation in solutions, as shown by Diesel[15] who precipitated spherulites of the mixed carbonates of iron, calcium and magnesium from solution, but in general they are much more readily formed in gels.

The feature which indicates that the jasper spherulites were precipitated in gels or similar structures is the development of concentric spheres, and it is contended by the writer that these represent a clear development of the Liesegang phenomena of rhythmical precipitation. The incidence of these phenomena in porous media and gels is discussed by Bradford[16], who shows how spherulitic aggregates collect material evenly around them and form enclosing spheres depleted in that material. Rhythmical repetition is typical of the Liesegang phenomena, which is, however, usually described in terms of parallel bands across a cylinder of gel.

It is virtually certain that gel or porous media formation played an extremely important part in the genesis

of the jaspers of the pyritic field, since spherulites occur in nearly all the jasper thin sections examined, irrespective of whether the jaspers are of sedimentary or hydrothermal origin, or whether they are found at San Domingos, La Zarza or Rio Tinto.

Other textures occurring with the spherulites, and themselves probably originating from gels or allied structures, include those which give radiating and brush polarization figures (illustrated in figures 3 and 4) and an ill-defined mosaic of anhedral quartz grains (fig. 5) Textures of this kind are common in flints, which may be of gel origin, and it is interesting to note that they have also been obtained synthetically by Van Praagh[17] in the hydrothermal devitrification of vitreosil, a form of silica glass. This is not surprising since glasses have much in common with gels, and similar patterns might well be exhibited from the crystallization of either.

In considering the mode of emplacement of the hydrothermal jaspers it is clear that in some cases they show evidence of replacement, and in other cases intrusive relations. During the formation of replacement jaspers it appears that there is an early phase of silicification and hematization in which quartz metacrysts grow in the country rock. These metacrysts may show growth zones outlined in included hematite, and they may be subsequently corroded by the later more intense phase of silicification.



Fig. 3. x120

'Brush' polarization phenomena in jasper vein quartz.



Fig. 4. x30

Typical 'brush' polarization textures in jaspers.

It is during this later phase that much of the rock is reduced to a permeable condition favouring the formation of spherulites. This condition necessitates that the rock should be interlaced with capilliary openings, as for example, in a gel. In some cases true silica gel will be formed in situ, but it is not contended that the formation of huge masses of homogenous gel are a necessary feature in the genesis of the jaspers.

Where the jaspers show definite intrusive relationships, it is probable that they have moved as a gel. Fig. 6 is an example of a microscopic vein which has probably crystallized from a gel. Silica gel veins have been found in nature, a notable instance being those cut during the driving of the Simplon tunnel, near its Italian entrance.

It is contended that the process of jasperization is intimately related to the processes of spilitization and sulphide mineralization which are discussed in the sections dealing with hydrothermal alteration and ore genesis.



Fig. 5. x120

Mosaic textures in jasper vein quartz.



Fig. 6. x30

Jasper vein.

Pyroclastic Rocks. Rhyolitic tuffs form an interesting development at San Domingos, and exert a marked structural control on dyke explacement. A belt of tuff extends along the northern contact of the middle porphyry dyke (squares A and B) and its eastern termination coincides with the end of the dyke. The tuff is a massive incompetent rock and has apparently localized a structural discontinuity along which intruding magma forced itself.

A rock which has all the field appearances of a tuff occurs along the southern margin of the large 'diabase' dyke, in squares D and I. Unfortunately none of the thin sections from this zone has yielded conclusive evidence of a tuff origin, but it is at least clear and of structural significance that this massive band of rock has influenced the splitting off of a thin separate parallel dyke on the southern contact of the main intrusion.

The rhyolitic tuffs resemble rhyolite in their field occurrence, but their origin is betrayed by distinctive bedding, and in thin section they frequently seem to contain radiolaria.

Tuffs are in all probability more widespread than has been shown on the map and some of the gritty bands noted in the sediments may be tuffaceous. Their detailed mapping, other than on the contacts of igneous rocks, has not been attempted. Volcanic agglomerates, which occur elsewhere in the pyrite belt, have not been observed in the San Domingos area.

Acid Igneous Rocks. The general term quartz porphyry has been used for convenience in naming these rocks, since it is the term commonly used in the literature for describing similar rocks elsewhere in the pyrite belt. (i.e.Williams D.[6]). For the purpose of this thesis it refers to rocks containing phenocrysts of quartz and alkali felspar and almost entirely devoid of dark silicates. The short term 'porphyry' has not been used, since some petrographers (i.e., Hatch and Wells) use it to denote a rock of syenitic composition, and G. Williams[5] has apparently used it in this sense in mapping the rocks at the La Zarza mine. (see p.35). Quartz porphyry is here intended to cover porphyritic microgranites, granophyres, quartz keratophyres, quartz monzonites and rhyolite porphyries.

The predominant type of quartz porphyry is highly silicious, with nearly all the felspar lying in the albite-oligoclase range. In some cases the felspar is almost pure albite, and then the almost complete lack of coloured minerals and white mica justifies use of the term quartz-keratophyre. Granophyres, notably developed in the small intrusions in the north-east corner of the map (squares D and E), typically show radiating intergrowth textures of quartz and albite.

The quartz porphyries of the Paiol Pequeno (magazine porphyries) differ from all others in the area in showing a higher degree of shearing and alteration. As it

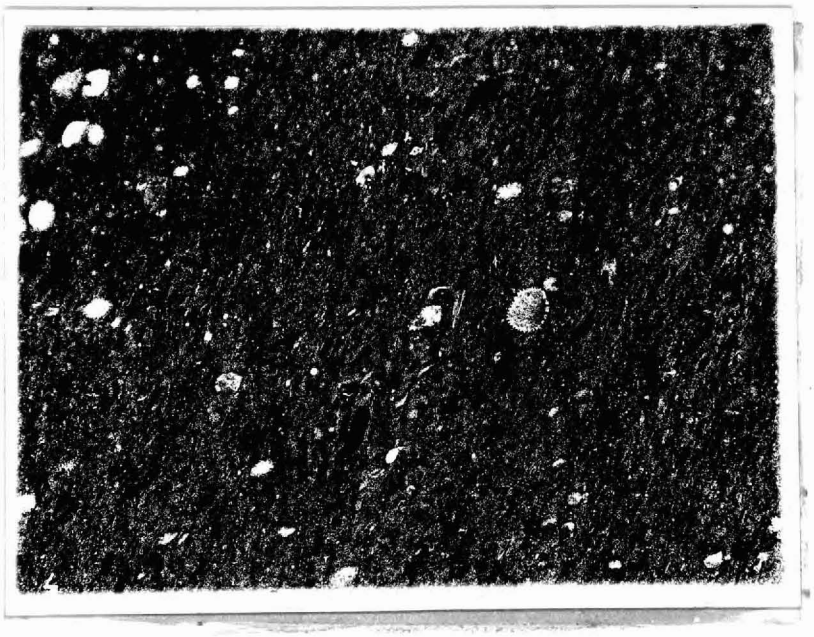


Fig. 7. x60

Radiolarian Tuffs. S.Domingo.



Fig. 8. x60

Granophyre. S.Domingo.

is hard to account for the shearing in terms of local structures it may be a product of auto-shearing and brecciation induced during intrusion. The possibility has been considered that the alteration was an accompaniment of ore intrusions below the present surface, but the lack of sulphides associated with the alteration seems to indicate that the solutions were non-sulphurous. It seems likely that a rock which has undergone auto-shearing will be susceptible to deuteric and late stage metosomatic alteration by a residual phase.

Quartz monzonites occur near Vale da Mota (square G) as a gradational variety of monzonite, but most of the quartz porphyries are too albitic to be classed as monzonites.

Rhyolite porphyries of flinty character are occasionally developed, and along the margins of the quartz-porphyries a flinty chilled facies and flow banding is sometimes developed.

Intermediate Igneous Rocks. These are widely developed and include the monzonite porphyries and most of the 'diabases' It should be stressed again that the terms 'porphyry' and 'diabase' are used here as terms current in mining parlance, but without precise petrological meaning. The petrological types included in the intermediate class are porphyritic microsyenites, monzonites, keratophyres, intrusive trachytes and trachy-andesites and porphyritic microidiorite. This

series of rocks grades right through the intermediate class from acid to basic, and represents a complexity of types.

The principal type shows a texture of felspar laths varying from ophitic to trachytic, accompanied by augite and some quartz, and set in a fine-grained matrix often crowded with microlites and a considerable amount of leucoxene. Free quartz can be absent and the pyroxene may have been totally destroyed during alteration. The felspars are almost invariably in the oligoclase-albite range, but some small varities showing simple twinning may be either potassic or acid plagioclase species.

The monzonitic and micro-syenitic porphyries show well developed phenocrysts and are notably more porphyritic than the other intermediate types.

Much of the complexity in the igneous rocks results from their saussuritization, spilitization and propylitization. That these processes have taken place is testified by the almost universal presence in the intermediate and basic rocks of the assemblage, Albite, Epidote, Carbonate, Chlorite and Pyrite, the significance of which is described elsewhere in this thesis.

Basic Igneous Rocks. The basic rocks all appear on the map under the term 'diabase'. They are essentially altered albite dolerites but since the albite may well have been formed from more calcic plagioclase as part of an alteration process, they may truly fall within the precise definition

of a diabase, as used by some geologists to signify an altered dolerite.

They show a pronounced ophitic texture and are always considerably altered. Seen in reflected light the leucoxene forms a typical pattern reminiscent of ophitic felspar laths.

The basic rocks grade into the intermediate class and are recognized in the field by their dark colour. They are obviously genetically grouped together with the trachytic and micro-dioritic rocks of the intermediate class and have undergone the same cycle of metosomatic alteration.

Faulting. Faulting within the sediments is extremely difficult to trace but there is undoubted evidence of regions of intense shear and interbedding-slip. Three faults which have displaced igneous rocks have been mapped in detail. The western one at Zambujeiro is interesting in that careful mapping by pitting has undoubtedly shown that it does not cause a displacement on the southern contact of the dyke in the way that it has on the northern contact. Movement along it seems to have been deflected along the southern contact, and the map suggests that the stresses which caused the fault may have been in operation prior to the intrusion of the dykes and thus have exerted some control on the shape of the intrusions.

Strong shear zones are associated with the rocks in the mine area, and the pattern and significance of the shears

is discussed in the section on structural controls.

San Domingos Ore Body. The disposition of the ore body in relation to the igneous rocks at the surface, and its dimensions in the opencast are shown on the surface map. At 240 metres depth the orebody is approximately 400 metres long and up to 100 metres wide. As the orebody descends to the lowest workings, at a depth of 360 metres, it diminishes in size.

Along the north wall of the orebody the western and eastern sectors consist of quartz porphyry, whilst the central portion is a zone of interdigitated slate and intermediate rock. The south wall is of intermediate rock, originally an augite micro-diorite, which, like all the rocks of the mine series, has suffered intense metosomatic alteration.

The ore contacts are always sharp on the south wall but are sometimes gradational on the north wall. Judging by the distribution of slate on the walls of the orebody it appears that much of the sulphide deposit originated by replacement of slate.

Details of wall-rock alteration and the mineralogy of the ores are given elsewhere in this thesis.

Gossanization. An extensive gossan capping which formerly lay over the orebody prior to the opencast operations testified to the extensive erosion of the upper part of the

sulphide deposit. An enigmatic zone of gossan also occurs at Bicados, in square H. It can be seen from the map that this particular zone extends for a considerable distance and in part appears to transgress the topography in such a way as to throw doubt upon its being entirely a transported gossan derived from the main orebody. Explorations below the gossan have been abortive and it is apparent that if the gossan has formed in situ it must be due to the erosion of a zone of disseminated sulphides. It is hardly likely to represent the roots of a vanished orebody, since the erosion of this would almost certainly have left extensive traces behind. It is concluded that the Bicados gossan originates mainly from a zone of disseminated pyrite, though the deposition of some transported iron oxides may have modified the gossan distribution in the valley. This conclusion does not, of course, rule out the possibility that ore may lie below the disseminated zone.

Stockworks. These are not of economic importance in the San Domingos mine since those carrying copper values are not sufficiently extensive to warrant mining. They occur in two principal zones, shown on the accompanying map, one in the vicinity of No.4 shaft and the other near the middle fault zone. The No.4 shaft stockwork occurs in a roughly vertical zone, but is sporadically distributed and shows higher values on some levels than on others. Its maximum development is on the 210 metre floor. The middle fault

stockwork appears on the upper levels of the opencast benches on the north wall and is well developed on the 122 metre and 150 metre floors. Exposures seen on the lower levels suggest that the stockwork is either diminishing rapidly with depth, or is enclosed within the porphyry and only visible on its fringe areas.

MINAS de RIO TINTO. SPAIN.

As the geology of the mines has been very thoroughly treated by D.Williams[6] it is proposed to give only a brief summary of the general geology as described by him, together with some slightly different interpretations of certain aspects in the light of new evidence.

The field work for this study was made possible by the generous co-operation of the Rio Tinto Company who provided accommodation and transport for which the writer expresses his sincere appreciation.

General Geology and Rock Types. The general relations of the district can be seen from the accompanying map, taken from the paper by D.Williams. The sedimentary rocks of the area consist predominantly of well cleaved slates, the quartzites so well developed at San Domingos being practically absent. The slates belong to the Visean stage of the Lower Carboniferous System and their cleavage strikes at about 100° true with a prevailing dip of about 80° to the north.

The 'slate conglomerate' lying in the porphyry to the north of the San Dionisio orebody is considered by the present author to be possibly of volcanic origin in part. Sections of some of the nodules appear to be tuffs, and one shows oval shapes which may be radiolaria. It is believed that these nodules, of volcanic origin, have undergone a certain amount of rolling and abrasion prior to compaction within sediments. Volcanic agglomerates in the pyrite belt have been reported by Collins[2], and since a section of a tuff was reported from the Rio Tinto area by Williams[6], this explanation of the slate conglomerate does not seem an improbable one. Reference can be made for other explanations, to the paper by Williams and the discussion on this paper by Edge.

The quartz porphyries are very similar to those of San Domingos already described, and include granophyric and keratophyric types. Marginal facies, well exposed at many places, are characterized by the segregation of innumerable porphyritic felspars.

The zone of metamorphosed chloritic rocks in the centre of the quartz porphyry to the north of San Dionisio is considered by the present writer to be a separate intrusion of trachyte, andesite, or diabase, now heavily chloritized. The reasons for this conclusion are as follows:

1. Thin sections, when illuminated by top light, show a leucoxene pattern identical with that observed in

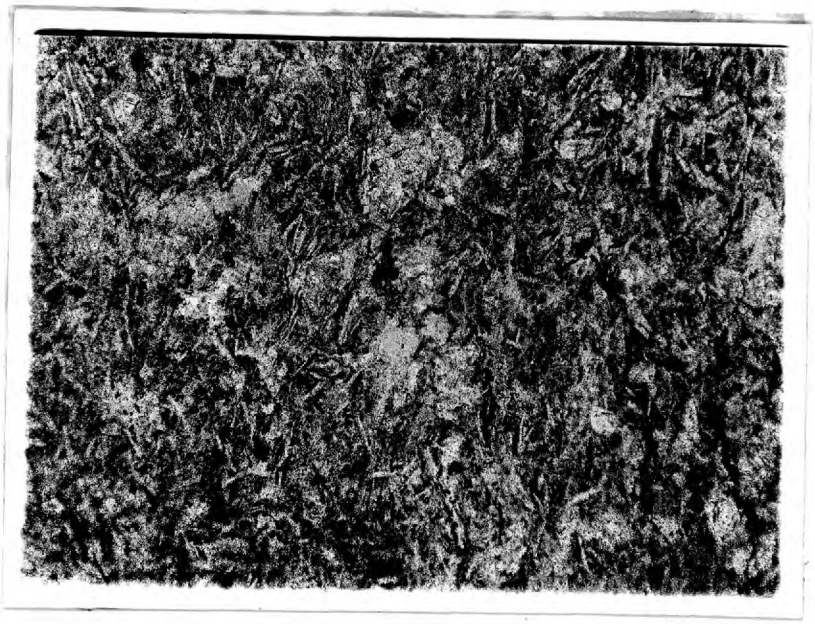


Fig. 9. x100

Trachytic texture in metamorphosed chloritic rock of Rio Tinto.



Fig. 10. x100

Leucoxene threads in Rio Tinto chloritic rocks. Top illumination.

chloritized rocks known to originate from intrusive trachytes and similar to the pattern developed in altered dolerites. This pattern is quite different from that seen in chloritized quartz porphyries and monzonites.

2. The frequent interdigation of slates with intrusions is much more commonly associated with intrusive trachytes and diabases than it is with porphyry. The pattern of slate pendants in the chloritic zone is similar to that in the 'Dolerites' (diabases) to the south of the Rio Tinto mines and in the San Domingos area.

3. It will be subsequently suggested that the Eduardo Fault is of pre-mineralization age. Since the chlorite of the chloritic zone is likely to be pene-contemporaneous with mineralization, its displacement by this fault has to be accounted for. One explanation is that there has been selective chloritization of a favourable zone which was dislocated by pre-mineralization faulting. An intrusion of diabase or similar rock crowded with slate pendants is just such a zone which experience shows would be selectively chloritized.

The basic rocks on the southern margin of the map are similar to those at San Domingos already described, and show ophitic textures and the development of albite associated with epidote, carbonates, and chlorite.

Jaspers are not conspicuously developed at Rio Tinto, their occurrence being restricted to the vicinity of

the western end of the Salomon dyke. Field relationships show that they were formed along porphyry contacts subsequent to the consolidations of the porphyry. Some of the jasper results from infilling along slate-porphyry contacts, and elsewhere its structure and field occurrence strongly imply a derivation by replacement of slate. All the microscopic textures which have been described as occurring in the San Domingos jaspers also occur in the Rio Tinto examples.

A highly siliceous capping of hornstone occurs on the ridge to the south of the Salomon opencast and is considered to have been mainly silicified prior to the sulphide mineralization, although some of the silica may have been acquired from solutions accompanying ore deposition. The occurrence of hornstones, silicified porphyries and jaspers at Rio Tinto has recently been fully described by D.Williams 18.

Faulting. The principal fault of the district, known as the Eduardo fault passes between the San Donisio and South Lode in an approximately magnetic north-south direction. The writer was exceptionally fortunate in being at Rio Tinto when a new drive on the 16th floor went through the fault zone. The broad zone of gouge and sheared rock was found to be heavily impregnated with perfect cubes and pyritohedra of pyrite; detailed examination of the crystals after they had been separated by panning, showed them to be completely

unfractured. This fact strongly suggests that the fault is either contemporaneous with the ore deposition or is of pre-mineralization age. The criteria of the chlorite zone displacement, previously used to assign a post-mineralization date to the Eduardo fault, is believed to be misleading for reasons which have already been given.

Post-mineralization movements have undoubtedly taken place as indicated by the minor faulting and slickensiding widely developed within the ore, and there has also been considerable faulting of the diabase in the southern part of the area.

The structural controls of ore deposition are discussed in a later chapter.

Rio Tinto Ore Deposits. The distribution of these deposits, which are nearly all related to the Salomon dyke, is shown on the accompanying map. They represent an enormous concentration of pyrite and have yielded well over 100 million tons of ore since mining commenced. It is not proposed to describe the spatial relations of the masses in detail as this has been dealt with by Williams. Mineralogical details and the distribution of metal values in the massive and stockwork are discussed in later chapters of this thesis.

The largest deposit is the San Donisio lode which attains a maximum length of about 1000 metres and reaches

a width of 280 metres. It lies on the contact of slate and porphyry but owing to the complexity of the porphyry contact, it lacks the characteristic lens shape of other Iberian pyritic ore-bodies. In the central and western parts of the orebody the porphyry contact forms a trough which pitches towards the east and has provided a locus for the development of massive ore; in the east the contact is vertical and the orebody has a more normal shape. Ore contacts are generally sharply defined, but there are occasional gradational contacts with the porphyry. Sometimes a veneer of slate intervenes between the massive pyrite and the normal porphyry footwalls, a feature which persistently occurs in other mines and suggests that the ore has often preferentially replaced slate.

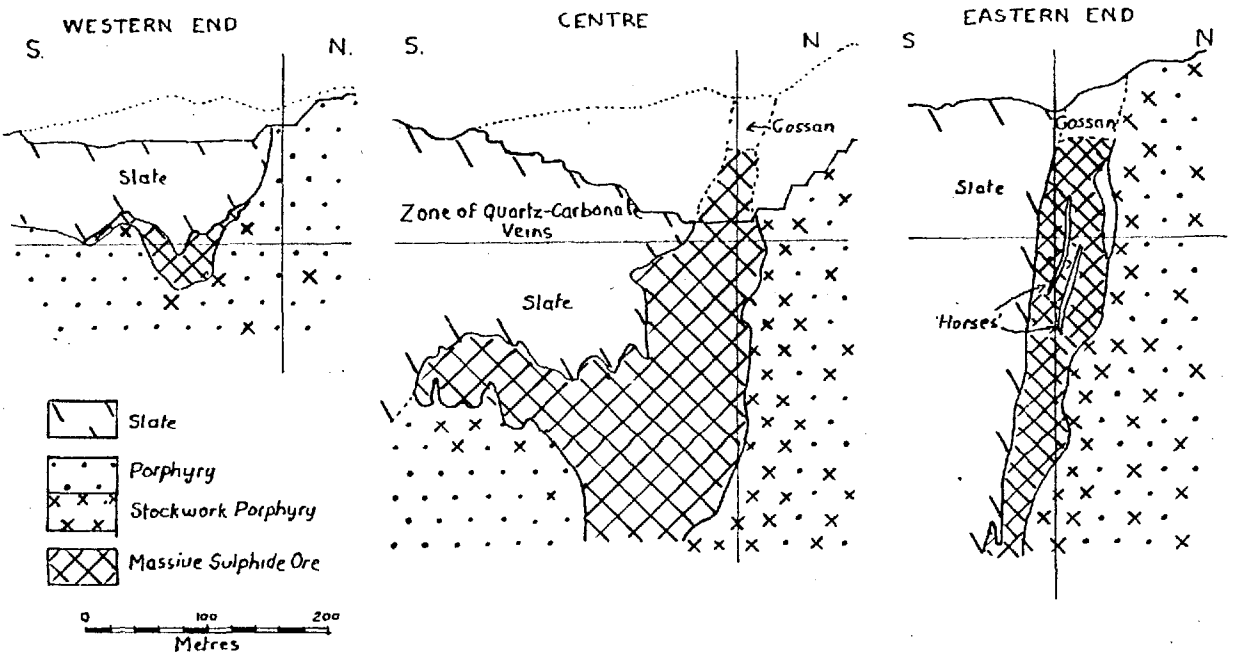


FIG 11 SAN DIONISIO LODE – CROSS SECTIONS.

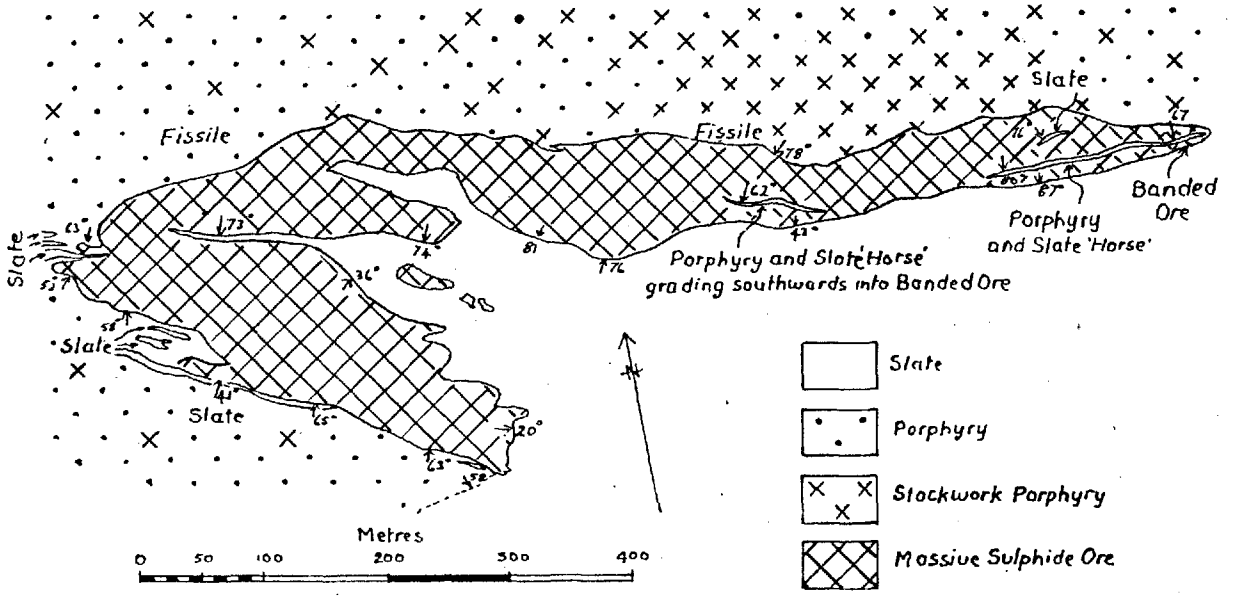


FIG 12 SAN DIONISIO LODE – TYPICAL FLOOR PLAN.

After D. Williams 1934

The Eduardo mass is virtually an eastward extension of the San Dionisio lode and stretches towards the Eduardo Fault. It is about 100 metres in length and is characterized by the occurrence of banded ores, the development of which is discussed in the chapter on mineralogy.

The South Lode lies on the southern contact of the Salomon dyke to the east of the Eduardo fault. It has an overall length of 1350 metres and averages about 35 metres in width, with a maximum of over 100 metres. It is a typical lens-shaped orebody developed on the porphyry-slate contact and, as in the San Dionisio Lode, a slate selvage frequently separates the porphyry from the massive sulphide.

The Planes mass lies at the eastern end of the Salomon dyke and where it has been mined underground the orebody lies partly on the eastward pitching contact of the dyke and in part it extends inwards into the porphyry. It seems likely that since the spatial relationship of the ore to the dyke is markedly similar to that of the jasper to the dyke at its western extremity, analogous structural controls operated in both cases. The mineralogy and distribution of ore types are of great interest and demonstrate the processes of ore formation very clearly, as discussed in later chapters.

North Lode is the collective name of the three deposits of Lago, Dehesa and Salomon, which are boat-shaped

masses with gradational contacts, enclosed within porphyry. Their massive ores have now been almost entirely mined out and operations are now practically confined to the underlying stockworks. Surviving remnants of the original slate roofs occur on the upper benches of the opencasts, and it is possible that the ore has resulted in part from the replacement of slate roof pendants in the Salomon porphyry dyke.

The Valle Lode, now worked out, is apparently isolated in slate about 100 metres from the northern contact of the Smelter Ridge porphyry, near Bella Vista. It had a maximum length of about 230 metres and was about 12 metres wide at the surface. Possibly the deposit is related to two porphyry stocks which contained feeding channelways for the ore forming fluids. The slates alongside the igneous contacts near the orebody show the development of porphyryoblasts and are adolinized as at San Domingos.

Stockworks. Only a brief description of the distribution of the stockwork is given in this chapter, the distribution of copper values being discussed in the chapter on the mineralogy of the ores.

Stockworks are extensively developed in the central and eastern sections of the north wall of the San Dionisio mass, but their extent in the deeper levels and under the orebody has not yet been explored. The zone of high copper values in the stockwork is rather narrow and runs close to the massive ore. In addition to the north

wall stockwork, a small network of cupriferous veins underlies the southern limb of the San Dionisio orebody, and extends upwards into the massive ore itself.

Pyrite stockworks exist through much of the north wall of the South Lode, but workable copper values are confined largely to two localized areas. The smaller one is situated near the eastern end of the opencast and plunges westwards at about 30° from the 11th floor before petering out on the 16th floor. The larger mass lies slightly west of the central part of the lode and extends from above the 15th floor to below the 25th floor.

The stockworks of the Planes mass occur in porphyry and, although of no economic value, they are of considerable academic interest in that they grade imperceptibly into massive coarsely crystalline pyritic ore.

The stockwork of the North Lodes, and Qebrantahuesos represent the roots of massive orebodies, now mined out. Salomon, the largest stockwork, has been proved for nearly 100 metres below the base of the massive sulphide deposit. At Qebrantahuesos a small block of stockwork has been proved to a depth of about 50 metres and is thought to have underlain an orebody now eroded away.

The Gossans. Gossanization and iron staining are widespread at Rio Tinto, and render the deposits very conspicuous at the surface. The gossans which formerly capped the massive deposits have been removed during open-

cast operations, but those which have resulted from the prolonged erosion of weakly mineralized porphyry are still in situ. The cappings vary between 10 and 40 metres in thickness and where they have been formed from massive ore, they are underlain by a zone of porous leached pyrites. When they have been derived from mineralized porphyry they generally lie on practically barren decomposed rock. The base of the gossans frequently carry gold and silver values, for which they have been worked.

False gossans, or bog-iron ores, are also extensively developed at Rio Tinto and testify to the magnitude of past erosion of the deposits. Only remnants of bog-iron ore deposits remain today, for they have themselves been eroded and re-transported due to the rejuvenation associated with comparatively recent Alpine uplift. The largest remnant is that of Mesa de los Pinos, which is 1600 metres in length and averages 150 metres in width and 6½ metres in thickness. Both the true gossans and the bog-iron ores have been described in detail by D.Williams[6,18].

LA ZARZA MINE. CALANAS. SPAIN.

The investigations upon which the present work is based were carried out during a three weeks stay at the mine, and the writer is indebted to the owners, The Tharsis Copper and Sulphur Co. Ltd., for their generosity in providing accommodation and facilities.

The mine is situated 55 km. north of the port of Huelva and about 20 km. west of Rio Tinto. The geology of the area around the mine is depicted on the accompanying 1/10000 sketch map.

Sedimentary Rocks. These are similar to those of the Rio Tinto area and are mainly composed of well cleaved slates with occasional gritty bands. Gordon Williams[5] has reported that bedding dips are usually low even through the dip of the cleavage is always steep.

Agglomerates and Breccias. These are notably developed at La Zarza as shown on the map, and underground. Their origin is exceedingly difficult to determine. Collins[2] considered them to be of volcanic origin but Cullis stated in the discussion on the Collins' paper that he was uncertain of this and suggested they might have been formed cataclastically. Gordon Williams believed they were contact breccias.

Hand specimens display whitish hard nodules of silicic appearance set in a sheared matrix which sometimes has the appearance of a tuff. Fig.13 illustrates a typical field exposure.

All the thin sections examined show the effects of intense hydrothermal alteration, but owing to the proximity of the breccias to ore it is impossible to be sure whether this alteration has been effected by the ore bearing solutions or by metamorphism associated with shearing. In some cases small oval shapes have the



Fig. 13. La Zarza Agglomerate.

appearance of altered radiolaria, which suggested that the agglomerates are of volcanic origin. However, the study of spherulitic growths, reported elsewhere in this thesis, has shown that spherulites of many different minerals can grow during hydrothermal alteration, and that if the rocks are sheared, cleaved or subjected to stress, these spherulites may develop oval shapes. In short, the simulated shapes of radiolaria can actually be formed by metosomatic action. Indeed, the only certain criterion for identifying radiolaria in hydrothermally altered rocks is the presence of regular internal patterns or edge markings. This diagnostic criterion has not been recognised in the La Zarza agglomerates.

Both rhyolitic and andesitic material occur in the fragments, and the rocks exhibit evidence of intense shearing, often amounting to mylonitization. It is considered by the writer that the rocks are probably contact breccias, though the possibility that they are sheared volcanic agglomerates cannot be denied. The available evidence is not conclusive and further careful microscopical study of rocks far removed from mineralization is required.

Quartz Porphyry. The amount of quartz porphyry developed in this area is less than at San Domingos and Rio Tinto, the principal light-coloured rocks being porphyritic microsyenite and monzonite. Quartz porphyries occur to the north and south of the mine series, but are not associated

with ore. Their felspars lie within the albite-oligoclase range and are similar to those in the San Domingos porphyries.

Intermediate Rocks. These include porphyritic micro-syenites and monzonites (mapped by Gordon Williams[5] as 'porphyries'), and trachytes. The micro-syenites occur in the Mesa porphyry and in the Sierra Blanca porphyry, both of which come into contact with the ore. They contain phenocrysts of plagioclase felspar, mostly in the albite-oligoclase range, and occasional orthoclase felspar, set in a fine-grained groundmass of quartz and felspar. Quartz-phenocrysts are absent and the rocks are somewhat darker in colour and less siliceous in appearance than quartz-porphyry. They frequently contain granular epidote, carbonate and chlorite, the chloritization being intense alongside the ore. Gordon Williams[5] erroneously stated that the greyish-green colour of the wall rocks is due to sericitization.

The trachytes have only been observed underground, where they are unmistakably developed alongside jaspers on a portion of the south wall on the 10th and 19th floors. They are believed to be of intrusive origin. In thin section they show a trachytic texture of sanidine and albite laths, and the rocks are strongly alkaline in character. Epidote is dispersed through them in extremely fine granules and carbonate is also present.

Basic Rocks. These can be classified as diabases. They exhibit the characteristics of similar rocks at San Domingos

and Rio Tinto, and consist essentially of ophitic albite set in a heavily chloritized groundmass. Their ferromagnesian minerals have been mostly destroyed and the presence of epidote or clinozoizite and carbonate implies the spilitic alteration of originally doleritic rocks.

Diabase is reported as occurring on the south wall of the Perrunal mass[5], and since this mass is continuous with the La Zarza orebody it is possible that the diabase corresponds to the trachyte observed by the present writer on the south side of the La Zarza deposit.

Jaspers. These are very conspicuous at La Zarza and form the capping of many hills in the district. The principal outcrops in the vicinity of the mine are those of Alcornocoso, Juncelejo and Chirondon, which occur on the margins of the porphyry and show both intrusive and replacement relationships. Jaspers exist underground alongside trachyte intrusions at La Zarza working, and on the margins of the diabase in the Perrunal workings.

The textures of the jaspers are similar to those of the jaspers at San Domingos and Rio Tinto, and are mainly the result of crystallization from gels. The greater abundance of jasper at La Zarza than in the other districts is considered to be largely due to the much deeper burial of the La Zarza ore below the present-day surface.

Exposures at La Zarza are ideal for studying the occurrence of jasper, and examples demonstrating all the

intermediate stages in the processes of silicification, hematization and jasperization can be found. The relationship of these processes to mineralization in regions above the ore can be studied in the remarkable opencast section below Los Silos, and also above the blind orebody at numerous points east of the opencast. Studies of these exposures, details of which are given in the chapter on ore genesis, have led the writer to infer that the jaspers and their associated manganese ores have been formed as an early phase, or advance front, of hydrothermal alteration which may remain entirely barren or may subsequently be followed by an intense phase of sulphide mineralization, depending upon factors to be discussed later.

Structures. Reconnaisance mapping has not revealed the existence of any transverse faults, but many of the rocks show evidence of mylonitization and the district has obviously been subject to considerable structural disturbance. The spatial relations of the intrusions are far more complex than might be inferred from a study of the surface map, a fact which becomes apparent when the underground geology of the concealed pyritic mass is studied. This complex arrangement of competent intrusive rocks associated with incompetent ore would undoubtedly have given rise to many couples and shearing movements during orogenic compression. The writer has found no evidence, however, to suggest that these couples were developed on a

regional scale by late stage orogenic movements, as suggested by Gordon Williams[5]. Fracture cleavage is developed locally in connection with interbedding slip or contact shearing, but it is not so widespread as illustrated on Gordon Williams' structural map. Every locality mentioned by Williams in connection with fracture cleavage was closely examined and the writer formed the opinion that local strike fluctuations of flow cleavage, especially near igneous contacts, had been confused with the development of fracture cleavage. In the experience of the writer fracture cleavage is a distinctive form of cleavage readily distinguished when seen in the slates of the Pyrite belt, and quite different from the cleavage mapped by Gordon Williams as fracture cleavage.

It is contended, therefore, that the orogenic pressures were more or less constant in direction and that shearing couples in a horizontal plane were developed by local adjustment during the compression of the rocks. This does not, of course, preclude the possibility of strike faulting and shearing by thrusting.

The Perunal - La Zarza Orebody. This orebody has not yet been fully explored and it may yet prove to be one of the largest pyritic masses in Iberia. It consists not of a single lens but of a number of lenses extending along the strike, either partially joined or arranged in almost en echelon fashion. Mineralization is known to extend over a length of nearly

3 Km., the width of the orebody varying mostly between 25 and 100 metres.

Chloritized porphyry (i.e., porphyritic micro-syenite and monzonite, but not quartz-porphyry), shown on the map as the Mesa porphyry, forms the north wall along the western part of the deposit. The en echelon arrangement of the orebodies displaces the mineralized zone northwards in its central portion so that the western extension of the Sierra Blanca porphyry forms the north wall of the zone at its eastern end.

In the western half of the ore zone, the south wall of the deposit is made up largely of slate, the remainder consisting of trachyte and diabase intrusions together with a small porphyry intrusion. The eastern half of the south wall is composed of porphyry, together with the agglomerate or breccia previously described.

Unfortunately, it is not possible to present a map of the complex underground geology. Most of the ore has been formed on slate contacts and where it apparently lies between igneous rocks, there are vestiges of a slate selvedge. This fact, together with microscopical evidence described in chapter 5, suggests that the ore has originated by replacement of slate.

Stockworks. Considerable pyritic dissemination occurs in the north wall of the La Zarza mass, but no data is available to the writer concerning the distribution of values.

Gossanization and Iron-Staining. A gossan capping formerly overlay the ore at the site of the present opencast, and it is presumably the erosion of this ore that has produced the discordant layer of bog-iron ore which lies in the valley to the south east of the opencast. Since the field relations of the gossans are much the same as those of Rio Tinto, described by D. Williams, they do not merit further consideration here.

The extensive iron staining of the rock above some of the concealed ore originated partly from the oxidation of dispersed sulphides in those rocks, and partly from the deposition of primary iron oxides from residual ore solutions. In some cases pyrite cubes in the rocks above the ore have been oxidized to limonite and weathered out so that they may be picked up loose on the surface.

CHAPTER 3.

PETROGENESIS OF THE ROCKS ASSOCIATED WITH PYRITIC OREBODIES.

The marked similarity of the structural and petrological environment of many of the world's pyritic deposits, which becomes evident on studying the literature, has focussed the writer's attention on problems of petrogenesis, the investigation of which might otherwise have appeared irrelevant in a study of mineralization. Principal emphasis is laid upon the role of late-stage magmatic and post-magmatic hydrothermal (i.e., deuteric) alteration in petrogenesis, for it is believed that these effects provide a common link between the rocks of pyritic provinces throughout the world, and are a clue to the origin of the orebodies themselves.

Deuteric Alteration in the Rocks of the Iberian Pyritic Belt.

Alteration in the Basic Rocks. The effects of post-magmatic alteration are, as would be expected, most pronounced in the true diabases. In them the plagioclase felspars have been considerably enriched in albite and often show a zonal arrangement, with more sodic felspar on the rim. These zoned felspars quite commonly have their cores replaced by chlorite or epidote, whilst their rims are clouded with micaceous flakes and clay minerals. Orthoclase phenocrysts may also be present, and these too frequently show zoning, whilst their comparatively large extinction angles suggest a sodic composition.

Epidote is liberally developed in the basic rocks, locally as coarse aggregates and small veinlets and elsewhere as minute grains which are only visible under high magnification. Sometimes the epidote forms rims around the felspars or their replaced cores. It may be profusely developed in some rocks, as in the diabase dyke on the northern side of the middle porphyry dyke (square A of the San Domingos map). This diabase dyke shows a progressive enrichment in epidote as it is traversed from the tuff to the porphyry contact, where the intense segregation of epidote imparts a bright green colour to the porphyry. In some of the diabase clinozoisite occurs with or in place of epidote, as in the diabase cut by the Naya tunnel at Rio Tinto.

Chloritization is virtually universal in the diabases and in many cases it has practically obliterated the pyroxenes. The more intensely chloritized dykes have a characteristic dark green colour, examples of which are the Nunes dyke at San Domingos (square D), and the diabase south of the hospital at Rio Tinto. Carbonatization is very common in the basic rocks and gives rise to micro veinlets and small patches of carbonate, some of which are pseudomorphic after felspar. Sericitization is rare and never extensively developed, occurring merely as minute scattered flakes in the groundmass and within the felspars.

The contact zones of the diabase dykes are sometimes so conspicuously hematized that the rocks develop a

purple colour, and in some of the basic intrusions in the vicinity of Zumbujeiro at San Domingos (square A) hematization has spread across the whole width of the dyke. A significant feature of the hematization is that although the groundmass of the rock may have been extensively replaced, the albite phenocrysts remain unattacked.

Jasperization, where it occurs, is usually associated with basic or intermediate rocks and is often accompanied by an extensive zone of related hematization. Silicification of the basic rocks without accompanying hematization is rare, although the segregation of secondary quartz in vesicles and small veinlets is not uncommon.

Leucoxene, characteristically abundant in the basic rocks, appears in small pools or in systems of parallel threads and has apparently resulted from the breakdown of titaniferous pyroxenes. Frequently the leucoxene pseudomorphs the cleavage of the pyroxene and sometimes inherits the rectangular mesh pattern of its two cleavages. The abundance of leucoxene is a feature common to meet albitized basic rocks, and especially of spilitic types, which are generally rich in titanium.

Although pyrite is not conspicuous, analyses carried out by Collins[2] indicate that most of the basic rocks carry pyrite, the average of his results being 0.197% FeS_2. Whether the pyrite is othomagmatic or postmagmatic has not been established.

Alteration in Intermediate Rocks. The alteration phenomena in the more melanocratic intermediate rocks of trachytic type are similar to those of the basic rocks. In the strongly porphyritic intermediate rocks of monzonite and micro-syenite type zoning in the felspar phenocrysts is frequently seen, and in many sections the felspars are pseudomorphed by carbonate. Intense chloritization of the lighter coloured intermediate rocks may give them a very distinctive green colour, much lighter than that of the diabase but quite different from the pistachio green of the epidotized rocks. Much of the chloritized Mesa porphyry (microsyenite) at La Zarza is of this colour.

Jasperization is strongly developed in association with some of the intermediate rocks, particularly with the porphyritic micro-syenites at La Zarza. (see p.)

Alteration in the Acid Rocks. The effects of post-magmatic alteration are readily apparent in the acid igneous rocks and have resulted in the widespread development of keratophyric and granophyric types. Sodic outer rims of the felspars are not common, but the inconspicuous though widespread occurrence of epidote suggests that calcium has been released during rock alteration. Vermicular intergrowths of quartz and albite are especially prominent in some intrusions, such as those depicted in the north east corner of the San Domingos map, and radiating granophyric textures and quartz-albite veins are often developed. Chlorite is usually present to some extent in the acid rocks and primary

ferromagnesian minerals are conspicuous by their absence. In some cases the intensity of chloritization clearly indicates that iron and magnesia have been introduced into the rocks by late-stage solutions. Jasperization and hematization are rare, the jaspers at the western end of the Salomon porphyry dyke at Rio Tinto being somewhat exceptional. Nevertheless, silicification is very common, especially on the margins of the intrusions, and produces extremely hard flinty aphanitic rocks which break with a conchoidal fracture. The textures produced in the silicified rocks are often similar to those formed in jaspers and resemble those produced hydrothermally by Van Praagh[17]. It seems likely, therefore, that at least some of the silicification is post-magmatic and hydrothermal. The segregation of these siliceous types is probably similar to the process of jasperization, apart from the hematite, and it is interesting to note that the previously mentioned jaspers at Rio Tinto are quite near to some siliceous segregations devoid of hematite.

Carbonization is rarely observed in acid rocks distant from mineralization channels, and pyritization is quantitatively similar to that in the intermediate, basic, and, according to Collins[2], sedimentary rocks.

Alteration in the Sediments. Contact alteration along dyke margins is characteristically of the adinole and spilosite type described by Agrell[19]. In its most intense form it is

typified by the growth of large spots in the slates, and although this degree of alteration is by no means universal, it can nevertheless be seen at many localities in the San Domingos, Rio Tinto and La Zarza areas. At San Domingos good examples can be seen at the Pinheiros diabase contact (square B) and alongside the diabase margins of square A, whilst at Rio Tinto there is a fine development of spotted slates close to the igneous contacts near the Valle Lode. The large spots of more intense alteration are composed of aggregates or laths of felspars, globular patches of carbonate or quartz, and chlorite spots. The felspars which include both albite and orthoclase, generally show considerable alteration to white mica and clay minerals.

Some of the tuffs adjacent to the diabase contacts (square A of the San Domingos map) have undergone pronounced adinolization, with the production of a massive grey-white rock of the type described by Agrell as normal adinole.

Spilosite types are characterized by the growth of much smaller spots, only visible in thin section. The spots may be of chlorite, sericite or quartz and in the latter case they often contain leucoxene. Inclusion of leucoxene in the quartz spots is a characteristic feature which is retained even if the sediments have subsequently been altered almost beyond recognition, a fact first detected by H.N.Rhoden, a student colleague of the writer's, and put to excellent use in mapping the complex geology of the intensely-altered north wall rocks of the San Domingos mine.

It has not been possible to study the extent to which spilositic rocks have been developed beyond the environs of the mines, but it seems likely that much of the contact alteration of slate leading to the formation of indurated margins alongside igneous rocks, is in fact a spilositic type of alteration.

The mechanism of spot formation and the growth of spherulitic forms during certain types of metamorphism is discussed on page 57 .

Data on the Rock Types associated with other Pyritic Deposits of the World.

U.S.S.R. The pyritic deposits of the Urals are in many ways very similar to the Spanish deposits, and the spilitic character of their associated rocks has been repeatedly described. Indeed, A.N.Zavaritsky[24], the principal student of the Ural area, has expressed the view that there is a genetic association between the spilite-keratophyre complexes and the pyritic orebodies.

Sweden. Gavelin[26], in an exhaustive study of the deposits of the Malanas district, reports the occurrence of spilitic keratophyres and effusive albite greenstones in rocks associated with the sulphide ore. The association has been complicated by metamorphism, some of the spilitic types having reverted to andesitic composition (Gavelin p.13), but the occurrence of epidote and calcite in vesicles certainly suggests that solutions were active during the post-magmatic

stage. Gavelin believes that the mineralization at Malanas is connected with the intrusion of the Revsund granite into the volcanics, and in a later paper[27] he describes this granite as being a late-orogenic migmatite-forming type. According to some schools of thought (exemplified by Cheng[28]) such a granite would be rich in sodic solutions, a point to be noted here for reference at a later stage.

Canada. The massive pyrite deposit of Flin-Flon in Manitoba is very similar in many respects to the Swedish deposits, and occurs amongst lavas which have been invaded by porphyries and granodiorites. The lavas, which contain amygdules filled with calcite, epidote, quartz or chlorite, have been recognized by Brownell and Kinkel[29] as spilites. The later porphyries and granodiorites are albitic, the latter rock typically showing zoned felspars with sodic margins.

The Horne Mine, Noranda, Quebec is another pyritic deposit associated with soda-rich rocks. Price[30] has mentioned pillow lavas amongst the surface flows which are intruded by 'meta-diabase' dykes. These dykes include albite diabases with radiating textures which strongly suggest a spilitic type of alteration.

The pyritic orebodies of the Eustis Mine, Quebec, are another example of the association between sodic rocks and pyrite, to which Stevenson[31] has drawn attention. The

presence here of olivine diabase, lamprophyre and camptonite dykes is interesting, for it has been recently shown by Vincent[32] that in the dyke swarms of the Skaergaard area, Greenland, these types have been successively intruded as magma fractions increasingly rich in volatiles.

U.S.A. The United Verde Mine, Jerome, Arizona, a massive pyrite deposit approaching the dimensions of the largest Spanish deposits lies in a Pre-Cambrian volcanic greenstone complex which has been intruded by quartz porphyry and augite-diorite. In the description of the geology given by Reber[33] the petrography is not dealt with in any detail but it is stated that the quartz-porphyry is frequently an albite rhyolite. A striking point is the frequent occurrence of jaspers on the diorite or quartz porphyry contacts, and from the description it appears that there are marked similarities between this district and the Spanish deposits.

The Shasta County area of California includes the Iron Mountain pyritic orebody described by Graton[34], and contains lava flows of meta-andesite, intrusions of alaskite porphyry, quartz diorite, and dykes which vary in composition between alaskite porphyry and a strongly basic type. The meta-andesite is characterized by amygdules filled with quartz, epidote, chlorite and calcite, whilst the strongly sodic alaskite porphyry consists mostly of quartz and albite, and might well be classed as a keratophyre. Small particles

of epidote, chlorite and magnetite are distributed through the alaskite but are nowhere present in important amounts. The dykes and sills which occur around the outskirts of the alaskite porphyry and quartz diabase are considered by Graton to represent all grades of differentiation from the original magma, of which the alaskite itself is the principal differentiate.

Australia. The Mount Lyell pyritic orebodies of Tasmania which have been described by Gregory[35], occur in a region of igneous schists, conglomerates and some non-schistose igneous rocks. The petrogenesis of the rocks has been considerably obscured by shearing, but nevertheless there is evidence of a rock-assemblage similar to that of other pyrite districts. Many of the schistose rocks are derived from quartz porphyry and where the felspars have been identified they are of albitic composition. Among the unsheared rocks are diabase porphyrites containing plagioclase felspar, and aggregates of chlorite and epidote which may be of deuteric origin; in general, however, it is not possible on the basis of Gregory's description to differentiate clearly between the deuteric and metamorphic alterations.

Cyprus. According to Hills[36] the pyritic orebodies of Cyprus are associated with and replace pillow lavas and have been formed at their contact with sedimentary rocks.

Other Areas. The data published concerning pyritic deposits

in other areas have not been available to the writer except in abstract form. It is noted, however, that the Norwegian deposits[37] of Roedhammer type occur on the contact of sodic granites, whilst those of Raron type accompany gabbro intrusions and those of Stardo are accompanied by jasper. The Leskedales type of deposit occurs between submarine effusive beds and is alleged to be of biochemical origin. The Turkish deposits[38] of the Esbiye-Gorete district in the Black Sea region occur amongst Tertiary lavas and tuffs, and the pyrite replacement deposits of Southern Antique in the Philippine Islands are associated with basaltic pillow lavas and cherts[39].

PETROLOGICAL FEATURES COMMON TO THE PYRITIC FIELDS, AND THEIR SIGNIFICANCE.

Spilitization and Related Phenomena. In the above review it will be noted that a certain cycle of events is repeatedly associated with the formation of pyritic deposits. An early volcanic phase is followed after a long interval by the intrusion of diabase and quartz-porphyry considerably antedating the ore, which is closely succeeded by the ascent of ore-bearing solutions. Sodic felspars, epidote or zoizite, calcite and chlorite are common to all the rock types, the felspars often showing zoning with increasing soda content towards the margins, and the other minerals forming in amygdules in the basic rocks. In some areas the early lavas form pillows and the environments can truly be called spilite-

keratophyric, whilst the other areas are also obviously related in mineralogical character to the spilite-keratophyre complexes. It seems clear that there is a genetic link between pyrite deposits and spilite-keratophyre suites, and we must therefore consider the processes involved in the formation of the complexes themselves before turning, in a later chapter, to the problem of ore formation.

In considering the case of the more obviously spilitic rocks containing zoned albitic felspars and amygdules filled with epidote, calcite and chlorite, there seems little doubt in the light of recent field and laboratory investigations that they have been affected by the circulation of solutions containing alkalis. In 1937 Eskola, Vuoristo and Rankama[40] showed that anorthite could be converted to albite by heating it with sodium carbonate solutions and silica in a bomb within the temperature range 260° - 330° c. They suggested that the undermentioned formula (A) represented the reaction. Turner[7], however, points out that this formula implies an increase in volume which is contrary to certain textural evidence seen in thin sections. He proposed an alternative equation (B) involving the removal of lime and alumina, the addition of soda and silica, with CO_2 playing the role of 'carrier' of soda and lime as carbonates.

(A) $CaAl_2Si_2O_8 + Na_2CO_3 + 4SiO_2 \rightarrow 2NaAlSi_3O_8 + CaCO_3$

Anorthite Albite

(B) $2CaAl_2Si_2O_8 + Na_2O + 2SiO_2 \longrightarrow 2NaAlSi_3O_8 + 2CaO + Al_2O_3$

Anorthite — Albite

The natural reactions involved in the formation of epidote during saussuritization have not yet been synthetically duplicated, but the fact that epidote forms by the breakdown of anorthite can be easily demonstrated in thin sections. Various equations can be given to satisfy the chemical requirements, of which the following two are examples:

$12CaAl_2Si_2O_8 + 2Na_2O + 6SiO_2 + 3H_2O \longrightarrow 6Ca_2Al_3(SiO_4)_3OH + 4NaAlSi_3O_8 + Al_2O_3$

Anorthite — Clinozoizite — Albite

$4CaAl_2Si_2O_8 + H_2O \longrightarrow 2Ca_2Al_3(SiO_4)_3(OH) + 2SiO_2 + Al_2O_3$

Anorthite — Clinozoizite — Quartz (in sol.)

Both the albitization and epidotization reactions tend to develop in the appropriate temperature range and Romberg[41] has recently examined the epidote-plagioclase equilibrium in detail. He has drawn up a provisional diagram for a falling temperature scale according to which anorthite is stable down to 400°c; below this temperature epidote starts to form and the felspar shifts progressively to a more sodic composition. Barth[42] has suggested a slight modification to allow for a pressure equivalent to a depth of 3 or 4 kilometres of rock, according to which the temperature range of reaction probably lies between 450°C and 250°C., which

corresponds approximately to the temperature range of pyritic mineralization.

It is evident that experimental, theoretical and field evidence all strongly support the theory that spilites have been formed by the extensive circulation of solutions during post-magmatic cooling; certainly this hypothesis applies to spilites carrying epidote, calcite and chlorite. It is a remarkable fact that the intrusives which follow the spilites in the pyritic fields may be separated from them by a considerable period of time, and yet they too show the influence of spilitic reactions. Thus the acid rocks change to quartz keratophyres with numerous characteristic textures and deuteric minerals such as epidote, whilst the basic rocks are altered to albite-diabase with a mineralogy similar to that of the spilites. It must be concluded that massive pyrite deposits are associated with cycles of magmatic activity in which the activity of volatiles has been a notable feature over a long period.

Jaspers. The conclusions concerning the high volatile content of magmas in pyritic provinces throws fresh light on the confusing associations of sedimentary and hydrothermal jaspers in the Iberian and Jerome (United Verde) fields. Both pillow lavas and rhyolitic tuffs are capable of introducing silica into the surrounding sea water, the former because the highly fluxed state of the lava facilitates the liberation of silica either by leaching or

by the release of volatiles into the sea, and the latter on account of their composition. This silica may be deposited as a gel, a process sometimes assisted by the activity of radiolaria, and may give rise to ordinary chert, ferruginous chert or jasper. A high ferruginous content may also be introduced into the sea by similar processes and may be deposited in the chert as hydrated iron oxide gel precipitates, or within the ordinary sediments to produce brilliant bands of red slate such as those observed by the writer in the Iberian belt.

After the volcanic episode and during the much later phases of intrusive activity, the circulating alkaline solutions which produce deuteric alteration are certainly capable of carrying considerable quantities of silica in colloidal form, and when the structural and physical controls are favourable these solutions deposit silica. The iron oxides which are also carried in these solutions have a greater mobility than the silica, and sometimes the jaspers on igneous-sedimentary contacts are surrounded by a halo of adinoles in which the matrix is strongly hematized and the felspars stand out as white spots. (e.g., jasper on north contact of porphyry near Vale da Moto, square G). This evidence, coupled with texture of the jaspers, leads to the conclusion that the formation of at least some of the hydrothermal jaspers may be a subsidiary effect of deuteric phenomena in igneous rocks. This conclusion is of

significance since it will be shown that jasperization can also be linked with mineralization, a fact which implies that there may be some relationship between deuteric alteration and mineralization. The genetical considerations which arise out of this possibility will be discussed in Chapter 7.

CHAPTER 4.

METOSOMATIC GROWTH FORMS AND WALL ROCK ALTERATION.

Metosomatic Growth Forms.

Spherulite and Spot Formation. A feature of considerable interest which has been noticed in the slates and to a lesser extent in other rocks is the formation of spots and spherulites. Investigation has shown that these structures are liable to grow in rocks not only during their soaking in hydrothermal solutions, but also during the processes of diagenesis, and it appears that spherulitic growth is conditioned by a certain degree of rock-permeability.

Spherulitic growth during wall rock alteration is best seen in the darkened slates which form near the ore-bodies. If sections of these slates are examined under a 4mm. objective using dark ground illumination they are found to contain innumerable spherulites of pyrite varying from 1 micron to 30 microns in size (Fig. 14). The spherulites consist of packed aggregates of pyrite granules which are sometimes elongated in a common direction (Fig. 15). As the ore is approached, the density of spherulites increases and they tend to form in bands; they become mingled with shapeless aggregates and anhedral pyrite and finally the banded ore merges into massive pyrite. It will be shown in the next chapter that these pyrite spherulites can also be detected in the massive ore by means of electrolytic etching and that

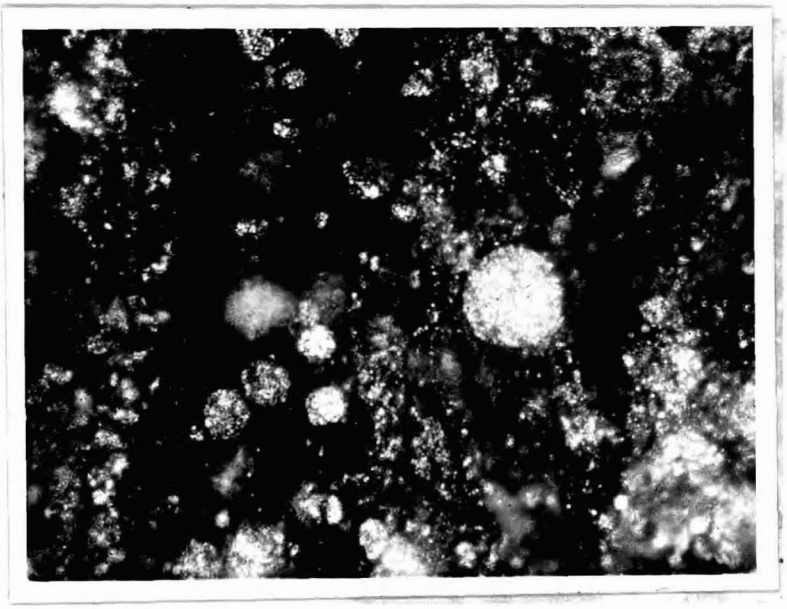


Fig. 14. x200

Pyrite spherulites in slate showing some preferential growth in bedding planes. Dark ground illumination.



Fig. 15. x200

Pyrite spherulites elongated in direction of schistosity in slate. Transmitted light.

they occur in all parts of the orebodies. This is one of the facts that makes a thorough understanding of their mode of formation important.

The origin of pyrite spherulites in slates has apparently not been explained satisfactorily to date. Schouten[43] gives illustrations of pyrite spherulites from many localities and argues at considerable length against the views of Schneiderhöhn[44] concerning their origin as fossil bacteria. He offers no explanation of their mode of formation other than that they originate syngenetically, and that they can be subsequently pseudomorphed by other sulphides by the agency of hydrothermal solutions. The work of the present writer, however, clearly shows that they can be formed entirely by hydrothermal solutions, as well as by diagenetic processes.

Laboratory Synthesis of Spherulites. A search of the literature on colloids and spherulitic precipitation has shown that banded precipitates and spherulites are readily formed in gels[13,14], and Bradford[16] has reported that banded precipitates can be formed in porous media such as columns of fine sand. It seemed logical from this that with the right conditions it should be possible to form spherulites in porous media other than gel even though no recorded instance of this has been found. Accordingly it was decided to reduce slate to a condition such as it might originally have had on the sea floor, and pass iron sulphide solutions

through it in an attempt to synthesise spherulites. In order to record the evidence the experiments were performed under observation with a photomicrographic camera, using a specially designed cell. The cell was fabricated out of sheet perspex and contained a small recess with tubes entering each side of it (Fig. 16). The tubes were prevented from blocking by means of small pads of asbestos, and the cell was packed with slate which had been crushed, boiled with HCl and neutralized with NaOH. This preparatory treatment of the slate had the effect of reducing it to a porous, partly gelatinized mush, a condition approximating to its state on the sea bed. The recess was then covered with a cover slip whose edges were sealed with rubber solution, and the whole was placed under the microscope, suction being applied to one tube whilst colloidal pyrite solution was fed through the other tube. The colloidal pyrite was prepared by fusing finely crushed pyrite with an excess of crushed sodium sulphide at 700°C. in a covered porcelain crucible, the fused mass being subsequently crushed and extracted with boiling distilled water so as to form a thick black colloidal solution.

The best results were obtained when the colloidal pyrite seeped around the edges of the cell, and thence started to migrate towards the centre. A run of 5 hours duration was made during which spherulites, identical to those observed in thin sections, were seen gradually to

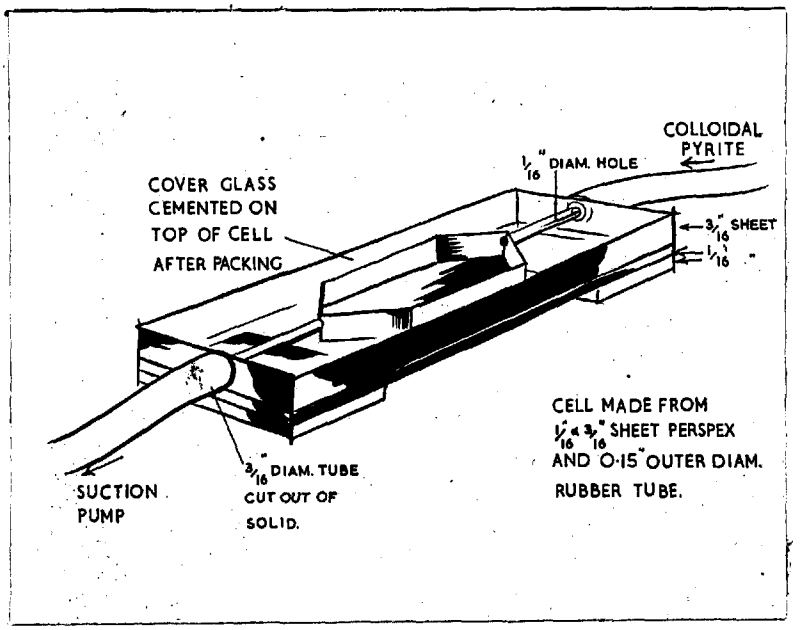


Fig. 16. Microscope stage cell for synthesizing growth of spherulites.

appear (Fig. 18). As expected from Bradford's work, banded formations also appeared, the bands advancing from centres rather than from a straight front, thus giving rise to colloform type textures (Fig. 19). In view of the innumerable colloform textures which have been found by the writer within solid rock (i.e., Fig.20) it is concluded that this expression of the Liesegang effect is undoubtedly one of the ways in which these structures are formed in nature.

It is not suggested from this experiment that the growth forms observed necessarily grew by a process of molecule by molecule metasomatic substitution, and it seems more likely that the spherulites pushed material aside as they formed. There is a suggestion that pressures are developed when spherulites grow in natural conditions since 'pressure shadows' are sometimes formed on either side of them (Fig. 21). Colloform textures are probably formed by rhythmic precipitation of sulphide within pore spaces, the bands of gangue left between the separate concentric zones forming pseudo-syneresis cracks. Radial growth lines were also observed in some of the synthetic growth forms as well as in colloform textures formed in rocks, and the writer concludes that the evidence of radial and concentric 'syneresis cracks' as criteria of gel origin must be regarded with suspicion.

It was not possible to identify by means of X-ray studies the material precipitated during the experiments as it rapidly oxidized to brilliantly coloured ochreous limonite.

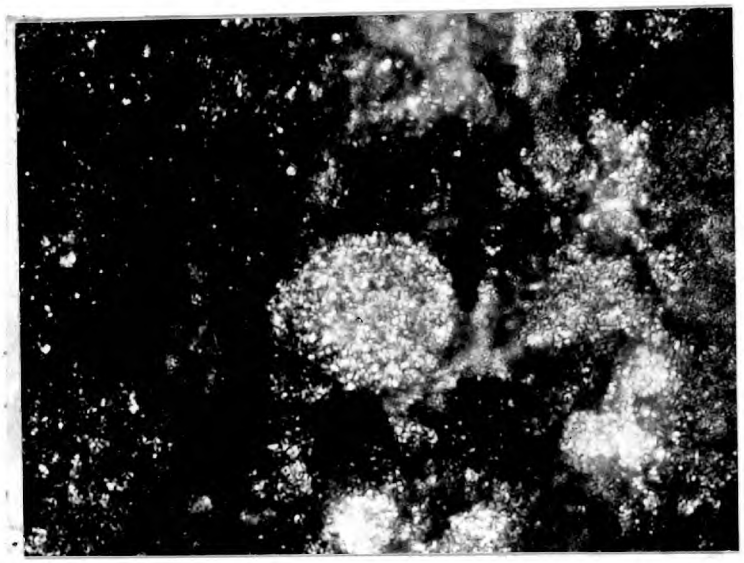


Fig. 17. x500

Natural spherulite in slate.

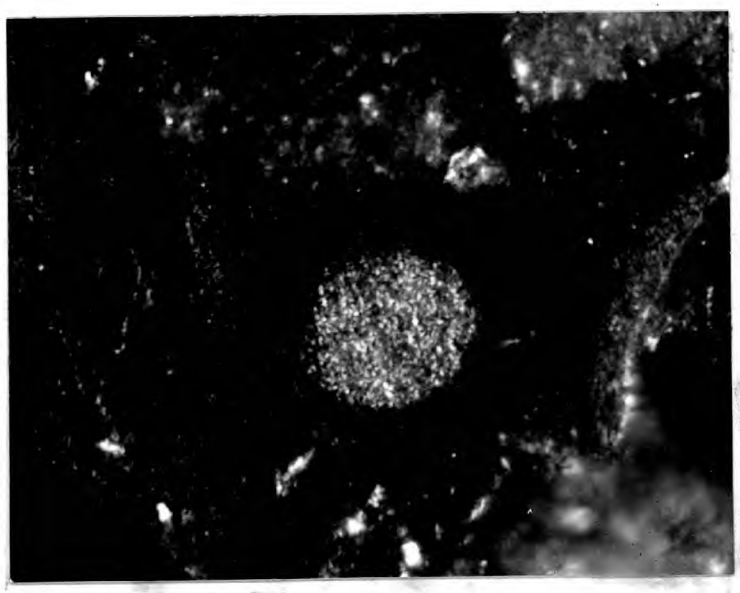


Fig. 18. x500

Synthetic spherulite in slate mush.



Fig. 19. x100

Synthetic colloform bands in slate mush.



Fig. 20. x100

Natural sulphide colloform textures deposited within a rock matrix.

Two types of precipitates were formed, one brassy yellow and the other chocolate brown, and although the writer considers that they were FeS_2 and FeS respectively, the investigation was primarily concerned with textures and positive identification of the minerals formed was not essential.

Diagenetic and Hydrothermal Pyrite Spherulites and the Formation of Black Shales. From the experiments made it is concluded that iron sulphides, formed by reducing bacteria under certain conditions of sedimentation will collect as spherulites. These conditions in which H_2S is liberated and in which carbonaceous matter forms in a partially colloidal deposit containing decaying organic matter, give rise to the typical black shale facies in which pyrite spherulites so often occur. Similar conditions may also prevail during the formation of coal, which also very commonly contains pyrite spherulites.

During ore formation replacement is effected in zones which have been subjected to severe leaching by solutions rich in halogens, alkalies, CO_2, H_2S etc. It requires no stretch of the imagination to visualize the softening of some rocks during this process and their alteration to the permeable state favourable to the formation of spherulites and colloform textures. The intricate distortion of slate often displayed on both microscopic and large scale suggests that such a softening has taken place.

The fact that the slates sometime turn black during the process of softening is partly due to the finely divided iron sulphide precipitated, (see page 66), but it may also be caused by the formation of carbon in a reducing environment. It is, in fact, suggested that black shales can arise by hydrothermal action, shearing or sedimentation under reducing conditions, and that all these types may occur in the pyritic ore fields where the sediments have a common geosynclinal-orogenic history.

Spot Formation in Adinoles. In addition to the pyrite spherulites formed hydrothermally in the wall-rock slates, spots of quartz and more rarely of carbonate, are also developed in the sediments. The quartz spots frequently contain leucoxene and needles of rutile and are identical with some of the spherulitic adinoles described by Agrell[19] (Fig.22). They are clearly produced in a manner comparable to the pyrite-spherulites just described.

The Mechanism of Spherulite and Spot Formation. Spherulites have been formed in the laboratory within ionic solutions [14,15] and gels[13,14] but it has been shown that whereas they are readily formed in gels, only a limited number of substances will crystallize in this way in ionic solutions, and then under specific conditions only. Thus Diesel[15] treated a solution of ferrous iron with a mixture of $CuCO_3$ and $MgCO_3$ and formed mixed carbonate spherulite precipitates, but only when the concentrations of Fe were greater than a



Fig. 21. x100

'Pressure shadows' alongside spherulite which consists of an aggregate of smaller spherulites.

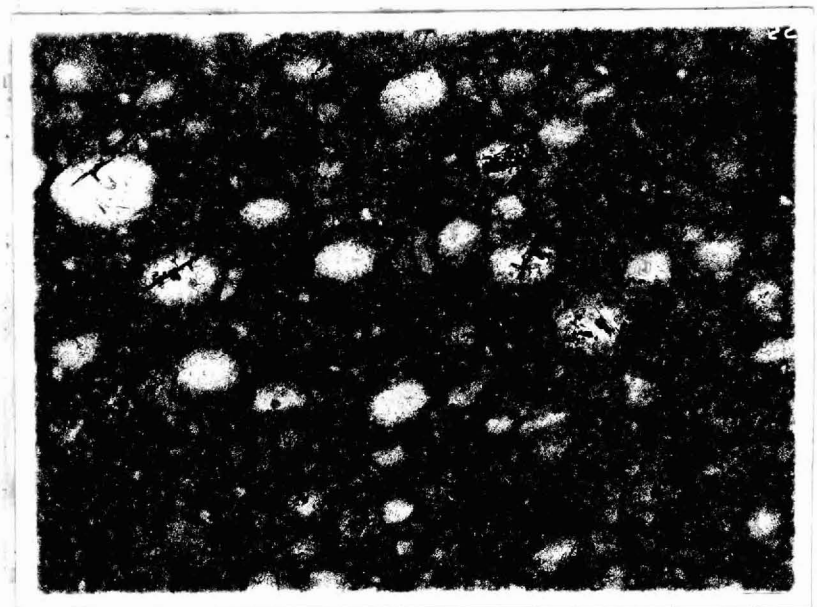


Fig. 22. x100

Spherulitic adinole with leucoxene in the quartz spots.

specified amount. Morse[14] considered that spherulitic precipitation was engendered by an absence of convection currents such as those encountered within gels. Lengyel[45] precipitated $NaHCO_3$, $CaCO_3$, $MgSO_4 4H_2O$, $Na_2S_2O_3 5H_2O$, $K_2Cr_2O_7$ and $Na_2Cr_2O_4$ as spherulitic groups of crystals at a temperature of 60° - 110°C. in solutions which were evaporated quickly. He found, however, that at lower temperatures, isolated crystals or regular groups appeared instead of spherulites, and that many strong electrolytes such as NH_4Cl, KCl, do not form spherulitic growths under any circumstances.

In considering some of the natural environments of spherulite formation, there is evidence that many of them are formed in porous media. Deans[46] has described spherulitic ironstones of west Yorkshire in which spherulites of siderite occur in fireclay, sandstones, mudstones, and chamosite ironstones. The spherulites show radial structures and contain inclusions of sediment, and in view of the association between spherulites and bands found in experiments, it is interesting to note that zonal structures are common in the fine sediments of these deposits. In addition to this example there are many other similar occurrences of spherulite growth taking place within porous media, instances being those within chalk, fullers earth, cement etc., whilst spherulites formed from solutions are also common.

Conditions favouring spherulitic growth from

solutions, may be summarized as follows:-

1. Precipitation or replacement within porous media, including gels. This is the most favourable environment for the growth of spherulitic forms.
2. Precipitation from solutions under specialized conditions such as very rapid deposition, absence of convection currents, or the presence of a colloidal phase.

In explaining these controls it is contended that during the migration of ions in solution towards a nucleus they will tend to grow in crystalline form providing they have freedom of movement over the growing crystal surface. If for some reason this movement is restricted, as for example by previous nucleation off the ions into less mobile colloidal particles, or by the enmeshing effect of a gel, then the ions are unable to take up their proper position in the growing crystal structure and remain at the point on the surface at which they arrive. Bradford[16] has shown that material suspended within a gel may be adsorbed to a nucleus at an equal rate in all directions, and the present writer concludes that it is this uniform influx of material coupled with a restriction of surface migration at the congested point of arrival which may cause spherulitic growth. This reasoning may be applied to porous sediments and the modification which arises if migration along the bedding or schistosity is easier than across it, probably provides an explanation of the fact that spherulites in slates are often

elongated in the direction of schistosity. (Fig.15).

Turning to the problem of spherulite formation in solutions, it is noted that this is facilitated by rapid evaporation, when it is conceivable that ions arrive at nuclei faster than they are able to arrange themselves into correct positions in crystalline structures, and consequently they form spherulites. However, it is more likely from our knowledge of the behaviour of supersaturated solutions, that in the first instance a colloidal solution will be formed by the rapid nucleation of the solution at innumerable points. The next step in the process is probably one of coacervation, that is the division of the newly formed sol into two liquids one rich in colloid and the other poor. The colloid-rich phase is commonly in the form of droplets[47] and in the case in question the rapidly changing environment will soon cause the flocculation of these coacervate droplets which, according to the theory already outlined, would give rise to spherulitic aggregates. The intermediate phases of nucleation at a large number of points, followed by coacervation, may well be involved in the formation of spherulites in gels, for although it has been suggested that the restrictive influence of gels may cause ions to aggregate directly as spherulites it is extremely probable that precipitation in gels first gives rise to colloidal dispersions which then aggregate in a manner resembling coacervation and possibly directly analogous to it. In the

writer's own experiments it was proved that colloidal particles aggregate to spherulites within porous media, and examination of black slates under very high magnification tends to corroborate this, for much of the sulphide appears to be present as little globules ranging in size right down to the limits of resolution of the microscope. Indeed it is likely that colloidal dispersion may account for much of the dark colour in some of these slates, for colloidal pyrite is black. It also seems likely that there may be several cycles of segregation, the minute globules visible in the black slates being the first result of cohesion of the colloidal particles, and the larger spherulites being an aggregate of these. In some cases even larger spherulites are found which have quite obviously resulted from the coalescence of smaller spherulites (Fig.21). Visible macroscopic evidence of this kind makes the sub-microscopic processes envisaged seem highly feasible.

Summing up the writer's views on the mechanism of spherulite formation, it is believed that they can be ascribed to the uniform migration of material to nuclei from all directions at such a rate or in such a form that the material cannot orient itself on arrival into crystalline structures. These conditions are likely to arise during the precipitation of matter within porous media or during the rapid evaporation of a solution, and in either case it is envisaged that an intervening colloidal phase will be formed

as part of the process. It is probably a fact that porous media facilitates the nucleation of ionic solutions at a large number of points, to form colloidal solutions, and this makes them particularly favourable for spherulite formation. The aggregation of the colloidal phase to spherulites is possibly analagous to the phenomena of coacervation and may take place in repeated cycles.

The conclusion that colloids play a major part in the formation of spherulites confirms and extends the findings of Bucher[48] who studied spherulitic formation in solutions.

The Growth of Euhedral and Anhedral Metacrysts. It has previously been deduced that spherulites form as the result of uniform migration of material to a nucleus from all directions in such a form or at such a rate that the material cannot orient itself into a crystalline structure. The converse of this rule can be applied to crystalline growth, and deposition from ionic solutions will be considered first. During slow precipitation from these solutions, nucleation will commence at a relatively few points and although it might be considered that a transitory colloidal phase must be formed, it will be exceedingly dispersed and hence will not tend to form coacervate droplets. The scattered nuclei, once formed, will continue to enlarge by ionic accretion following the normal course of crystalline growth. A similar mechanism is involved in the growth of

metacrysts in unleached massive rock, for a colloidal phase cannot be involved here owing to the inability of colloids to migrate in a system where the only available channelways are grain boundaries, crystal discontinuities, sub-capillary fissures, etc. Perfection of crystal growth will depend to some extent upon the rate of arrival of ions at a nucleus compared with the rate of their surface migration around that nucleus, so that slow crystalline growth will attain greater perfection than rapid growth, a deduction in accord with common experience. Uniformity of ionic accretion will also be a controlling factor and distortions of the crystal lattice will be liable to occur when portions of the growing surface are fed preferentially, as for example when there is a consistent direction of flow of the solution past the crystal, or when a fracture in the rock provides a rapid flow to one point on the surface only.

Where crystalline growth takes place from colloidal solutions the same fundamental principles already outlined can be applied. In free solution crystalline growth will be aided if precipitation is slow and the colloidal dispersion is practically stable. Thus in some cases if a crystal is suspended in a colloidal solution it will provide a seed upon which crystal growth will continue. Similarly crystal growth from colloids may take place within a porous rock providing precipitation is slow. Distorted forms may arise in the intermediate case between crystalline and spherulitic

growth, or when permeability within the rock is non-uniform and prevents the even influx of particles to nuclei. For reasons already given, a colloidal phase is likely to be involved during precipitation within a porous rock, even if the solution introduced into the rock was originally ionically dispersed.

Summing up, it is concluded that euhedral crystalline growth is favoured by slow precipitation and uniform permeability, whilst anhedral growth is symptomatic of more rapid precipitation and non-uniform permeability. Metacrysts can only be deposited in unleached massive rock by ionic solutions, but colloids can precipitate euhedral and anhedral metacrysts in addition to spherulites within porous rock.

"Pressure Shadow" Aureoles. Pyrite crystals in the slates and other wall rocks are occasionally surrounded by aureoles of quartz, chlorite or sericite, and this feature which is common to many pyrite mineralizations, has been the cause of speculation by numerous writers. The aureoles may envelope the crystals completely and show a fibrous growth orientated perpendicularly to the crystal faces, or they may grow preferentially in the direction of rock schistosity (Fig. 23). The latter type is common and has led to the belief that the growing crystals of pyrite force apart the schistosity of the host rock to form crevices in which the aureoles grow. These crevices have been considered as 'pressure shadows',

a term coined by Pabst[49] to describe the aureoles. Mugge[50], who was the first to examine them crystallographically, deduced that the degree of crystallographic orientation in the fibres depended upon the rate of opening of the alleged crevice. One of his conclusions was that if the rate of opening of the crevice was les than the minimum growth rate of the crystal grains, they all remained in contact with the opposite side and had an equal chance of growth no matter what their orientation. A fibrous aggregate would then result with fibres normal to the opposite side but with no particular crystallographic orientation. Pabst[49] put this argument to test and found that in fact the fibres were not crystallographically orientated. He concluded that if Mugges's deductions were true, pressure shadows must grown under the conditions of slow opening which have been cited. Pabst's findings have recently been confirmed by Fairbairn[51] who examined specimens from the Campbell Shear Zone, Con Mine, Yellowknife and found the pressure shadows showed no lattice orientation. He also found that pressure shadows can be used to obtain the sense of movement in a shear zone by taking orientated specimens and cutting sections parallel to the lineation and normal to the foliation, a fact which clearly demonstrates that in some cases at least their orientation is controlled by the stress applied to the host rock. Bain[52] has differentiated between two types of pressure shadows, one in which the aureole surrounds the pyrite on all sides

(called a 'rotational fringe'), and another in which the aureole is distributed symmetrically about a plane through the pyrite (called a 'compressional fringe'). The first type is presumed to signify the opening of the wall rock to mineralization in three space directions and is said to be associated with high grade gold ores, whilst the second type is indicative of straight compression and is found in low grade ores.

Turning to examples found in the writer's own area, these were first commented upon by Demay[53] but his theories on a magmatic stage origin were subsequently disproved by D. Williams[6] who, together with De Magnee[54], gives good illustrations of the pressure shadows. De Magnee affirms the views of Mugge, Pabst, and Bain by stating that the aureoles are caused by pressure or stretching phenomena accompanied by filling. The present writer, however, does not believe that this is the sole cause of their formation. Many cases are found where the fringe is of equal width all the way around the pyrite crystals and even if apparently showing some rotation, the aureole may be so wide as to render its origin by infilling impossible. The fringes must therefore sometimes originate partly at least by replacement, the pyrite faces forming nuclei from which growth proceeds. The fibrous growth is analogous to the formation of radiating structures in some spherulites and also to radiating structures in the synthetic colloform textures

described on page 60. These fibrous structures are by no means universal in spherulitic and colloform textures and the same observation applies to aureoles, so that their formation obviously takes place only under a limited range of conditions. It is further noted that Mugge's criterion of absence of lattice orientation, indicating fringes growing in slowly opening crevices, is based on the premise that if crystal growth from nuclei within the crevice is more rapid than the rate of opening, there is no preferential direction of growth stimulating orientation. Precisely the same argument applies to fringes formed by replacement, so that this criterion can only be used to rule out growth in comparatively rapidly opening crevices.

For reasons which have been given it is concluded that aureoles may develop by replacement, by the infilling of slowly opening crevices, or by a combination of the two processes. Their formation will be controlled by the existence of pressure gradients, and preferential replacement will therefore take place within pressure shadows. If distortion of the rock takes place at an intermediate stage of fringe formation, the direction of growth will change and so give rise to curved fringes which indicate the sense of shear in the rock. If no gradient exists across a crystal-host rock interface then aureoles will not grow, but if, for example, slight rotation initiates a growth by forming low pressure zones on the crystal faces, the fringe will continue

to grow wider by a 'seeding' effect. That this has taken place is abundantly clear from the extremely common occurrence of examples such as those shown in Fig. 24 .

It is not possible to be certain about the relationship in time between the pyrite crystals and their fringes. In some cases aureoles may grow as part of the same process which brings about the growth of the pyrite crystal, for the growth of that crystal implies a redistribution and transport of material. Fringes developing contemporaneously with metacryst formation would be analogous to fronts of alteration advancing from a centre. On the other hand the aureoles could be formed long after the crystal by the subsequent migration of material through the rock. Such a migration could be caused for example, by metamorphism or shearing leading to a redistribution of quartz and chlorite. The time problem is difficult to answer on geological evidence alone, but is seems likely that it could be investigated by laboratory experiments, perhaps on the lines of those made on spherulites as described on page 58 . Until a positive answer is forthcoming on this time relationship it is certainly unsafe to deduce alteration paragenesis from the evidence of aureoles.

WALL ROCK ALTERATION.

Alteration in the Slates. Alteration of the slates adjacent to the pyritic masses is not as extensive as in the igneous rocks, and away from the immediate environs of the ore



Fig.23. x30

'Pressure shadow' orientated in direction of schistosity.

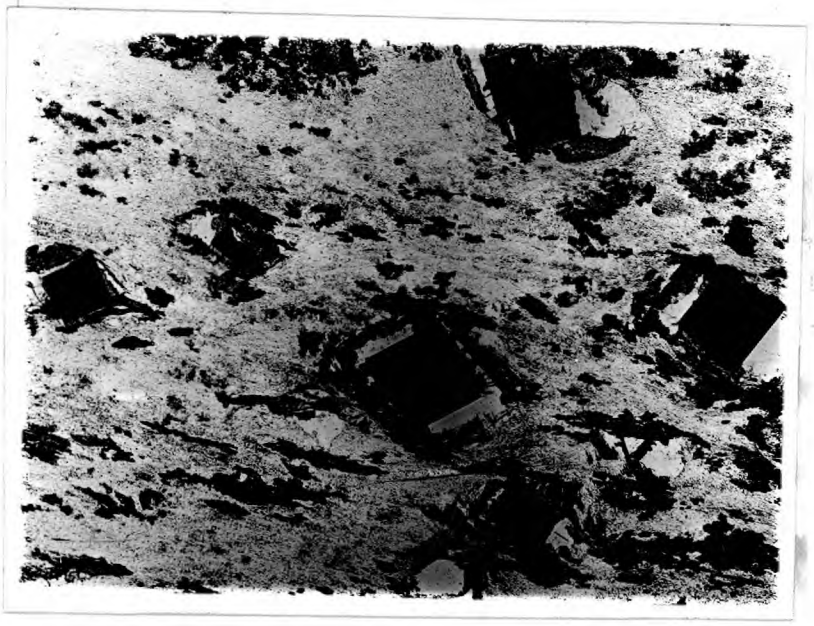


Fig.24.

Typical 'Pressure Shadows' surrounding pyrite cubes.

contact it is not easily recognisable to the unaided eye. Sericitization, which is the most widespread hydrothermal alteration in slate, may be intense close to the ore, and chloritization is also common. Pyritization is often accompanied by a darkening of the slates and this phenomenon has been discussed on page 66 . The development of adinole and spilosite rocks of the quartz spot type is a feature which may prove to be even more extensive than sericitization, but it is often quite invisible in the hand specimen. Kaolinization may be prominent in zones adjoining pyritic oxidation, and is caused by acid waters derived from oxidation.

Alteration in Porphyry. The principle modes of wall rock alteration in the porphyry are sericitization and chloritization. Although sericitization may be intense, its intensity by no means as widespread as that of chloritization. The chloritized porphyry appears in thin sections to consist of practically nothing but quartz and chlorite, the silica liberated during the chloritization of the felspars often forming secondary growths upon pre-existing quartz grains. Often much of the silica in the rocks has been redistributed during hydrothermal soaking and although the silica content may remain similar to that of fresh rock, only a few corroded primary quartz phenocrysts survive.

The titanium content of the porphyry is considerably lower than that of the diabase, and one of the

distinguishing features of the porphyry after intense chloritization is its low content of leucoxene compared with that in diabase. Another characteristic is the formation of the cerium and yttrium-bearing epidote, allanite. Rao[55] has shown that yttrium is nearly always present in the porphyries (about 50 p.p.m.) whilst it is absent from the diabase and sediment. Presumably it substitutes for Ca in the felspars, owing to its similarity in ionic radius, and is liberated on the breakdown of the felspars. Allanite occurs as minute crystals within the chlorite, giving pleochroic halos. Although present in small amounts it is well distributed so that it forms useful criterion for distinguishing heavily chloritized porphyry from other rocks.

Spherulitic and colloform growths of pyrite are rarely formed in the porphyries except near the ore contacts, where they may be well developed, especially in the sericitized rocks which have been sheared (Fig. 25). Some of the shapes assumed by quartz and chlorite in highly chloritized rocks are almost spherulitic in form and may indicate growth from highly saturated solutions, and possibly colloidal aggregation. Aureoles are common around pyrite crystals in porphyry, as described on page 69 .

Alteration in Diabase. The alteration pattern in the diabase is very much more difficult to delineate than that of the porphyries due to the difficulties of identifying some of the finely granular minerals which are formed. Intense

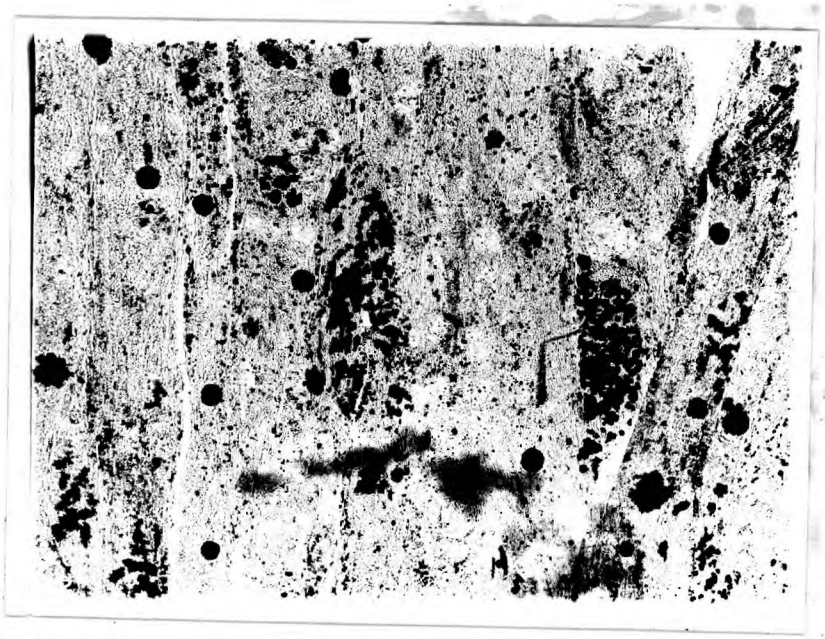


Fig. 25. x100

Spherulitic pyrite in schistose sericitized porphyry.

chloritization is a feature of some of the diabase and the high titanium content of the rock remains as a characteristic pattern of leucoxene. Very close to the ore there may be intense sericitization giving way outwards to a carbonate rich zone. It is this latter zone which raises some of the problems of mineralogy for both carbonate epidote and possibly jarosite as well can occur in extremely fine granular forms. All three minerals exhibit variation in relief, the carbonate being distinguished by its low relief in certain orientations relative to the plane of polarization, whilst the other two minerals retain their high relief in all positions. Epidote is very much more common in the basic rocks owing to their higher calcium content, and it occurs not only as a deuteric mineral but also as a wall rock alteration species. The original presence of calcium also presumably accounts for the much higher proportion of carbonate minerals liable to occur in the basic rocks.

Spherulites and colloform textures of pyrite are quite common in the diabase, although the sections require careful searching by top illumination to reveal them. In particular a spherulitic type rather similar to those formed of iron oxides in jasper (Fig. 1.) appears in the diabase and apparently not in the other rocks. The very fine outer ring of pyrite developed around a central pyrite spherulite suggests that when permeability conditions favourable to spherulite growth are developed, they are

sometimes slightly different from those developed in slate. Gels vary a great deal in their physical structure and this difference between the breakdown products of slate and diabase is not really surprising. It can be concluded from the textures observed that permeability may be developed easily in diabase and it might therefore be expected that diabase would be susceptible to replacement. In fact this is not so, for the rock readily breaks down in the ore channel to form an impermeable barrier of gouge-like material, undoubtedly containing much colloidal material, but in a flocculated form.

The Distribution of Wall Rock Alteration at Rio Tinto and San Domingos.

Rio Tinto. The north walls of both the San Dionisio and South Lodes are characterized by a narrow zone of sericitization often only a metre or so wide which separates the ore from an intensely chloritized zone which extends well beyond the limits of the underground workings. The sericite zone, which has developed in highly sheared rocks, has an unusual localization which is discussed on page 92 .

Hematization is sometimes observed along the ore contacts, and more rarely jasperization. The latter has been described in detail by D.Williams[18] who deduces that jasper formation generally preceded that of the pyritic orebody, although there may have been a certain amount of post-sulphide jasperization. His conclusion that jasperization

has a close genetic relationship with pyrite mineralization is in close agreement with that of Reber[33] who studied the much more extensively developed jaspers at the United Verde Mine. Williams believes also that at least part of the silicification which produced the silica rocks of Salomon may be connected with mineralization.

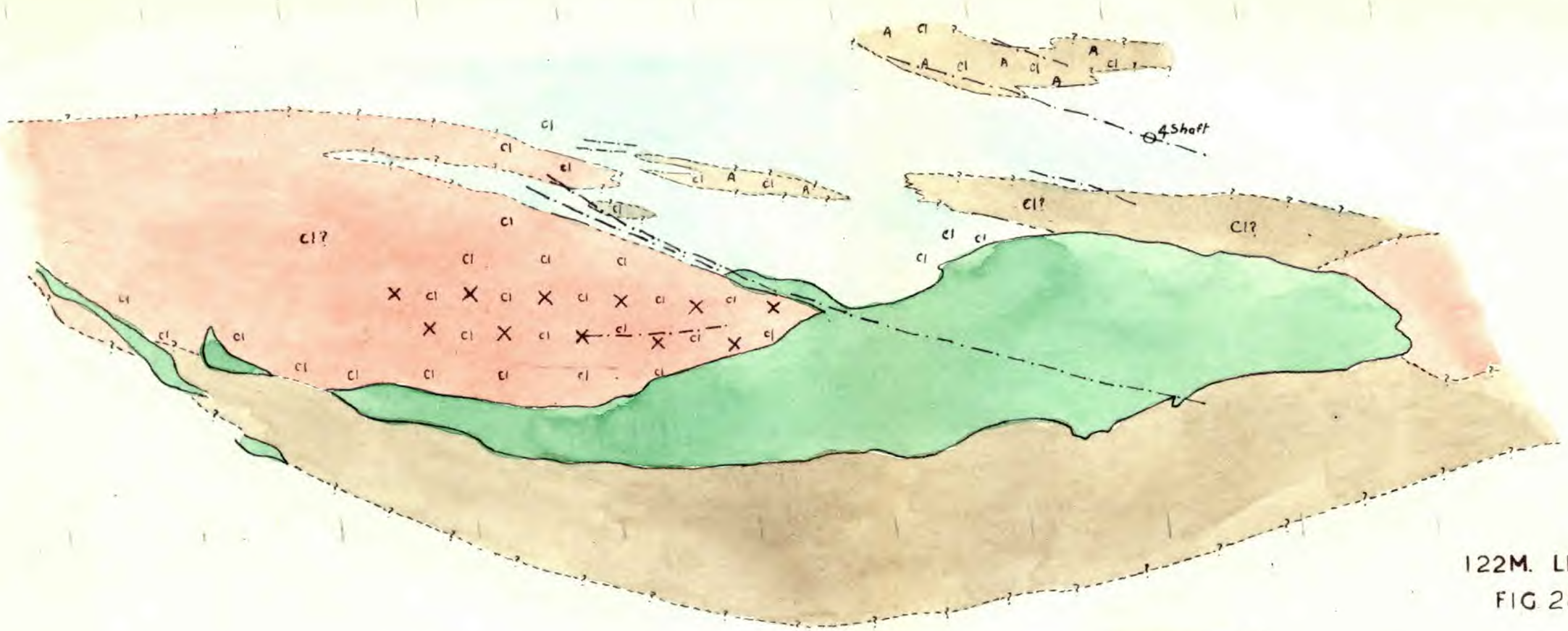
Alteration in the cupriferous stockworks is almost entirely chloritization, except in their extreme fringe areas where sericitization sometimes occurs. It was originally hoped that alteration might be of some value as a mineralogical guide in the search for cupriferous stockworks, and to investigate this possibility a large number of sections were cut from samples taken at points throughout the stockworks. Although the results of this study provide basic data on the alteration associated with mineralogical channels, they also show that wall rock alteration, as determined under the microscope, is not likely to be of assistance in predicting stockwork trends.

San Domingos. The wall rock alteration pattern and the somewhat intricate lithology of the north wall has been worked out by a number of undergraduate students from the Royal School of Mines working under the direction of Dr. J.S.Webb. Simplified reductions of two of the maps prepared by one of these students, N.R.Rhoden, are given in Fig. 26 &27.Since a detailed study of the distribution of wall rock alteration at San Domingos has not been within the

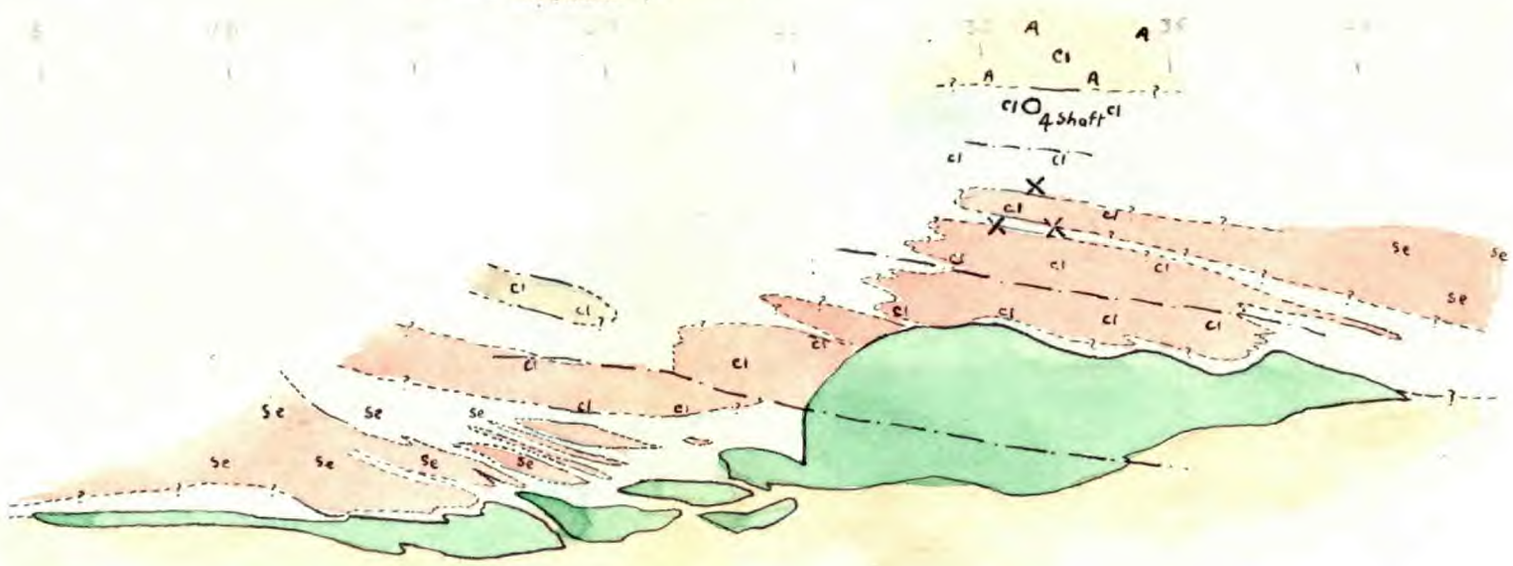
present writer's province of research, it does not call for a lengthy description here.

Study of Fig.26&27 shows that whereas chloritization occurs throughout the north wall on the 122 metre level, it is confined to the central portion of the north wall on the 300 metre level whilst sericitization appears at each end of the orebody. This trend is continued down to the 360 metre level where sericitization spreads across the whole of the north wall and chloritization is localized in the basic dykes of the wall. Thus the overall picture of alteration in the north wall is one of chloritization in the upper levels giving way to sericitization in depth, first at the extremes of the orebody and later in the centre as well. Information concerning the south wall is much more scanty owing to the complete absence of underground workings. The limited information based on borehole evidence shows that an innermost zone of chloritization , which is often absent, gives way laterally to a 'sericite' zone and then to an epidote carbonate zone, beyond which the rocks are similar to the normal deuteric-altered diabase of the district. The innermost zones of alteration on the north and south walls sometimes carry gypsum, particularly in the sericitized zones. It is interesting to note that barite occurs in analogous positions at Rio Tinto. These sulphates were formed during a late stage in mineralization and it may be significant that the barium contents noted by Rao for

S. DOMINGOS.



122M. LEVEL
FIG 26



270 M. LEVEL
FIG. 27

Slate

Porphyry

Diabase

Pyritic Ore

Chloritization

Sericitization

Stockwork

SCALE 1:2000

unaltered San Domingos porphyry vary between 70 and 400 p.p.m. whilst a sample of normal Smelter Ridge porphyry from Rio Tinto contained 1000 p.p.m. of barium. Hematization is occasionally developed on and near to the ore contacts, particularly those of the south wall, and more rarely nodules of jasper are found. These nodules, like those of Rio Tinto, usually carry crystals of pyrite.

The Genesis of Wall Rock Alteration.

In considering the problems of wall rock alteration at Rio Tinto and San Domingos, two principle queries arise. The first concerns the nature of the controls of sericitization as distinct from chloritization, and the second refers to the composition of the hydrothermal solutions which have affected the alteration. Answers to these queries could provide valuable clues in searching for the entrance channels of mineralization besides throwing additional light on ore genesis.

Sericitization and the Alteration of Felspars. The most up-to-date studies of the alteration of felspars have been made by Gruner[56] and O'Neill[57]. Gruner investigated alteration of felspars in HCl solutions whilst varying the concentration of K and Al, and found that kaolinite forms only below 350° ± 10° C., whilst muscovite forms above this temperature to as high as 525°C. Pyrophyllite may form over the whole range from 300° to 525°C. K felspars are stable at 400°C. and probably also Na felspars providing

the concentrations of the corresponding alkalies are high. O'Neill extended Gruner's work and investigated alteration in K_2S solutions and in basic, neutral and acid solutions of NaCl and KCl at 250°C to 400°C. He found that in the presence of excess K ions potash and soda felspars alter to kaliophylite in solutions more basic than about 0.10 M K_2S and 0.08N KOH. In less basic solutions and in solutions as acidic as 0.001 N, potash felspar alters to soda felspar in the presence of an excess of Na ions, the reaction being reversed in the presence of excess K ions. For a short range of concentrations more acidic than 0.001 N, soda felspar is stable for the time of the experiments, but in 0.020 N HCl soda felspar alters to pyrophyllite. In the presence of excess K ions soda felspar alters to muscovite in solutions as basic as 0.010 N.

Some of the conclusions that can be drawn from Gruner's and O'Neill's work are that sodic solutions above 350°C in the environment of wall rock alteration (i.e.,with alumina presumed to be available) will alter albite to pyrophyllite if they are neutral or acidic, but will not alter albite if they are more than weakly basic. Potassic solutions will alter albite to muscovite or pyrophyllite if they are weakly alkaline to acidic, but will form kaliophyllite in strongly alkaline solutions. The term 'sericitization' is generally taken to mean the formation of small flakes of muscovite, although some authorities consider that it includes hydromuscovite as well. It is

virtually impossible, however, to distinguish between pyrophyllite, muscovite, and talc in thin section and moreover X-ray pictures of pyrophyllite are very similar to those of muscovite, especially if it has any $Al_2(OH)_3$ mixed with it. According to Gruner it was this difficulty that caused Norton[60] to make errors in his identifications when studying hydrothermal alteration. To make matters worse the thermal analysis characteristics of muscovite, pyrophyllite and talc are distinctly similar. It is apparent, therefore, that their separate identification is indeed a difficult proposition. In view of this, and the fact that Gruner's and O'Neill's results show that muscovite and pyrophyllite are almost certain to be commonly formed together, it is suggested that the term 'sericitization' be used to cover muscovite-pyrophyllite alteration, and if chlorite is being formed contemporaneously in the presence of Mg, then talc might be included as well. It may be significant that in one of the few published papers containing comprehensive X-ray and analytical data on naturally occurring hydrothermal sericite (Sales and Meyer [61]), the recorded alkali content of the sericite is well below the theoretical amount, and one wonders whether this might not be due to the 'sericite' being in fact an intimate mixture of muscovite and pyrophyllite.

These observations have been made to show that there is little point in differentiating muscovite from pyrophyllite when attempting to apply the results of Gruner

and O'Neill, unless there is evidence to show that one of the two minerals is not present in the sericite zone. According to the proposed new terminology, one can say that 'sericite' zones are formed in weakly basic to acid solutions containing alkalis.

Turning next to the problem of whether the hydrothermal solutions which effect sericitization have an excess of sodium or potassium ions it can be shown that knowledge of the fields of formation of the micas is insufficient to give a direct answer. Gruner's and O'Neill's work was carried out with either Na or K solutions and only two experiments were made with mixed solutions. In these two cases O'Neill made the experiments without the presence of free alumina and the albite used did not break down, a result which could easily have been predicted from the trends of Gruner's work. It is known that albite will break down to muscovite in acid solutions containing excess K and it will break down to pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) in acid solutions containing excess Na. Both products have the appearance of sericite and it would be extremely interesting to know what effect the Na:K ratio in hydrothermal solutions has on the Na:K ratio in the 'sericite' product. There are reasons for believing that 'sericite' zones which show the addition of K could have been formed by solutions containing more Na than K, since K enters the mica lattice very much more readily than Na. Two facts substantiate this deduction, namely:

(1) Paragonite was not formed in any of Gruner's and O'Neill's experiments and there is only one doubtful record of it having been formed artificially[62]. The synthesis which, by analogy with the formation of muscovite, would be expected to yield paragonite, always yields pyrophyllite.

(2) Potash clays are formed in sodic environments and they include potash-bearing hydro-muscovite.

It is suggested that once albite becomes unstable during hydrothermal alteration Na will migrate in the solutions because there is no breakdown mineral which will fix Na. Some K however will be fixed in muscovite. The direct proof of this is in experiment and fortunately Dr.G.Van Praagh, who has carried out autoclave work on quartz, has taken an interest in the problem. Experiments on albite, aimed at extending Gruner's and O'Neill's work, have commenced and initial results are encouraging.

Assuming that the hypothesis on the migration of Na and fixation of K is correct certain predictions can be made. It is well known that modern juvenile waters nearly always contain Na and K, with Na in considerable excess over K [63]. During the passage of these heated waters through igneous rocks, the first effect to be expected would be one of albitization of the plagioclase felspar, as shown by the work of Eskala[40], Gruner and O'Neill. The Na content of the rock may increase slightly and the K content will remain constant since K will be retained in orthoclase.

In the sodic environment the orthoclase will break down next but most of the K will be fixed in muscovite which will be stable in the new conditions. With the continued passage of solutions and consequent rise in temperature the albite will break down, mostly to pyrophyllite but partly to muscovite, and it is maintained that it is the transference to this stage which is most commonly observed in hydrothermal vein wall rocks. The breakdown of albite causes a considerable drop in Na, for, as has been explained, there is no alteration mineral to fix the Na, but K will remain constant or increase slightly because muscovite is stable (Gruner) and albite will yield a small amount of additional muscovite depending upon the Na:K ratio of the solutions.

The behaviour of the alkalis predicted above is precisely in accordance with the chemical analyses of wall rock alteration made at Butte[61], where K remains more or less constant or increases very slightly as the ore is approached. It is interesting to note that at Butte K remains practically constant as the 'sericite' zone is traversed, illustrating the danger of attempting to evaluate the distribution of K on mineralogical grounds.

So far we have considered weakly basic to acid solutions, but if the original emanations are rich in CO_2 and carbonates, muscovite will no longer be stable and pyrophyllite will be formed. The rising solutions will therefore leach the alkalis proportionally near their sources, and will not go through the cycle described until

they have partially neutralized themselves by wall rock attack. When this carbonate wall rock attack takes place it will inevitably increase the proportions of K to Na in the solutions as can be deduced from our knowledge of the average composition of rocks. The potassium picked up at deep levels will be deposited at higher levels by the processes which have been outlined, and it is fairly reasonable to assume that the greater the leaching of K in depth the greater will be the substitution of Na by K higher up.

Again these predictions are fully supported by the best field evidence available on the behaviour of rising solutions, namely the investigations by means of boreholes in Yellowstone Park reported by Fenner[64]. He says (on p. 300)

".....we perceive that the potassium that is so important in substitution processes in the felspars is not derived (except perhaps in small degree) from the igneous body but from carbonate attack upon the felspars of roof rock at a lower level than the borehole attained. In short, the potassium is picked up at lower levels by one process and deposited at higher levels by another. The surprising thing (not dependent upon theory or inference) is that in the upper levels substitution of potassium for sodium goes on until the waters are so depleted of potassium and enriched in sodium that the ratio of the two becomes

1:34. This, however, is established with almost as much certainty as if the experiments were performed in the laboratory."

In considering the effects of carbonate attack we have predicted what the process is likely to be where solutions are streaming up channelways. Horizontal migration in walls will be much slower and chemical gradients steeper. The total release of alkalis on the inner walls will give rise locally to solutions containing possibly as much as a 50:50 ratio of K to Na, or even more K in a potassic rock. Any such solution migrating into the walls will give rise to a K rich 'sericite' zone with a high muscovite to pyrophyllite ratio. Naturally this migration will be two-way and may be of the type suggested by Gruner where SiO_2 moves out and K moves in along with Al_2O_3, perhaps as $KAlO_2$. This type of alteration might be expected in association with some replacement deposits, for the rocky constituents formerly occupying the site of the ore have presumably migrated in solution during their replacement. In such a case, however, the formation of a true K rich zone (not just a 'sericite' zone) will depend upon how much of the replaced material went straight up the ore channel without advancing into the wall as a 'front'.

Much of the argument put forward from time to time in support of the hypothesis of the major role of K solutions as ore transporting media and agents of wall rock alteration, is based upon the existence of 'sericite' zones. The

principle obstacle to this theory has always been the fact that sericitic alteration is extremely common and natural emanations of potassic solutions, as seen on the surface today, are quite rare.

Fixation of Calcium. Under certain conditions calcium is fixed or even increased slightly during wall rock alteration. This is possibly because, according to Eskala[40], at temperatures above approximately 360°C oligoclase is the stable plagioclase felspar instead of albite. In determinations made on the products of a bomb experiment carried out by Van Praagh, in which an approximately neutral solution containing KCl and $NaHCO_3$ was used, the writer found that part of the product of alteration from albite ($Ab_{90}An_{10}$) was oligoclase ($Ab_{75}An_{25}$), the secondary material being in well crystallized form and notably different from the original crushed material. This experiment was carried out at 450°C and confirms the findings of Eskala. It is inferred that solutions above 360°C carrying calcium are liable to substitute some calcium for sodium in albitic rocks. This change will proceed as long as the plagioclase felspar remains stable, and when it ultimately breaks down the calcium may then be fixed as calcite if free CO_2 is present.

Chloritization. It is unfortunate and surprising that no attempt has ever been made to make a systematic study of the fields of formation of the chlorites, and consequently we

must rely on a few disconnected experiments for data. All these experiments (except the unrecorded ones of Gruner) have been summarized by Moring and Ingerson[65] and it appears that chlorites have only been synthesized in neutral or alkaline solutions. The lowest temperature at which they have been synthesized is 400°C and the highest 600°C, but the association of chlorites with epithermal deposits indicates that they can be formed hydrothermally at low temperatures. Gruner mentions in his paper on felspars that Mg ions are evidently not capable of combining with SiO_4 groups to form new Mg silicates in acid solutions, but gives no data concerning his experiments other than that they were made on talc with 0.175 N or stronger HCl.

Combining the results of all the existing work one can make the tentative conclusion that chlorite can be formed in a range extending at least between epithermal temperatures and 600°C in basic, neutral and possibly weakly acid solutions.

Controls of Chloritization versus 'Sericitization'. If the assumption is made that Fe and Mg ions do not greatly affect the pH or temperature range of formation of sericite, then it might be concluded that contemporaneous 'sericitization and chloritization can take place at all hydrothermal temperatures providing the solutions are weakly alkaline, neutral or weakly acidic. Unfortunately no experimental work has been carried out to verify this assumption, but

it seems likely to be true from considerations on the nature of the ore forming fluid (see Chap.7). It is at least fairly safe to assume from the existing experimental work that decidedly acid conditions will not give rise to chlorite, a conclusion of particular importance to the present study since a late acid phase undoubtedly existed during the pyritic mineralizations. The presence of gypsum, barite and alunite in unmistakably late stage relationships, shows that acid solutions were active and it is likely that some sericitization was effected by these solutions. The fact that the sulphate veins generally occur in heavily sericitized ground adds weight to this argument.

Although late stage reactions could account for some 'sericitization', much of it is difficult to explain in this way. It is a notable feature at San Domingos that 'sericitization' occurs on the upper levels as an outer zone, separated from the ore by a belt of chloritization. This outer zone is not usually heavily sericitized whilst the chlorite zone may consist almost entirely of a chlorite-quartz aggregate. It is suggested that in pH, conditions that are suitable for the formation of either chlorite or 'sericite', the latter is the lower energy form in quartz porphyry because limited amounts of muscovite and pyrophyllite can be formed in such a rock with very little chemical change beyond a slight leaching of Na. Intense chloritization of quartz porphyry on the other hand necessitates the

introduction of a considerable amount of Mg and possibly some Fe, in addition to strong leaching of alkalis, and is clearly a change requiring high energy.

In diabase the conditions are different since chloritization can take place with practically no interchange of material. Providing chlorite is stable not a great deal of 'sericite' is likely to be formed; intense 'sericitization' will only take place if conditions become acid and chlorite is unstable.

In testing these conclusions by applying them to the observed field relationships it is found they explain many features. The normal alteration pattern in quartz porphyry of an inner intensely chloritized zone and an outer more weakly sericitized zone, is accomplished, according to the theories outlined, by the circulation of solutions of such a pH and composition that either chlorite or sericite can be formed, the two alteration zones presumably moving forward as 'fronts' in the manner described by Sales and Meyer[61]. According to these theories alteration of basic rocks will be mostly chloritization, which may account for the fact that basic dykes on the north wall of San Domingos are chloritized in regions where porphyry has been sericitized. The picture in the south wall diabase, however, is very different for in contrast there is an inner zone of intense sericitization, which contains appreciable amounts of sulphate and iron oxides and is

presumed to have been formed in the late acid hydrothermal stage. A similar narrow zone of sericitization and sulphates occurs in porphyry along most of the north walls of the San Dionisio and South Lodes at Rio Tinto, and is sometimes only a metre or so wide. This extreme localization may be controlled by shearing along the contact which is believed to be associated with movements after the emplacement of the ore. It is perhaps significant that some of the gypsum and barite veins occur in an unfractured state in fissures cutting the ore, and it is possible that the late stage acidic solutions circulated during a regional pressure relied shortly after the main phase of mineralization. During this period the acid hydrothermal solutions must have passed through the shear zones formed on contacts and elsewhere, causing characteristically intense but localized sericitization and the deposition of sulphates, minor sulphides and oxides. This localization is sometimes even more noticeable in the stockworks, where sulphate veins cutting through heavily chloritized ground are bordered by an extremely narrow sericitized zone. The fact that these sulphate veins are rare in the stockworks suggests that the late acid stage was probably of minor extent, and its effect in 'tight' ground such as that of the stockworks was very limited.

Distribution of Trace Elements in the Altered Wall Rocks.

This problem was investigated by Rao[55] who found certain

characteristic trends during wall rock alteration. In sericitized rocks Rb and Ba are considerably enriched regardless of the original nature of the rock. Mn, La, Ni, Li and Sn show occasional enrichment but do not suffer leaching. Cr at times exhibits a tendency to be leached, but no significant changes were observed with regard to other elements. During chloritization, Rb, Ba, Sr, and frequently La, are strongly leached, Co and frequently Mn show considerable enrichment, especially in acid rocks. When chloritization is intense V and Cr are partly leached and all the other trace elements are also removed in varying degrees.

In addition to the above mentioned trends it was found that at San Domingos the Mn-content of the altered rocks vary systematically with depth, being high (in all rock types) on the 240-270 m. levels of the mine and progressively lower both above and below this horizon.

It is clear from Rao's work that the trace element changes are in accord with what has been said about the relative magnitude of chemical changes taking place during sericitization and chloritization. The only trace element changes accompanying sericitization are the introduction of Rb and Ba. As has already been pointed out sericitization does not necessarily imply the addition of K to a rock, and the introduction of Ba or Rb by no means proves that K has also been introduced. The breakdown of the existing K felspar by hydrothermal solutions will form

muscovite and pyrophyllite and Ba and Rb can enter into the lattice of the muscovite. Providing Ba and Rb are present in the hydrothermal solutions they are almost certain to be introduced into a rock when sericite is formed regardless of whether or not K is increased. Similar substitutions of elements already present can take place by the other trace elements listed by Rao, and there is nothing in his results which proves that there has been a wholesale migration and interchange of material in the sericitized rocks, even though in some cases there might have been.

By contrast, trace element behaviour in the chloritized rocks proves that a considerable interchange has taken place. The strong leaching of Rb and Ba for example shows that K-bearing minerals must have been removed, and since Na as a rule migrates before K, the trace element data support the deductions already made of strong base leaching.

Summarized Conclusions on Wall Rock Alteration.

(1) In the absence of detailed X-ray and analytical data the 'sericitized' zones can only be regarded as liable to contain one or more of the minerals muscovite pyrophyllite, talc and hydromuscovite.

(2) Direct determination of K is the only satisfactory way of studying the distribution of K in wall rocks. Computations from mineralogical analyses of 'sericite' are very likely to give erroneously high values of K.

(3) The presence of 'sericitized' zones does not imply that the hydrothermal solutions were dominantly potassic. 'Sericitization' could be carried out by solutions containing excess of Na over K, probably even if K is actually increased in the 'sericite' zone. The reason for this is that when muscovite and pyrophyllite are the stable species replacing felspars, they fix the K already present and perhaps withdraw some extra from the solutions, whilst Na will migrate since no mineral left will be capable of accepting Na into its lattice.

(4) A small or moderate amount of 'sericitization' in quartz porphyries scarcely alters the bulk composition of the rock. It is a lower intensity alteration than chloritization, providing it has formed at a pH conducive to chlorite formation.

(5) Chloritization of the intensity normally found in quartz porphyry wall rocks implies considerable change in bulk composition. It is a higher energy form of alteration than sericitization when caused by solutions capable of yielding sericite.

(6) Intense sericitization may be the result of a 'front' mechanism, the K being displaced by the encroaching chlorite zone, which itself advances in front of ore mineralization.

(7) The principle phase of wall alteration was probably effected in conditions between weakly alkaline and weakly acidic, preferably the former.

(8) Late stage sericitization is associated with late stage acidic hydrothermal activity. It is accompanied by the deposition of sulphates and is particularly localized along shear zones on ore contacts etc.

(9) Chloritization in the basic rocks may be of lower grade than that of the quartz porphyry since it does not imply the same change in bulk composition.

(10) The idealized picture of wall rock alteration is of advancing fronts of sericitization followed successively by chloritization and sulphide mineralization. Localized sericitization on the ore contacts follows as a separate phase after the principle mineralization, and may be separated from the earlier alterations by an appreciable time gap.

CHAPTER 5.

THE PYRITIC ORES, THEIR MINERALOGY, TEXTURES, DISTRIBUTION OF VALUES, VARIATIONS IN THERMO-ELECTRIC POTENTIAL AND TEMPERATURES OF FORMATION.

Mineralogy and Textures.

Mineralogy. The massive ores of the province can be classified under a number of headings as follows.

1. Crude pyrites ore having a specific gravity of 4.5 to 4.8, carrying from 47 to 50% of sulphur, up to 1.5% approximately of copper, up to 4% zinc, 1% Pb and 1% As, with seldom more than 3% or 4% of combined silica and alumina. In addition small amounts of various other elements may be present. This type represents the bulk of the ore of the province and is a hard, grey, fine-grained rock.

2. Dull grey pyrite, softer than the above, heavily fractured and subject to fairly rapid oxidation on exposure to air.

3. Banded pyritic ore consisting of fine-grained pyrites with parallel bands of gangue material.

4. Coarsely crystalline ore, generally with a fairly high percentage of gangue.

5. Fine-grained cupriferous pyrite, a yellowish hard and compact variety breaking with a conchoidal fracture.

6. Veined cupriferous pyrite; one of the above types

cut by ramifying veinlets of chalcopyrite.

7. Complex ore, a bluish grey variety carrying comparatively high values of zinc and lead and sometimes showing banded structures. The banding is complex and consists of alternate bands of varying richness in chalcopyrite, pyrite and sphalerite, together with galena. This type of ore may contain barytes gangue.

8. Magnetic pyrites -- an unusual intensely ferromagnetic variety yielding an X-ray picture characteristic of pyrite.

All of these ore types are present to a greater or lesser extent in both the San Domingos and Rio Tinto deposits, but the La Zarza mass does not possess any richly cupriferous varieties, most of its ore assaying less than 1% copper. In addition to making a detailed study of the ores from the mines mentioned above a small number of specimens from the Tharsis, Concepcion, Poderosa, and La Pena masses have been examined. None of the sections studied has shown hitherto unrecorded minerals, and the writer has little to add to the mineralogical (as opposed to textural) descriptions already published. The following minerals have been observed:-

Principal Primary Minerals in Order of Their Paragenetic Sequence. Arsenopyrite, pyrite, chalcopyrite, sphalerite, galena, hematite, goethite. Hematite and goethite occur principally in contact ores and are sometimes formed during the initial phases of mineralization.

Primary Minerals Occurring in Very Minor Quantities. Tetrahedrite, enargite, famatinite, chalcostibite, bornite, bournonite, jarosite (?)

Secondary Sulphide Enrichment Minerals. Chalcocite, covellite.

Goasan Minerals. (Reported by Williams[18] but not studied by the present writer). Goethite, turgite, hematite, jarosite family, anglesite, cerussite, barite, scorodite, clinoclasite and cerargyrite.

In addition to the above minerals whitneyite, umangite, hauchecornite, ullmanite and perhaps berthierite have been reported by Bateman[4], but despite careful search the present writer has been unable to confirm their presence. Since Bateman has also given a full description of the mineralogy of the ores no further reference to it is now necessary.

Electrolytic Etching. Test were made with this form of etching to determine whether it could yield more information concerning the structure and texture of the sulphides than provided by ordinary etching. A considerable number of experiments were made using some of the electrolytes employed successfully in metallography and also with dilute normal etch reagents. Etchants tested at various dilutions were HCl, HNO_3, H_2SO_4, chromic acid + H_2SO_4, chromic acid + HCl, chromic acid, potassium permanganate, picric acid, oxalic acid, phosphoric acid and ammonium hydroxide. By far

the most successful results were obtained with 5% chromic acid, a 50% dilution of concentrated ammonium hydroxide providing a poor second best. Phosphoric acid appeared to have possibilities as an etchant for chalcopyrite but the application was not thoroughly investigated.

The apparatus used for electrolytic etching is illustrated in Fig.28 . Specimens must be either unmounted or mounted in a conducting bakelite, preferably with the face of the mounting briquette made of non-conducting bakelite[66,67]. A sufficient voltage is applied to pass about 50-60 milliamps, this voltage usually lying between 3 and 15 volts, and etching is continued for between 3 and 10 minutes depending upon the specimen. Massive fine-grained pyrite generally requires a short period only, whilst disseminated pyrite requires a long time. It is usual to protect one half of the polished face from etching by means of a film of rubber solution, or better still, a piece of waterproof adhesive tape. By means of this expedient an unetched surface is preserved for normal determinative work and studies of paragenesis. Etching takes place by a combination of anodic dissolution and the oxidizing attack of the electrolyte, and is particularly selective because pyrite displays a large variation in conductivity associated with a slight change of composition.

Textures revealed by electrolytic etching and their interpretation. The results achieved by the electrolytic

etching of pyrite are very much superior to those obtained by ordinary etching, and in consequence hitherto unsuspected detail in the sulphide has been revealed. Part etching has therefore been applied as a routine to all polished sections of pyritic ores. Figs. 29 and 30 demonstrate the effect of this etching. After etching a specimen, a suitable area was photographed (Fig. 29) and a circle deeply engraved around the area. The specimen was then repolished and the encircled area rephotographed (Fig. 30). The etched textures disappeared during repolishing, but in order to confirm that they were still present in latent form and had not been entirely removed the specimen was re-etched. It was then found that the same type of structures reappeared although altered slightly in their configuration. In this example the etching reveals pyrite pseudomorphs after early-formed arsenopyrite faces, whilst the black material on their etched surface is finely divided pyrite probably of similar origin to the colloform pyrite. It is clear in this case that very much more information can be obtained from etched surfaces than from plain polished surfaces.

Perhaps the most significant textures revealed by electrolytic etching are the spherulites. These occur in patches and streaks, in specimens collected from all parts of the pyritic masses. Fig. 31 shows a cluster of these spherulites under the 8 mm. objective, whilst fig. 32 shows an individual spherulite highly magnified under a 2 mm. oil

immersion objective. Their resemblance to spherulites developed metasomatically in country rock (pages 56 - 67) is unmistakable, especially when allowance is made for the fact that these photographs are of polished sections whilst the surfaces of the spherulites seen in thin sections are unpolished. Their occurrence in streaks, shown in fig. 33 , is strongly reminiscent of the formation of spherulites in bands within slate. Fig. 34 and fig. 35 demonstrate their occurrence in globular patches in close association with colloform type textures. Fig. 36 shows their elongated growth which is a common feature, and the development of a later generation of crystalline pyrite on top of the spherulites.

Although the spherulites are not very prolific in any given section they are widely distributed and have been found in samples taken from all parts of the San Dionisio (Rio Tinto) and San Domingos orebodies, whilst numerous random samples from the South Lode, La Zarza orebody and other masses also show them. They are considered to be similar to the spherulites which have been described as developing progressively during the metasomatism of slate and other rocks, and which have been synthesized in the laboratory. They are believed to be excellent criteria of replacement origin.

The textures which are most prolific in massive pyritic ores are the colloform types. Figs. 37, 38 and 39

are photomicrographs taken at progressively increasing magnifications showing a typical colloform texture in which the colloform and spherulitic textures have a common ancestry. The colloform structures assume a variety of habits, including granular aggregates (fig. 40), bands (fig.38), and radiating fibrous aggregates (fig.41). Some of these textures exhibit the criteria claimed by Edwards[68] as diagnostic of gel deposition, and yet examples such as Fig.42 show that radiating and banded colloform textures can form within rock without the presence of what are normally conceived as 'open spaces'. The close association of many of the colloform textures with spherulites suggests that a high percentage, if not all, of them were formed in other than 'open spaces'. This is in contradiction to the opinion of Edwards who states, "The apparent restriction of sulphide gels to ores deposited in limestones, or else to epithermal deposits, suggests that they develop only where open spaces permit a process of rapid chemical precipitation of sulphides ....." Undoubtedly colloform textures can form from gels in 'open space', and the present writer found that when colloidal pyrite was left standing in a beaker it tended to precipitate in the course of a day or more as a nodular gel. At present, however, there is no criterion for differentiating between colloform textures formed in open spaces and those formed by replacement, and in fact the two may be very closely related. The best

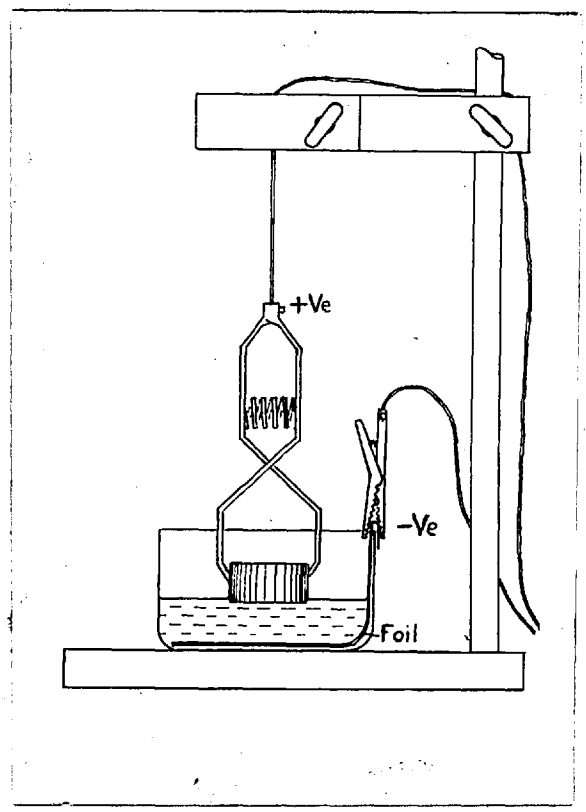


Fig. 28. Apparatus for electrolytic etching.



Fig. 29. x150

Electrolytically etched massive pyrite showing palimpoest cruciform twins (probably after arsenopyrite), and colloform growth on the crystal surfaces.



Fig. 30. x150

Same area as Fig.29. unetched.

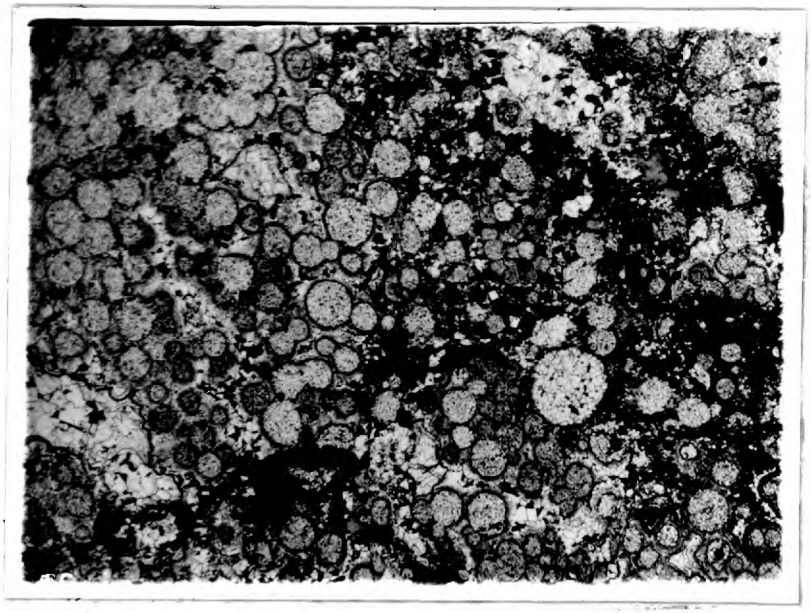


Fig. 31. x1000

Spherulitic textures in massive pyrite. Electrolytically etched.

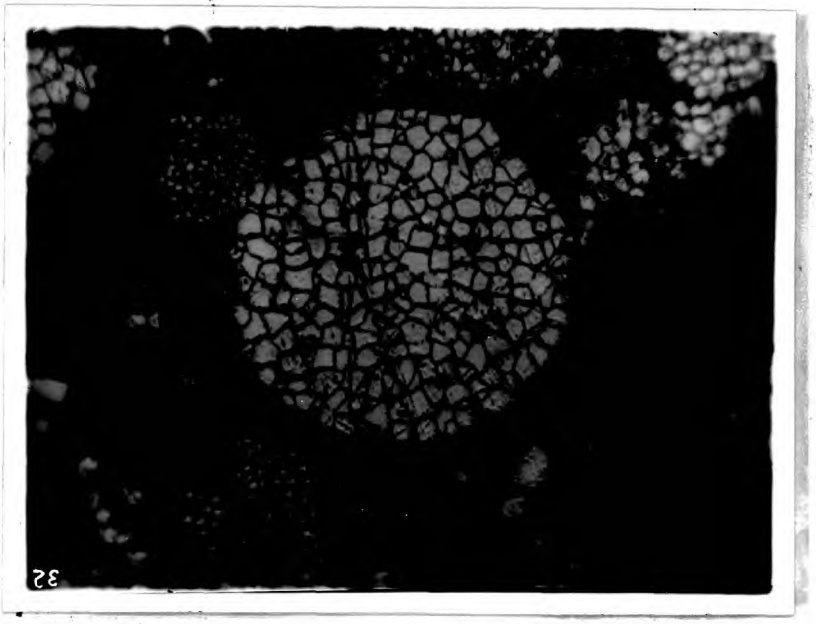


Fig. 32. x2000

Spherulite in massive pyrite. Electrolytically etched.



Fig. 33. x200

Spherulites formed in streaks within massive pyrite. Electrolytically etched.

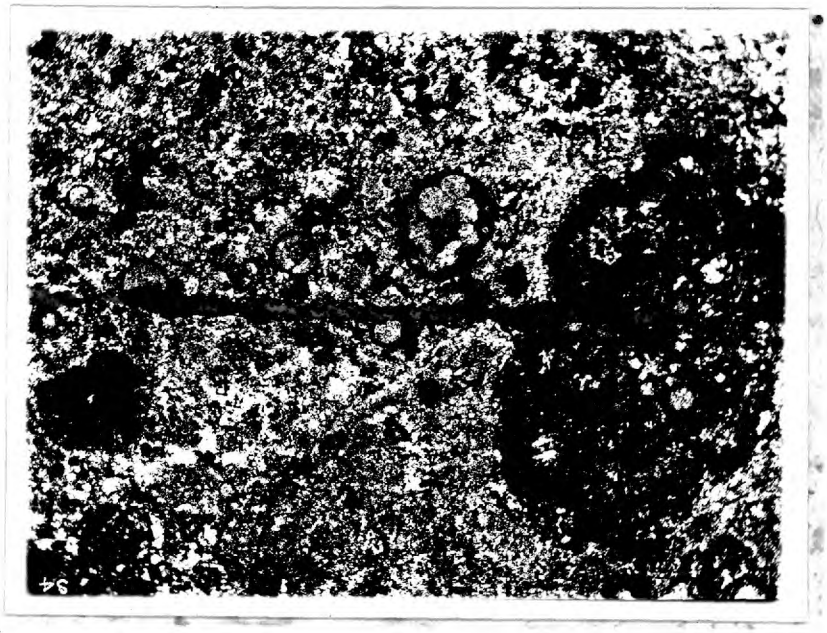


Fig. 34. x200

Globular patches of spherulites in massive pyrite. Electrolytically etched.

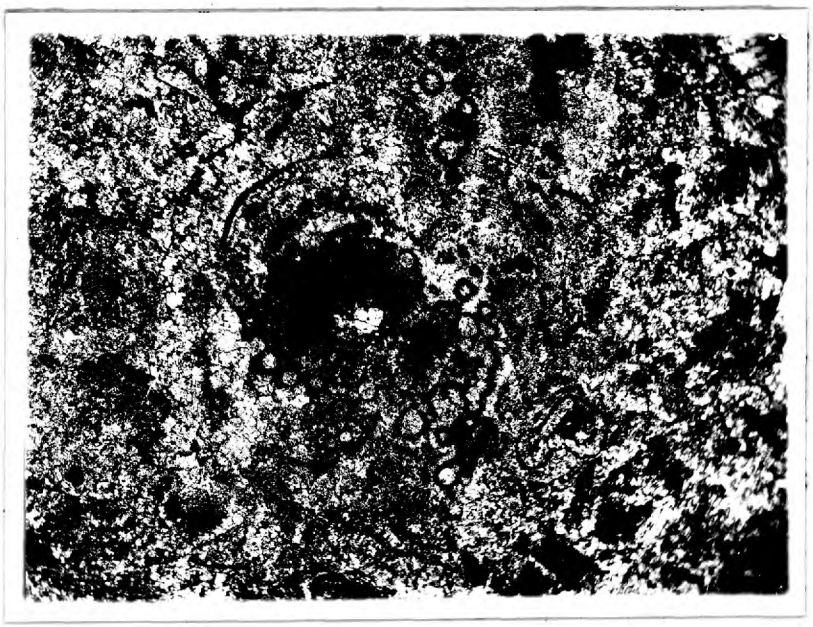


Fig. 35. x200

Spherulites closely associated with colloform textures in massive pyrite. Electrolytically etched.



Fig. 36 x1000

Oval spherulites with superimposed growth of crystalline pyrite. Electrolytically etched.

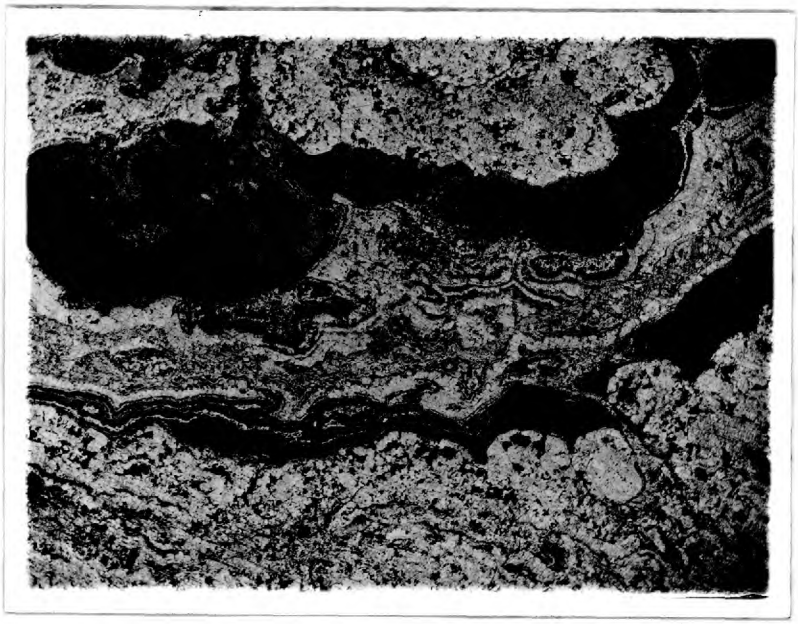


Fig. 37. x30

Colloform bands in massive pyrite.
Electrolytically etched.

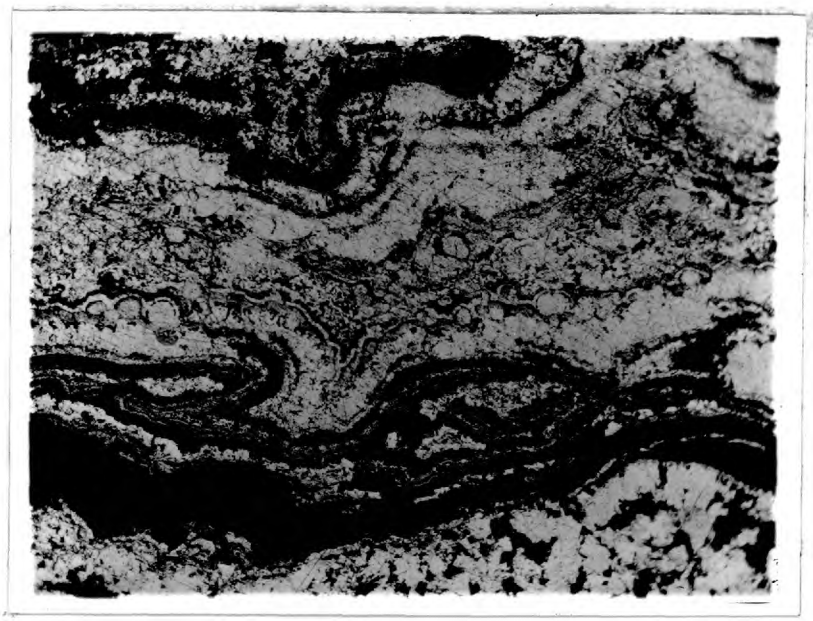


Fig. 38. x100

Higher magnification of Fig.37 showing association of spherulites with colloform bands x100



Fig. 39. x500

High magnification of Fig.37 showing close relationship between spherulitic and colloform grow ths.

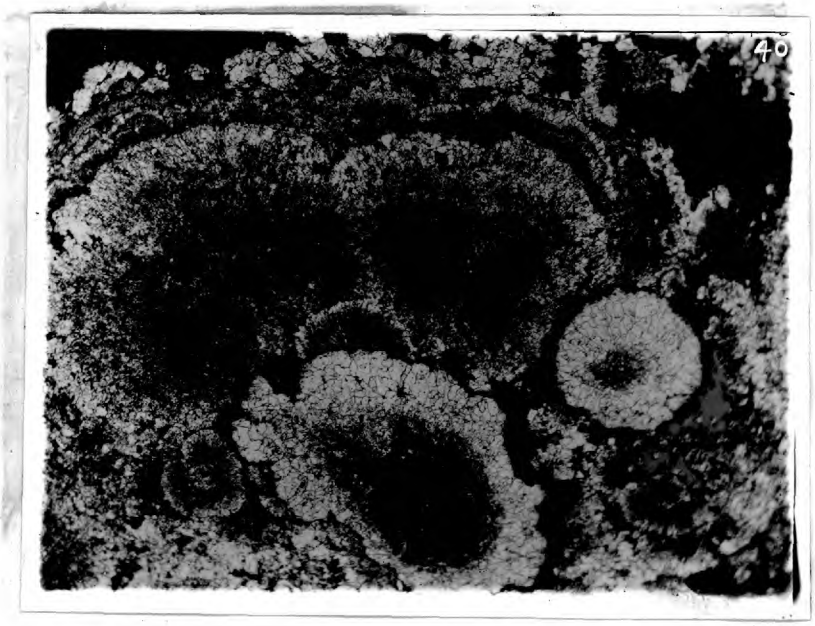


Fig. 40. x30

Granular type colloform textures in massive pyrite. Electrolytically etched.

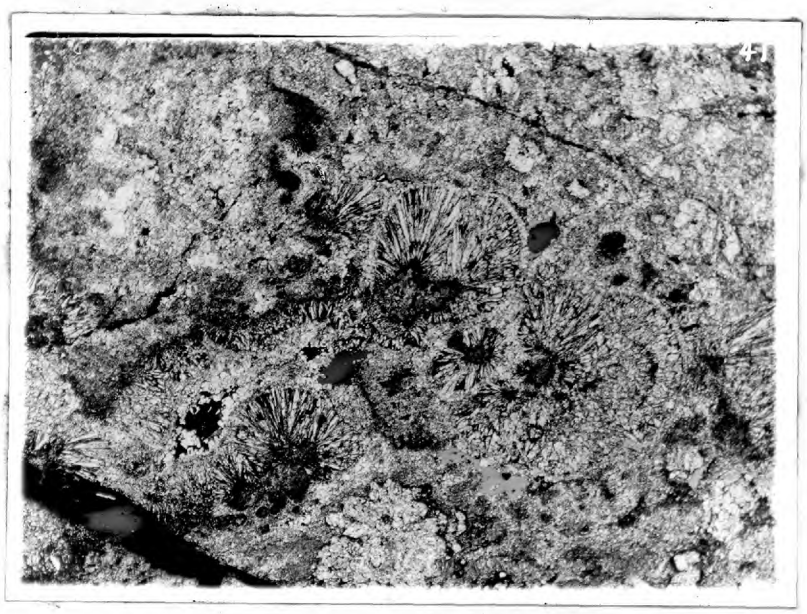


Fig. 41. x30

Radiating structures in colloform growths. Electrolytically etched.

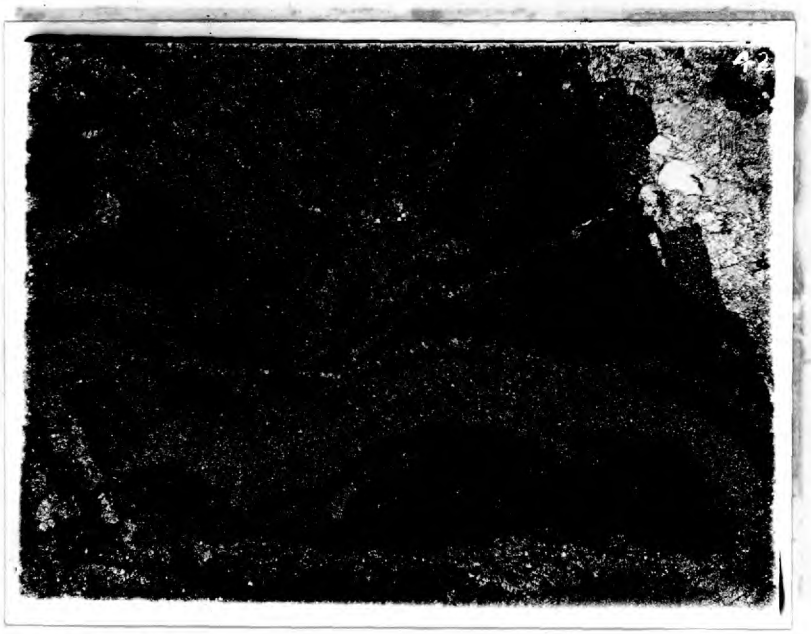


Fig. 42. x30

Colloform pyrite within rock material. Textures showing radiating and concentric structures. Oblique illumination of thin section.

interpretation of the existing field and experimental evidence that the writer can offer is that replacement colloform textures are the result of rapid deposition within heavily leached rocks. Prior to deposition the sulphides almost certainly existed in a colloidally dispersed condition, even if they originally entered the rock in ionic solution. The curved surfaces of the colloform textures are the result of migration through the porous rock and the structures are an expression of the Liesegang effect. These surfaces are not necessarily "manifestations of surface tension effects in viscous material" as suggested by Boydell[69], although there may be a fundamental similarity between the formation of a gel in open space and the precipitation of colloidal material within porous media.

Over 80 per cent of the sections examined were found to contain colloform textures together with very fine grained pyrite, and it is concluded that high energy leaching and rapid deposition were major ore forming mechanisms. The textural evidence of spherulites and colloform textures and their distribution give practically undisputable proof of the hydrothermal origin of the orebodies and confirm the arguments of Finlayson, Collins, Bateman, and D.Williams, whilst refuting the magmatic theories of Vogt, Edge and G.Williams. One of the principal facts used by these 'magmatists' to support their hypotheses is the existence of sharp contacts between ore and country rock. Microscopical examination of these contacts, however,

reveals colloform textures on them, and some of the sulphide contains skeletal remains of replaced rock, apparently in a state resembling a colloidal dispersion of gangue. This gives rise to clouded varieties of pyrite and chalcopyrite which for a long time defied identification (Fig.43). It seems that colloform replacement is very prone to yield sharp contacts, possibly due to the limited capacity of colloidal particles to migrate. It is only when a considerable amount of ionic sulphide colutions pass into the wall rocks that gradational contacts are formed.

Occasionally contacts are found where slates have been bent or buckled. This is due to the effects of differential movement during the period of mineralization, for it can be proved (see structural investigation, on p.130) that movements went on before, during and after ore formation. Much of the ore channel must have been in a semi-plastic state, and it is quite likely that some of the ore itself was remobilised after deposition if it was subjected to stress before it had consolidated. Movement in the non-rigid mass could account for the frequent occurrence of broken colloform textures.

Chalcopyrite is rarely seen in colloform textures and when it is, it is impossible to be certain that it is not merely pseudomorphing earlier-formed colloform pyrite (Fig.44). The principal colloform phase of replacement was probably an early rapid deposition of pyrite relatively free from chalcopyrite, and the main deposition of chalco-

pyrite (with some pyrite) took place later under conditions which were not favourable to the colloform type of replacement.

Wholly crystalline massive pyrite is uncommon and is believed to originate from the total replacement of wall rocks under conditions of slow metasomatism by ionic solutions. Some of the best examples of this are seen in the Planes orebody at Rio Tinto, where the stockworks merge into massive ore. When electrolytically etched this massive ore shows crystals with excellent growth zones (Fig.45), a feature believed to be indicative of slow growth.

Crystalline pyrite within the normal massive fine grained ore is believed to be of two ages. The early solutions formed metacrysts (and spherulites) in the wall rocks and these crystals were then enveloped by later solutions which carried out colloform deposition with the formation of more spherulites. Later still, as the intensity of hydrothermal activity diminished the pore spaces and skeletal gangue left in the newly formed ore mass were infilled and replaced by crystalline pyritic growths. Thus the colloform textures are found growing on the early-formed metacrysts and spherulites, whilst crystalline growth is superimposed on all the earlier forms (Fig. 36). Some fractures formed in the early pyrite may be infilled by later pyrite (Fig.46), and these fractures also provide loci for other late stage minerals.

Banded structures in the ores and their interpretation.

The occurrence of two types of banding has already been mentioned. The type which consists of alternating bands of pyrite and gangue is usually considered to be formed by the metasomatism of schistose rock, preferential replacement having taken place along planes of schistosity. That which is formed in complex ore (figs. 47 and 48) consists of bands of pyrite, sphalerite, chalcopyrite, galena and gangue, and cannot be explained so simply. The banding is usually less perfect and the adjacent rocks are not necessarily schistose. J.C.Allen has described the occurrence of these ores in the San Telmo pyritic orebody in Spain where they are exceptionally well developed, and it appears that the banding there is formed entirely within ores on contacts between ordinary pyritic ore and complex ore, and not on wall rock contacts. It is also significant that these pyrite-complex ore contacts are sometimes very sharply defined by a gouge or sterile parting, whilst elsewhere they are gradational. Allen has ascribed these features to the injection of a liquid or plastic mass probably in colloidal form, but to the present writer the sterile partings and gradational contacts suggest replacement and are analagous to the slate veneers and gradational contacts formed between massive pyritic ore and wall rocks. It is believed that late solutions rich in the constituents of blende and other minerals, replaced 'horses' left in the

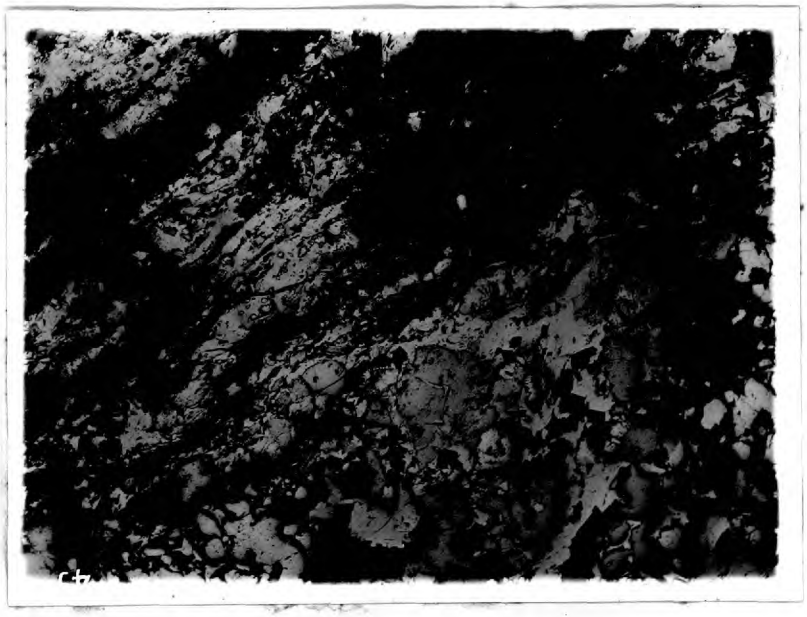


Fig. 43. x100

Contact ore containing sulphide clouded with gangue particles.

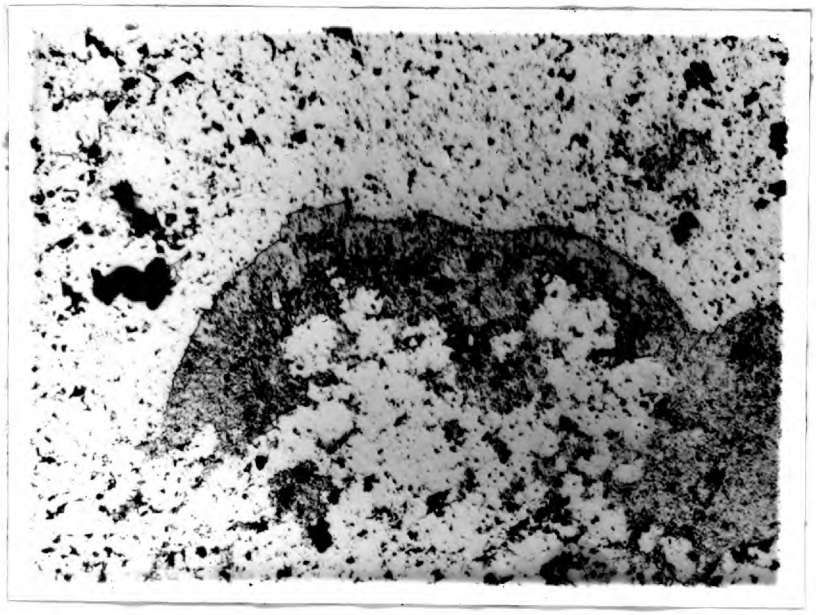


Fig. 44. x100

Colloform chalcopyrite possibly pseudomorphic after colloform pyrite.

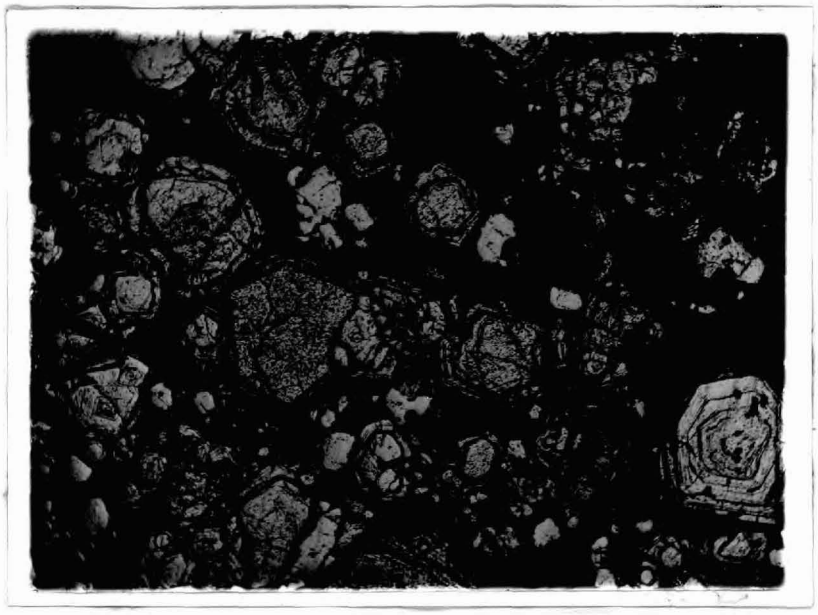


Fig. 45. x100

Planes ore showing zones resulting from slow crystalline growth. Electrolytically etched.

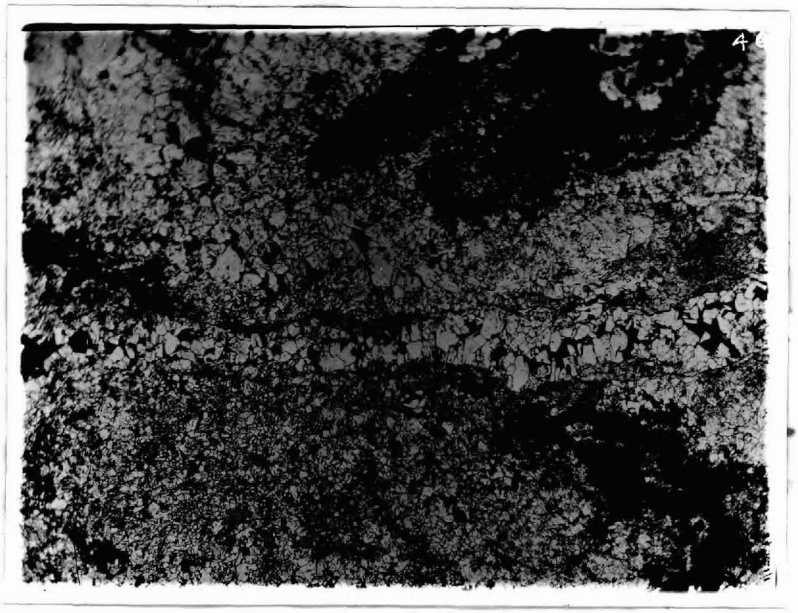


Fig. 46. x100

Two generations of pyrite one cutting the other.

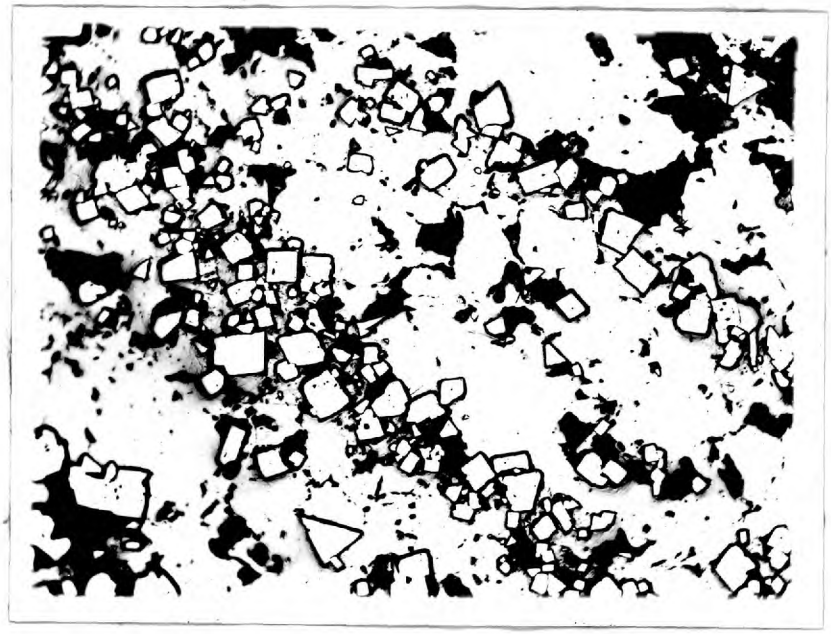


Fig. 47. x100

Banded ore with euhedral pyrite.

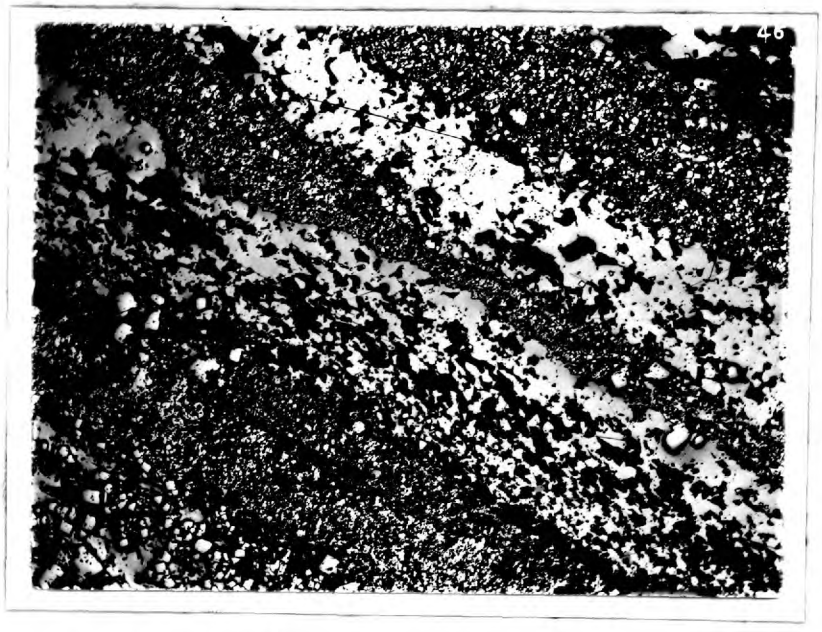


Fig. 48. x100

Banded ore.

early-formed pyritic mass, but in some cases were unable to replace the highly altered outer skin of the 'horse' in immediate contact with the pyritic ore. 'Horses' are common in most of the pyritic masses and are reported by Allen within all the ore types at San Telmo. A distinctive feature of the mineralization at San Telmo is the magnitude of the late stage zinc-barytes phase which apparently partially reproduced the conditions of early pyritic mineralization by converting some of the rock being replaced in to a porous mass. Under such conditions rhythmical precipitation can take place within the porous media in the manner described by Bradford[16], and this process probably accounts for the banding. Comparable mineralogical banding cannot take place during the colloform phase of pyrite mineralization because this phase is virtually monomineralic, though some of the banding near the margins of the pyritic masses may be due to this cause. It is in fact quite likely that during the replacement of schistose rocks the Leisegang effect may considerably intensify the banding, especially since spherulites sometimes accompany the banding (cf. Bradford's experiments).

The theory of complex mineralogical banding being due to rhythmic precipitation during replacement is capable of accounting for the frequent occurrence of distorted bands of variable thickness since the heterogeneity of the porous media would be expected to cause these effects. On the other hand it is extremely difficult to visualize the formation

of some of these multi-mineralogical bands as palimpsest structures inherited from schistose rocks.

Newhouse and Flaherty[71] have described banding due to metamorphism, and their criteria have been used in searching for evidence of pressure effects in the banded ores. No such effects have been found, and their absence has also been noted by Williams, who examined the reputedly pressure-banded ores of the Eduardo Mass at Rio Tinto.

Disseminated and Stockwork Ores.

Mineralogy. All the more common minerals seen in the massive ores are present in the stockwork and disseminated ores, where they exhibit the same paragenetic relationships. They include the primary sulphides arsenopyrite, pyrite, chalcopyrite, sphalerite, galena, bornite, tetrahedrite, enargite, and famatinite, the secondary sulphides chalcocite and covellite, the oxides hematite and goethite, and the primary hypogene sulphates barytes, alunite and jarosite (rare). With the exception of pyrite, chalcopyrite and sphalerite, the sulphide minerals are but rarely seen in polished and thin sections. The two antimony-bearing minerals noted in the massive ore, chalcostibite and bournonite, and have not been recognized in the disseminated ores, but two additional minerals giving microchemical reactions for arsenic and lead, have been detected. One of these is galena white, strongly anisotropic, scratched by a needle, etched black by HNO_3, stained brown by KOH and

negative to HCl, and is probably either baumhauerite ($5PbS,4As_2S_3$) or rathite ($3PbS,2As_2S_3$). The other mineral is greyish white, isotropic or weakly anisotropic, scratched by a needle, tarnished by HNO_3 fumes, gives negative reactions to HCl and KOH etch reagents, and is probably legenbachite. $6PbS\ (Ag_1Cu)_2S2As_2S_3$. Owing to the small amount of material available it was not possible to get X-ray confirmations of these two identifications.

The stockworks are generally confined to the massive porphyry and usually contain a few primary minerals only, whilst the disseminated ores which lie in fissile porphyries flanking the massive ores have been affected much more by late-stage mineralization processes and acid waters liberated during the oxidation of the pyritic masses. In consequence secondary copper minerals, iron oxides and hypogene sulphates are not uncommon in the latter ores whilst the gangue may be dominantly of sericite or sometimes quartz and clay minerals, instead of the quartz-chlorite aggregate characteristic of the stockworks.

Textures of the stockwork and disseminated ores. The massive stockworks consist of ramifying veinlets of sulphides generally cutting massive porphyry and with disseminated sulphides impregnating the interstitial rock. Occurrences of stockworks in slate have been reported[6] in the Iberian belt, but they are rare. The walls of the sulphide veins seldom match, and it seems most probable that the veins have

resulted mainly by replacement of the walls of small fissures. Contrary to expectation the veins do not appear to assume any systematic orientation with respect to the presumed direction of orogenic pressures. The sulphides in the veins are mostly coarse-grained and allotriomorphic and in this respect differ from the interstitial sulphides which are frequently idiomorphic and, unlike the vein material, show pronounced growth zones after electrolytic etching (fig. 49). This fact leads to the conclusion that the vein material was probably deposited rapidly in comparison with the idiomorphic pyrite, but in conditions unsuitable for the growth of colloform textures, which are never observed. The spatial distribution and mineralogy of the stockworks suggest that they are the feeding channels of the massive orebodies.

The disseminated ores formed in the wall rock immediately adjoining the pyritic masses may merge into stockworks or be developed separately. Their contactswith massive ore are usually well defined but a gradation from massive pyrite into disseminated ore is not uncommon. In contrast to the massive pyrite, the disseminated ores are usually coarsely granular, the pyrite varying generally from idiomorphic crystals in fringe areas to allotriomorphic aggregates close to the orebody. Colloform and spherulitic pyrite sometimes occur in the latter region, and on the basis of arguments already given it is reasoned that disseminated ores close to the massive deposits have

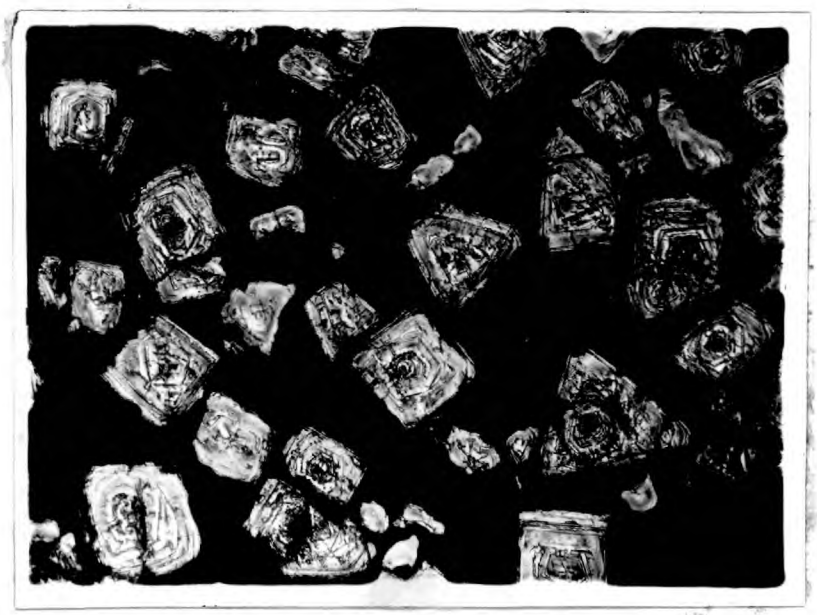


Fig. 49. x100

Disseminated pyrite metacrysts showing crystalline growth zones. Electrolytically etched. Phase contrast illumination.

resulted from comparatively rapid replacement whilst those in the fringe areas have developed more slowly.

Distribution of Metal Values and Thermo-electric Potentials.

Pyrite geo-thermometer. Although it has been known for about a hundred years that the electrical properties of pyrite and other minerals are highly variable, F.G.Smith[72] in was the first to attempt to correlate these properties with temperatures of formation. He found that both the specific resistance and thermo-electric potential of electronically conducting minerals are related to the degree of perfection of crystal growth in the minerals. He also postulated that in a given set of conditions the degree of perfection in minerals is related to their temperature of formation, an assumption which has not been rigorously proved but which has been substantiated by limited experimental work. It was therefore deduced that the electrical properties of minerals are related to their temperatures of formation, and an instrument was devised to facilitate the simple and rapid recording of the thermo-electric potential of minerals. Pyrite was chosen as the most suitable mineral for use owing to its ubiquity and the comparatively high thermo-electric currents it produces. Calibration of the instrument was carried out with various specimens whose approximate temperature of formation was known or had been deduced, and tests were then made on a large number of specimens from a variety of deposits. It was found that the

temperature estimates obtained in these tests were consistent with what would be expected from geological reasoning and it was claimed by Smith that in some deposits several generations of pyrite could be recognized. However, an important point made by him is that comparisons must be confined to pyrite deposited under similar conditions, otherwise an additional variable will affect crystal perfection and hence temperature readings. Thus it would not be permissible to compare hydrothermally deposited pyrite with pyrite formed by fumarole gases.

In view of the results obtained by Smith and the apparent plausibility of his arguments the present writer has experimented with the method. An instrument was built on the lines described by Smith, using a miniature soldering iron fitted with hot and cold probes made of stainless steel, and a sensitive potentiometer circuit. This instrument was in fact modified from an earlier one, built by G.A.Collins[73], a research student at the Imperial College, in which the probe was made of copper. The present writer found copper unsatisfactory because a film of oxide formed on the probe immediately it was heated, and a simple experiment showed that this film considerably affected the readings obtained. The instrument was calibrated by means of two specimens kindly sent from the University of Toronto by F.G.Smith, and calibrated on his original instrument. The crystal marked 150°C gave a reading of +45 millivolts and that marked 550°C gave -18 millivolts. The zero voltage point is,

according to Smith, 390°C., and a calibration curve was drawn on graph paper using the three known points.

Temperatures of ore deposition. In applying the pyrite geo-thermometer to the Spanish ores it was noted that fine-grained pyrite gave consistently lower temperature readings than coarse crystalline varieties, even when the two types occurred together within the same specimen. This fact is to be expected from theoretical considerations, since the temperature readings obtained on the instrument are believed to be a direct function of crystal perfection. Smith has observed in a personal communication that "fine grained pyrite should give a lower temperature reading than coarse grained pyrite even if deposited at the same temperature. This has been noted even in large single crystals, in which the part near the axis of growth (trunk of the lineage structure) gives readings sometimes 150° higher than the more imperfect part corresponding to the infilled branches of the lineage structure". It is obvious from this that great care must be exercised in interpreting results obtained with the pyrite geo-thermometer. The calibration material sent by Smith was of a coarsely crystalline variety of pyrite and therefore only measurements made on similar material are likely to be of the correct order. Most of the readings from stockwork material should therefore be approximately correct, whilst those in the fine grained massive ore should be lower than the true temperature of formation. Fortunately the fine grained pyrite contains

occasional metacrysts of coarse crystalline pyrite and it is possible to establish that the mean difference between the two pyrite types is very approximately 100°C. For this reason 100°C has been arbitrarily added to all the readings made in massive ore. This adjustment can also be deduced from observations made on ex-solution textures of chalcopyrite in sphalerite. Buerger[74] has shown that sphalerite and chalcopyrite are capable of some degree of solid solution at temperatures above 350°C to 400°C and solutions of chalcopyrite in sphalerite unmix at about these temperatures. Solutions of sphalerite in chalcopyrite develop at rather higher temperatures and unmixing occurs at about 550°C.[75]. When these data are compared with pyrite geothermometer results obtained from massive pyritic ore, it is significant that ex-solution textures of chalcopyrite in sphalerite are seen occasionally in the higher temperature ore but never in the lower temperature ore. These lower temperature ores are generally zinc-rich and it will be shown subsequently that they form a well defined class which usually gives pyrite geo-thermometer readings of less than 230°C. If 100°C is added to this figure then a dividing line between ores carrying sphalerite with ex-solution textures and those ores which do not is established at approximately 330°C. This addition of 100°C seems justified from a consideration of Buerger's results, and furthermore it keeps the maximum temperature of formation of the massive ore at just over 500°C, in conformity with

the absence of ex-solution sphalerite in chalcopyrite.

Turning to the stockwork ore where temperature readings do not require correction, it is noted that the maximum temperatures recorded are 500-550°C, an observation which again accords well with the fact that ex-solution textures of sphalerite in chalcopyrite are apparently not developed in stockworks. Ex-solution textures of chalcopyrite in sphalerite are, however, extremely common in the higher temperature stockwork ores such as those of Salomon, and indeed are very much more prolific there than in the high temperature massive ores. This is presumably due to the fact that the sphalerite cooled more quickly within the disseminated ore than within massive ore, and hence the chalcopyrite had less time to migrate to the grain boundaries as it unmixed. In those stockwork ores which, according to the pyrite geo-thermometer, formed below approximately 350°C, the sphalerite does not contain ex-solution textures, a fact which shows a good correlation between Buerger's findings and the pyrite geo-thermometer results. This is particularly well illustrated in the north wall stockworks of South Lode at Rio Tinto, where the temperature readings lie mostly in the range 280°C - 340°C.

It can be concluded from the consistency of results obtained with the pyrite geo-thermometer and their close correspondence with temperatures deduced from ex-solution phenomena, that a reasonable reliance, perhaps to

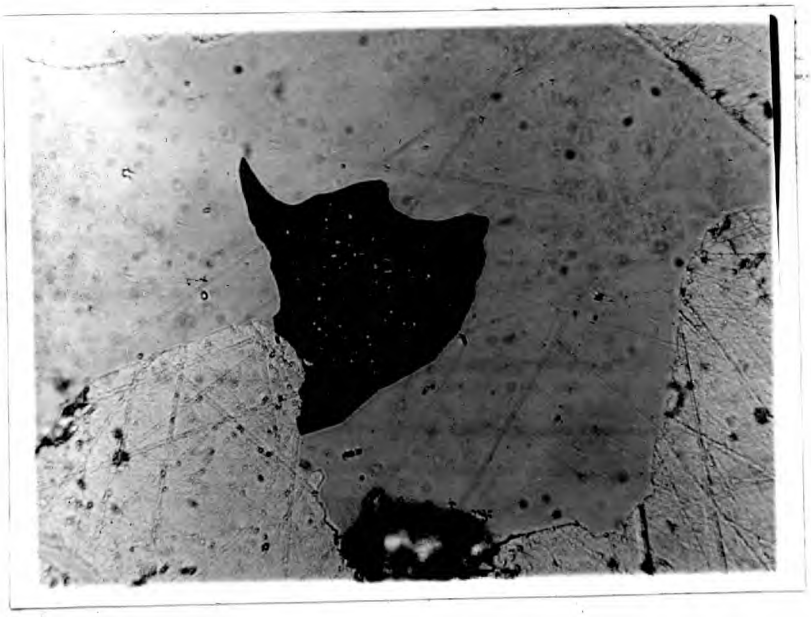


Fig. 50. x500

Ex-solution spots of chalcopyrite in sphalerite. Stockwork ore.

within ± 50°C., can be placed upon the figures. Temperatures obtained for the stockwork roots of orebodies (Salomon, Quebrantahuesos) vary mostly between 400 and 500°C., whilst stockworks alongside massive orebodies usually give figures between 250°C and 350°C close to the ore, but further away range from 350°C to 500°C. Occasionally figures as low as 200°C are obtained close alongside the ore, where the pyrite has been deposited more rapidly than in the main stockwork (see p.111), this represents an intermediate class between stockwork and massive pyrite. For this reason an unknown correction factor between 0 and 100°C must be added to the readings, which means that reliable observations cannot be taken in this zone. Massive pyrite gives corrected temperatures lying principally between 250°C and 330°C, with a few readings up to 500°C. Coarsely crystalline ore from the Planes mass is an exception since it gives uncorrected readings between 370°C and 450°C., figures which require no correction because the ore has a high degree of crystalline perfection and has clearly originated as an advanced stage of stockwork formation.

According to Lindgren's[63] classification, mesothermal deposits are formed between 175°C and 300°C and hypothermal between 300°C and 600°C. The Iberian pyritic deposits can therefore be considered to overlap from mesothermal to hypothermal, with the massive ores lying mainly in the mesothermal range and the stockworks lying principally in the hypothermal range.

Distribution of Metal Values in the Ores and their Correlation with Temperature Data.

Distribution of values in the stockworks. A selection of chemical analyses of massive pyritic ores and disseminated ores are given in Table I. In comparing broadly the distribution of metal values in the stockworks with that in the massive ores, it is convenient to express the metal values as a percentage of the total sulphur content for this is an approximate way of comparing the percentage of non-ferrous sulphide against pyrite in each ore type. The following results are derived from the Table I.

Assay No.	Material	Percentage of Metal expressed as a percentage of S content.			
		Cu	Pb	Zn	As
1.	Cupreous Pyrite	2.56	2.65	4.34	1.03.
2.	Low Grade Cupreous Ore.	2.03	1.98	2.20	0.59
3.	Crude Ore.	1.22	2.35	2.92	0.79
4.	Crude Ore.	1.36	2.40	3.42	0.96
5.	Low Grade Ore.	2.42	2.54	4.37	1.06
6.	Planes Ore.	0.27	0.27	0.31	0.34
10.	Stockwork Ore.	13.29	0.40	3.17	0.99
11.	Stockwork Ore.	9.59	0.53	4.76	0.04
12.	Stockwork Ore.	8.73	0.50	3.22	0.50
13.	Stockwork Ore.	11.60	0.36	3.49	0.85
14.	Stockwork Ore.	14.63	T	5.76	1.95
	Mean for Massive Ore (excluding Planes)	1.92	2.38	3.45	0.89
	Mean for Stockwork.	11.57	0.36	4.08	0.87

The striking points of this table are that the ratio of copper to sulphur is about six times greater in stockwork ores than in massive ores, and the ratio of lead

TABLE I. ANALYSES OF RIO TINTO ORES.

Assay No.	Description.	S	Fe	Cu	Pb	Zn	As	Sb	Ba	Ni	Co	Mn	SiO_2	$BaSO_4$	Al_2O_3	CuO	MgO	TiO_2	Sn	P	H_2O. by diff.	Au ozs.	Ag.	Sg.	SO_3
1.	Typical Cupreous Pyrite.	47.56	40.87	1.22	1.26	2.06	0.49	0.03	0.012	T	0.005	0.004	3.46	0.23	0.62	0.11	0.45	0.016	0.005	0.006	1.592	0.6	44.6	~~4.6~~	
2.	Low grade Cupreous Ore.	49.05	43.49	1.01	0.47	1.08	0.29	0.06	0.015	T	0.005	0.01	1.20	-	0.36	T	0.05	T	-	T	1.82	-	-	-	0.49
3.	Crude Ore.	49.29	42.67	0.60	1.16	1.44	0.39	0.02	0.005	T	0.007	0.005	2.42	0.07	0.36	0.06	0.31	0.020	0.004	0.010	1.159	0.4	35.5	-	
4.	Crude Ore.	47.92	41.68	0.65	1.15	1.64	0.46	0.04	0.006	T	0.007	0.005	2.76	0.27	0.88	0.19	0.18	0.022	0.004	0.013	2.123	-	-	-	
5.	Low grade.	47.31	41.32	1.14	1.20	2.07	0.50	0.06	0.011	T	0.003	0.004	2.51	0.46	0.77	0.20	0.18	0.018	0.004	0.007	2.233	-	-	-	
6.	Planes.	47.73	42.86	0.13	0.13	0.15	0.16	T	T	T	0.005	T	4.22	0.16	1.63	0.17	1.06	0.025	0.005	0.010	1.555	-	-	-	
7.	S.Domingo Cupreous Ore 240.	49.25	44.65	1.78	0.11	1.30	0.45	0.12	0.02	0.06		-	0.15	-	0.88	0.25	0.09	-	-	-	-	-	-	-	
8.	Tharsis Ore.	49.35	43.64	0.71	0.62	2.19	0.37	-	-	-	-	0.02	0.74	nil	0.34	0.48	0.32	-	-	-	1.22	0.9	21.5	-	
9.	Tharsis (Furnace size	50.20	43.53	1.20	0.69	2.14	0.52	0.025	0.008	T	-	0.075	0.18	-	0.26	0.30	0.25	-	0.010	0.004	0.012	0.8	54.0	-	
	(Fines	49.88	43.91	0.69	0.79	1.60	0.46	0.025	0.006	T	-	0.056	0.37	-	0.69	0.38	0.29	-	0.020	0.008	0.051	0.4	30.0	-	
10.	Chlorite. (Stockwork)	10.08	15.73	1.34	0.04	0.32	0.10	-	-	-	-	-	57.26	-	11.11	0.44	3.10	-	-	-	-	0.1	3.7	-	
11.	Chlorite Heads. "	13.26	17.29	1.27	0.07	0.63	0.005	-	-	-	-	-	51.30	-	7.09	0.67	3.60	-	-	-	-	0.1	8.9	-	
12.	Chlorite Heads. "	16.18	19.89	1.41	0.08	0.52	0.08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.13	9.5	-	
13.	Chlorite Heads. "	14.05	19.54	1.63	0.05	0.49	0.12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.20	15.80	-	
14.	Chlorite. "	10.24	15.55	1.50	T	0.59	0.20	-	-	-	-	-	59.32	-	9.69	0.14	2.75	-	-	-	-	-	-	-	

to sulphur is about six times smaller. Zinc and arsenic are closely similar in each type of ore.

In considering the possible cause of this distribution of values it must be borne in mind that the stockworks probably represent the feeding channels of the massive orebodies and that all the ore solutions therefore passed through them. It follows that the physico-chemical conditions must have been different at the present site of the massive orebodies from those existing in the stockworks, otherwise the solutions would obviously have formed massive deposits in the present stockwork zones. It must also be true that the conditions most favourable to pyrite deposition are not necessarily the same as those conducive to the deposition of other sulphides. Some may be deposited at higher pressures and temperatures and others at lower, in addition to which the range of conditions over which the sulphides are deposited will vary. It is suggested, for instance, that chalcopyrite is deposited entirely within the range of pyrite but over a more limited span, with its peak of deposition at a slightly higher temperature than that of pyrite. A roughly converse set of conditions applies to galena, whilst sphalerite and arsenopyrite can be considered, for the purposes of this argument, to have similar depositional ranges to that of pyrite. In short, it is suggested that the distribution of values is a function of pressure-temperature zoning. It has already been shown by the distribution of ex-solution textures and pyrite

geo-thermometer results that the depositional temperatures of the deep stockworks average up to 150°C higher than those of massive ore, and it will be shown subsequently that there are strong indications of temperature zoning within the massive ore. There appears therefore to be a good case for the theory that the mechanism of pressure-temperature zoning is one of the controls in the formation of the cupriferous stockworks.

So far the effects of paragenesis on the distribution of metal values have not been considered; nevertheless, it seems very probable that the progressive change in composition of the hydrothermal fluids had a marked effect on the localization of the cupriferous stockworks. For example, the early solutions may have been relatively poor in copper, and the feeding channels did not necessarily remain in the same place throughout the mineralization period, since earth movements are known to have continued through the period of ore formation. A shift of feeding channels might involve the deposition of separate barren and cupriferous stockworks, as occurred in the Horne Mine, Noranda. A further point is that the chalcopyritic mineralization which continued after pyrite deposition had ceased was probably effected by a substantially reduced volume of hydrothermal fluid. This late stage chalcopyritic mineralization would ascend through a more localized network of fissures than the earlier phases, giving an inner core of higher copper values to the stockwork. It is

probably these factors which give the copper values within the stockworks their somewhat 'spotty' character. It is stressed, however, that these are not the only controls, otherwise zinc would have approximately the same distribution as copper, for it is of very similar paragenetic age. The figures given prove quite conclusively that zinc is in fact distributed in quite a different way to copper.

Summarizing the conclusions on stockworks:-

1. Hydrothermal fluids which formed the massive orebodies arose through fissures which are now stockworks.

2. The ratio of chalcopyrite to pyrite is much higher in stockworks than in massive ore, partly because the temperatures and pressures of deposition were higher in the stockworks. The distribution of values in stockworks is, in other words, a function of pressure and temperature.

3. The distribution of values within stockworks is a function of the change of composition of the mineralizing fluid with time, coupled with shifting or depletion of the feeding channels.

When applying these conclusions to the prediction of stockwork trends it can be surmised from (2) that the extent of stockwork formation is determined by pressure and temperature gradients. If a massive orebody of the Salomon type roots entirely in porphyry then gradients may be low and very extensive stockworks may be formed. If on the other

hand the orebody pinches out in depth on an igneous contact, then gradients are likely to be high and the stockworks possibly rich but very localized. The distribution-control outlined in conclusion (3) is fortuitous and structural studies have failed to reveal any means of predicting in detail the likely distribution of values.

Distribution of values in massive ores. Zinc and copper values in the San Domingos deposit show a distinct antipathetic arrangement, a fact first observed by Webb and clearly illustrated in his assay plans (Fig. 51 and 52). The present writer has carried out a detailed thermoelectric study of 114 well distributed samples collected on the 240 metre level under Webb's instructions, and has found a good correlation between pyrite geo-thermometer readings and assay values. The results are summarized on the three-dimensional graphs or stereograms. Figs. 54 , 55 and 56 represent temperatures plotted against average assays for the block of ore from which each sample was taken, whilst Figs. 57 , 58 and 59 show temperatures plotted against assays of the actual specimen. Study of the stereograms leads to the following conclusions concerning ores on the 240 metre level.

1. Ore containing more than 4 % Zn is deposited only at temperatures less than 330°C (corrected).

2. Ore formed above 330°C contains more than 0.5% Cu and the ratio $\frac{\text{Cpy.}}{\text{Cpy.+ Sph}}$ is greater than 3:10.

These facts combined with the general appearance of the graphs are strongly suggestive of temperature differentiation. Zinc-rich ores are formed only at low temperatures whilst copper-rich ores tend to be formed at high temperatures. This relationship can be illustrated in one stereogram by plotting the ratio of $\frac{\text{chalcopyrite}}{\text{chalcopyrite + sphalerite}}$ against temperature, and it can be seen that the stereogram based on block assays shows the relationship more clearly than that in which specimen assays are used. This is considered to indicate that the results are not spurious due to solid solution or the effects of mechanical admixture in the pyrite, a criticism that has been made from time to time. Actually this criticism has little foundation in fact, since spectrographic studies of pyrite made by Hawley[77] in conjunction with thermo-electric studies by F.G.Smith showed no direct correlation between trace element content and temperature reading. Furthermore, observations taken on individual chalcopyrite or sphalerite grains are instantly recognisable, the former giving extremely high results and the latter giving no current at all.

The relationship between temperature and assay values is perhaps most clearly seen in In Fig. 53 . This is a floor plan of the 240 metre level at San Domingos, showing a well defined zone in which all samples gave temperature readings above 330°C (corrected). Comparison of this plan

SCALE 1:2000

>2·0 per cent Cu

1·5-2·0 " " "

1·0-1·5 " " "

<1·0 " " "

COPPER

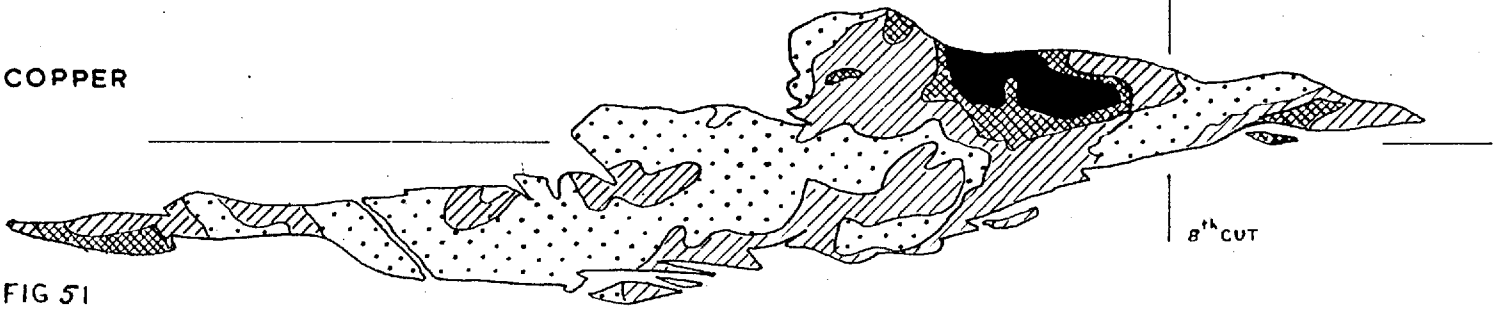


FIG 51

>5·0 per cent Zn

3·0-5·0 " " "

2·0-3·0 " " "

<2·0 " " "

ZINC

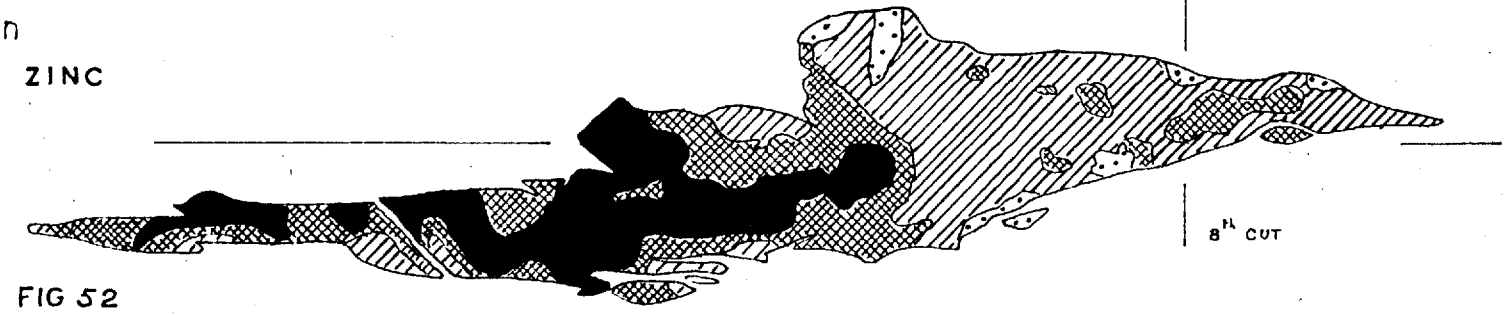


FIG 52

330°-500°C

280°-330°C

+ Sample Locations.

PYRITE GEO-THERMOMETER
TEMPERATURE DISTRIBUTION

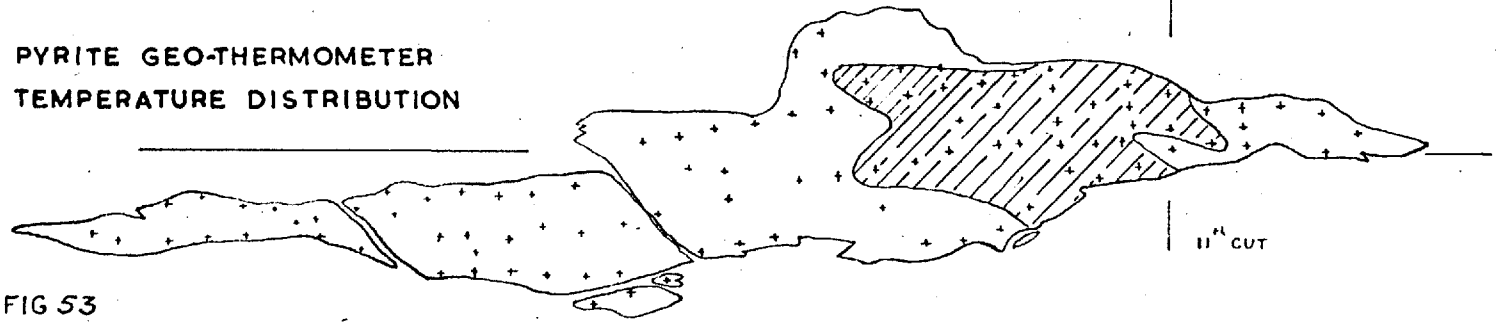


FIG 53

Cu, Zn AND TEMPERATURE DISTRIBUTION ON THE 240 M. LEVEL S. DOMINGOS

STEREOGRAMS OF Cu & Zn DISTRIBUTION PLOTTED AGAINST PYRITE GEOTHERMOMETER TEMPERATURES. 240 FLOOR S.DOMINGOS.

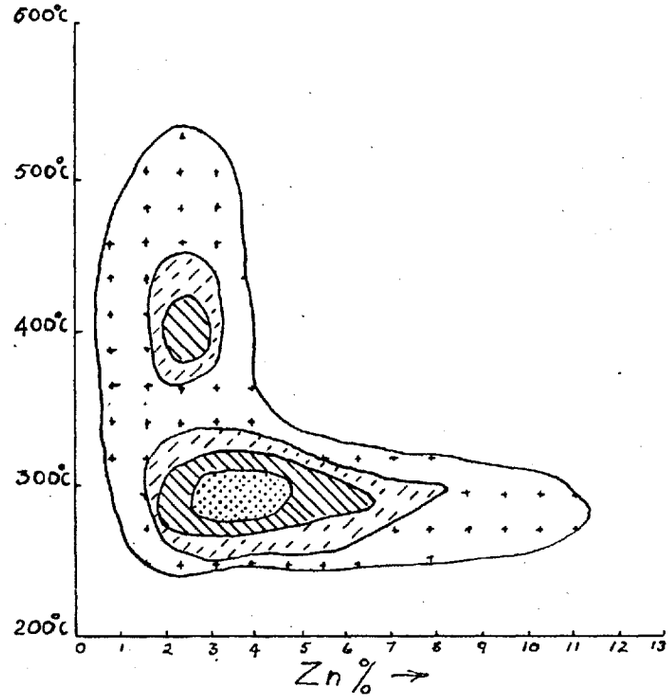


Fig. 54

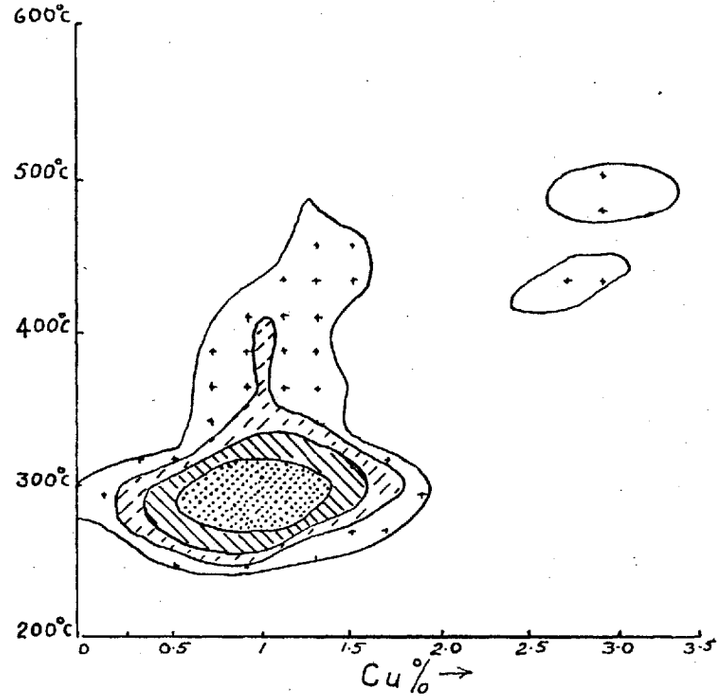


Fig 55

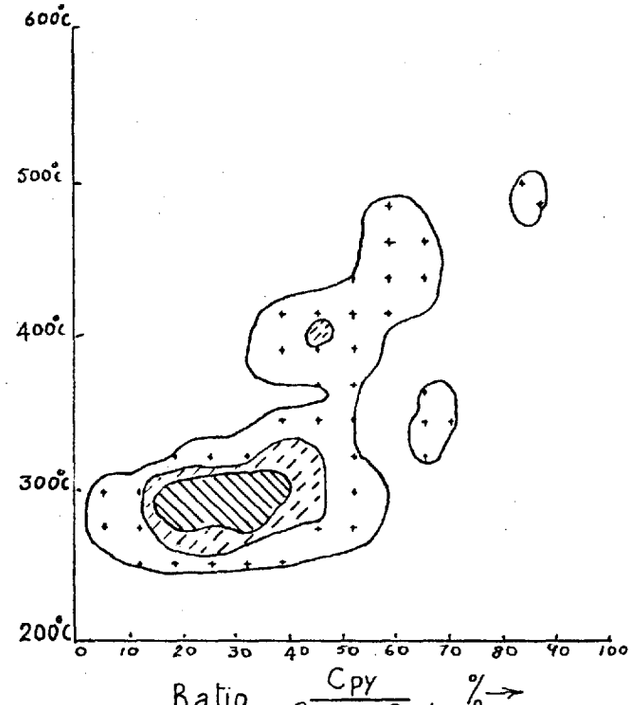
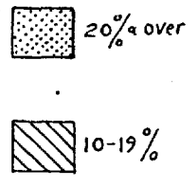


Fig56

MEAN BLOCK ASSAYS



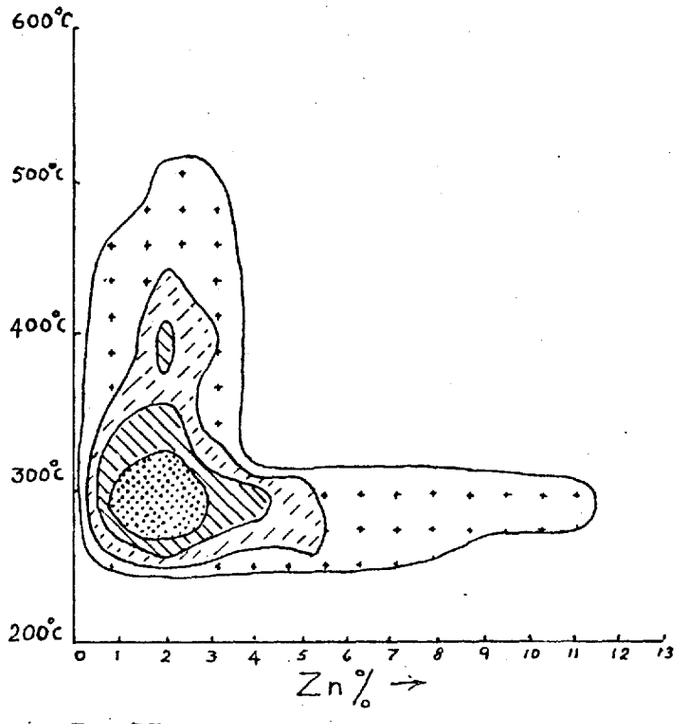


Fig. 57

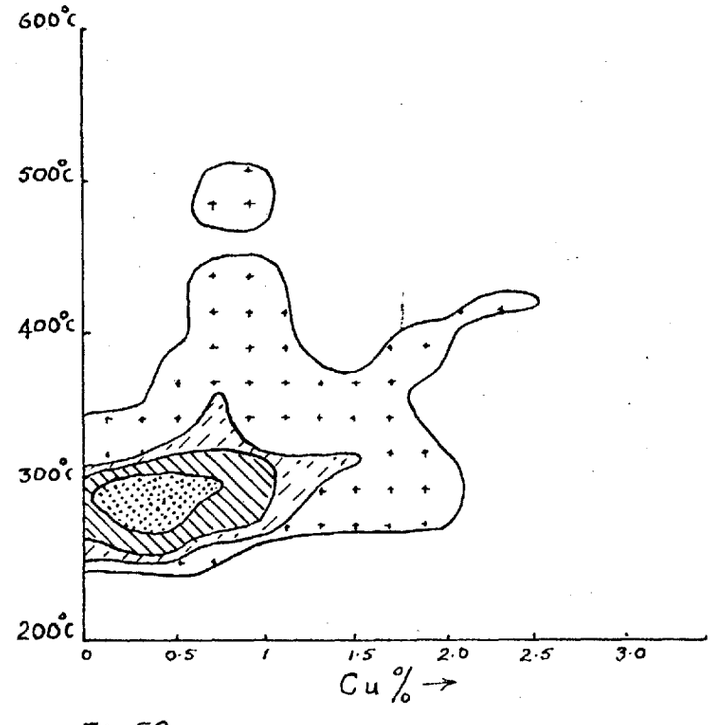


Fig.58

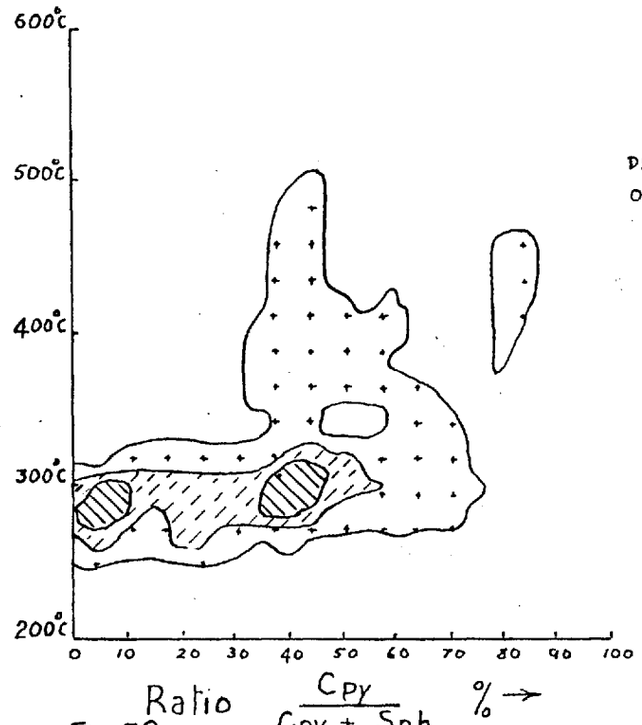
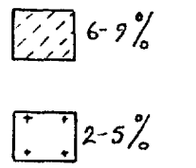


Fig.59



DENSITY DISTRIBUTION OF OBSERVATIONS.

SPECIMEN ASSAYS.

with the appropriate assay plans shows clearly the effects of temperature differentiation. It will be noted that zinc differentiation in the low temperature areas is more clearly developed than the copper differentiation in the high temperature areas, a feature which is probably due to the greater mobility of zinc and the fact that zinc continues to migrate in the cooling orebody after the copper has been fixed.

Gavelin[26] has produced detailed evidence of the differentiation in place of certain Swedish pyritic ores. According to him the paragenesis in some of these deposits is unquestionably sphalerite ------ chalcopyrite ----- galena, and yet the ores tend to divide into two classes, one poor in copper and richer in lead and zinc, and the other showing the reverse relationship. It is hard to conceive how this could happen except by migration of the elements after the ore was emplaced and before the crystallization of the later sulphides. This Swedish evidence adds weight to the argument for differentiation in the San Domingos ore.

The mode of differentiation of the pyritic masses propounded here is not difficult to imagine, for it has already been pointed out that the principal ore-forming phase due to rapid replacement of a zone which had previously been reduced to a leached and softened state by early hydrothermal liquors. The resultant early-formed mass would be highly porous and permeable, a fact substantiated by the

evidence of electrolytic etching which shows that the later solutions deposited crystalline pyrite in the interstices around earlier colloform and spherulitic textures. It was the existence of this semi-permeable mass which permitted the incoming zinc solutions to seek lower temperature areas and the copper solutions to find higher temperature zones. The distribution of values only became complicated after the mass solidified completely, for the still later solutions were then confined to relatively few fractures and differentiation was consequently restricted. Deposition then took place near the feeding stockworks, giving the type of cupriferous enrichment described by Williams[6] at Rio Tinto (p. 623).

The secondary enrichment, superimposed on the primary ores has been fully described by earlier authors.

Summarizing the conclusions on the distribution of values in massive ore:-

1. Initial differentiation took place in situ when the first-formed pyritic ore was in a permeable state. Later solutions, richer in copper and zinc than the early ones, tended to migrate to high and low temperature zones respectively.

2. As the main mass became impermeable, still later solutions migrated along cracks and fissures to superimpose a distribution of values spatially related to the stockworks.

3. Secondary enrichment imposed upon the primary distribution of values was largely confined to upper levels of the orebodies.

CHAPTER 6.

CONTROLS OF MINERAL LOCALIZATION.

This subject is, for convenience, discussed under two principal headings, the first, "Local Ore Controls", deals with factors influencing the deposition of individual ore masses, and the second, "Regional Ore Controls", is concerned with the localization of pyritic ore-fields.

LOCAL ORE CONTROLS.

Structural controls. Shear zones appear to be the most obvious structural control, and their invariable presence in association with the Iberian ore-bodies has been remarked upon by Finlayson[1], Collins[2] and Edge[3], all of whom visited a large number of mines. The localization of orebodies by shear zones is also repeatedly noted in the literature describing pyritic replacement deposits in other parts of the world. The shear zones are most commonly developed along the contacts between dissimilar rocks, such as porphyry and slate, and in analysing the environments of 36 orebodies in the Iberian belt, Edge recorded 25 on igneous contacts. Of the remainder, some are located on contacts between quartzite and slate (e.g., Tharsis), and a few occur wholly within igneous rock.

Although the term 'shear zones' has been used it does not necessarily imply that a great deal of comminution took place, but rather that there was some differential

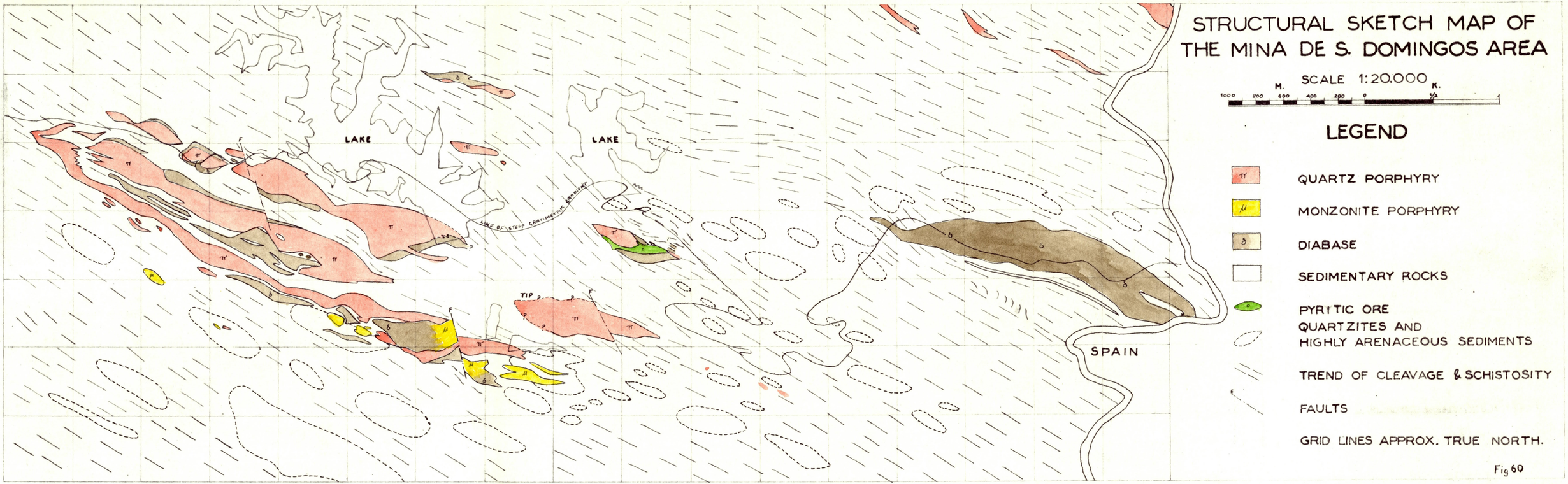
movement along the ore zone, which provided necessary openings for the passage of hydrothermal fluids. D.Williams suggested that 'pressure slacks' may have been formed by the differential movements, especially along porphyry contacts transecting the cleavage of the slates, or along crests and troughs in the invading porphyry. Ore solutions are visualized as migrating into these zones of low pressure and depositing their metallic content.

The greater part of the writer's own structural investigations have been carried out at San Domingos. The accompanying 1 in 20,000 structural sketch map of the Mina de San Domingos area, Fig. 60 , was prepared from a 1:10,000 map of the area, and shows the interpolated cleavage trends as well as the line of steep gravimetric gradient delineated during the geophysical investigations of a team under the direction of Dr. Bruckshaw. It will be noted that the line of steep gravimetric gradient is deflected considerably to the south slightly to the east of the mine and then swings back to its previous strike. These deflections appear to show some relationship to the alteration of cleavage trend, and it is not unlikely that both features are caused by some major structural discontinuity in depth. Orogenic compression acting on such a discontinuity may have provided a couple which fissured the rocks and formed deep seated channelways to tap the ore solutions.

During underground structural investigations at San Domingos all the shear zones exposed in the various

levels were mapped and the data extrapolated on to the 240 metre floor plan (Fig. 61). It was found that the middle shear zone could be followed from the wall rocks into massive ore, where it was traced along slickensided joints. This latter fact implies that earth movements were taking place below, during and probably after mineralization, for the middle shear zone is often heavily mineralized where it cuts the wall rocks. The evidence of drag folds and tension gashes shows that the south wall of the orebody had a tendency to be displaced to the east with respect to the north wall, even though the movement might have been small. This movement can be readily explained in terms of the broader structures, for a glance at the structural sketch map of the area shows that the mean strike of the ore zone lies at an appreciable angle to the regional trend of the cleavage. It follows from this relationship that a couple may have developed in the ore channel with the southern half of the couple directed eastwards. This is by no means the only possible explanation of the couple, but it is the most straightforward. At any rate the couple certainly existed and probably accounts for the curving and splitting of the middle shear zone to form a 'horse tail' pattern. It also provided a mechanism for creating the network of fissures which are pre-requisite for ore formation.

Turning to the Rio Tinto structures, the discovery that the Eduardo fault was formed before or during mineralization raises the question of whether this not inconsiderable



STRUCTURAL SKETCH MAP OF THE MINA DE S. DOMINGOS AREA

SCALE 1:20.000

M. 1000 800 600 400 200 0 K. ½ 1

LEGEND

- QUARTZ PORPHYRY
- MONZONITE PORPHYRY
- DIABASE
- SEDIMENTARY ROCKS
- PYRITIC ORE
- QUARTZITES AND HIGHLY ARENACEOUS SEDIMENTS
- TREND OF CLEAVAGE & SCHISTOSITY
- FAULTS
- GRID LINES APPROX. TRUE NORTH.

Fig 60

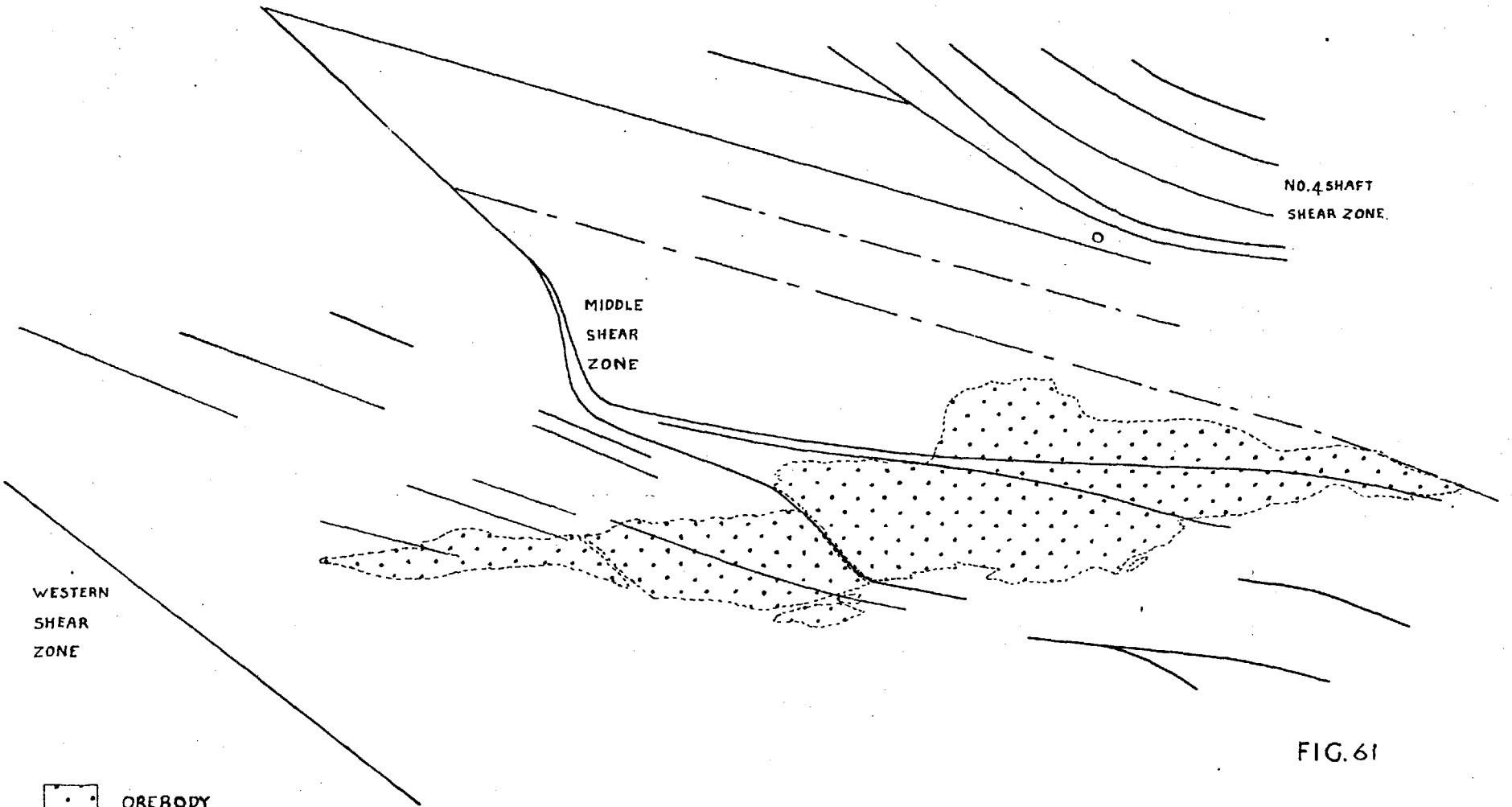


FIG. 61

PATTERN OF PRE- AND INTRA-MINERALIZATION SHEARS AT SAN DOMINGOS.

IDEALIZED PLAN OF 240 M. LEVEL REDUCED FROM DATA OBTAINED AT ALL LEVELS.

fault was directly connected with ore formation. This is certainly not unlikely, for many other massive sulphide orebodies show a close genetic relationship with faults, as exemplified by the Horne Mine, Noranda[76], Flin Flon Mine, Manitoba[78,79], Britannia Mine, British Columbia[80] and the United Verde Extension Mine[33]. The Eduardo Fault was presumably caused by ultimate failure of the rocks under the applied stress of a couple, and it is possible that the same couple caused differential contact movements and crackling of the porphyry associated with ore formation. The magnitude of this fault implies that the structural disturbance descends for a considerable distance and was thus capable of providing ore channels from depth, whilst the couple may also have caused widespread fracturing of the Salomon dyke.

In the La Zarza property the principal structural control appears to have been the spatial distribution of the igneous intrusions rather than transverse faulting. The strike of the Mesa Porphyry is approximately E-W whilst the trend of the cleavage is 110° so that a strong couple certainly existed along the southern contact during the period of regional compression from the south. This fact probably accounts for the localization of the Perunnal mass and the western portion of the La Zarza orebody. The eastern extension of the La Zarza mass occurs in en echelon lenses, the trend of the ore zone lying E-W, at an angle of20° with the cleavage. Limited underground reconnaisance mapping indicates that the sub-surface geology is somewhat complex,

but it is clear that much of the ore has formed on E-W igneous contacts. Like the western part of the orebody the eastern section of the mass is therefore probably localized in zones where couples tended to produce differential movements. Similar types of controls are presumably exercised in a vertical sense, for the dips of the igneous contacts at La Zarza show wide divergences from the cleavage dips. Indeed the general complexity of the intrusives has probably made the area propitious for ore formation.

Lithological controls. The influence which rock types have had on replacement is principally connected with their physical characteristics and breakdown products rather than their bulk chemical compositions. The reason for this is illustrated by a comparative study of the compositions of rocks commonly associated with the orebodies. Three typical analyses are quoted below from the papers by D.Williams[6] and Collins[2].

It will be noted that the differences between the chemical compositions of these three types are not pronounced, and there is no basis for assuming that the variations which do exist have influenced the susceptibility of the rocks to replacement by sulphide masses.

Physically the various fresh igneous rocks & highly arenaceous sediments are fairly similar, all being massive and subject to fracturing and jointing. These types naturally differ considerably from fresh slates which are

TABLE III.

	A	B	C
SiO_2	63.12	70.76	60.22
Al_2O_3	17.39	9.63	16.59
Fe_2O_3	0.79	1.40	1.45
FeO	5.01	4.46	3.87
MgO	1.92	3.89	4.85
CaO	0.96	2.32	3.31
Na_2O	2.24	3.50	1.92
K_2O	3.29	1.21	0.81
MnO	0.02	n.d.	n.d.
Cu	--	0.03	0.07
ZnNi	--	0.32	0.34
S	--	0.69	1.68
P_2O_5	0.27	0.07	0.12
CO_2	n.d.	0.08	0.24
H_2O+	3.08	1.20	2.30
H_2O-	0.35	--	--
Fe as FeS_2	n.d.	0.60	1.54
TiO_2	0.78	--	--
C,organic	0.62	--	--
	99.84	100.16	99.31

A = Dark bluish - grey slate, 100 m.south of San Dionisio orebody.[6].

B = Quartz Oligoclase Porphyry, N.Wall of Cueva de la Mora Opencast[2].

C = Quartz - Andesite Porphyrite Footwall, Cueva de la Mora 180 m. level[2].

often capable of absorbing movement by slippage along cleavage planes and hence are not so liable to fracture. It is inadequate, however, to consider the properties of fresh rock alone for the early hydrothermal solutions will modify them prior to mineralization. In the case of a zone containing porphyry, diabase and slate, differential movements would tend to fracture the porphyry and diabase. If hydrothermal solutions gained access to these fractures, they would tend to migrate through them to regions of lower pressure. Diabase however has a tendency to break down in hydrothermal channels to form clay products which seal the fractures, whereas porphyry retains its massive character, and consequently the migrqting solutions, qnd hence the stockworks, are largely confined to porphyry. When the migrating solutions arrive at a point where the physico-chemical conditions are correct for deposition, then replacement commences. The ideal characteristics for stockwork formation are not necessarily the same as those favourable to replacement; in fact slate appears to be the rock most easily replaced. The early stages of hydrothermal leaching are apparently capable of reducing slate to a permeable state (Chapt. 4) in which pyritic solutions can flood the entire rock and deposit fine-grained relatively homogeneous ore, replete with colloform textures.

Although the propensity for slate to be leached to a porous state is an aid to replacement it may be unfavourable to the large scale movement of solutions, and

it is probably for this reason that the ore fluids rise through stockworks in massive porphyry and then deposit their contents principally by replacement of slate. Diabase is usually unfavourable to both ore transport and replacement, and Edge[3] reports that only three mines out of a total of thirty six are associated solely with basic igneous rocks and sediment. Quartzites may sometimes provide channelways for ore solutions, but the association of orebodies with quartzites is uncommon, presumably because the chances of fracture systems in quartzites tapping the deep seated source of the solutions are less than those of fracture systems in porphyry.

Physico-chemical controls. Lindgren[63] has pointed out that the fundamental reason for the deposition of ores in veins and allied epigenetic deposits in the upper crust is probably that the metals were in solution in hot waters which, during their ascent, gradually encountered conditions favourable for deposition. He places temperature as first amongst these conditions. This conclusion, however, is presumably based on the assumption that the metals are transported in ionic solutions, for the stability of colloidal solutions may in certain circumstances be much more affected by pressure changes than temperature changes. This applies particularly to mixed metal-alkali sulphide sols, for Kania[81] has shown that the presence of H_2S is of great importance in maintaining the dispersion of these sols. At hypothermal temperatures a high pressure is probably required to maintain

a stabilising concentration of H_2S, for according to Kania increase in temperature is accompanied by a strong tendency for the CO_2 in solution to force the H_2S out. Decrease in temperature may thus tend actually to increase stability, whilst decrease in pressure will cause flocculation. Once flocculation has been initiated in a sol by what may be a comparatively small change, it is liable to proceed at a very high rate when compared with the speed of precipitation from ionic solutions due to an analogous change in conditions. In the next chapter it will be shown that colloidal phenomena may have played a major role in the formation of massive pyritic deposits, and if this is true then it is highly probable that pressure has been one of the principal controls of ore deposition. On the basis of this theory it would be expected that the dimensions and shapes of the stockworks would be closely related to pressure gradients and the quantity of ore solution available. From structural considerations lens shapes, sometimes arranged in en echelon fashion, would be the shape expected of 'pressure slacks' in which the ore masses formed, whilst the extent of stockwork formation would depend upon pressure gradients in the porphyry adjoining the mass. Stockworks near contacts might be of limited extent whilst those buried deep within porphyry dykes might be very extensive. There is actually some corroboration in fact of both these predictions.

REGIONAL CONTROLS.

In Chapter III it was shown that massive pyritic deposits are generally associated with soda-rich igneous rocks of acid and intermediate type. Frequently an early volcanic phase, spilitic in character, has been intruded by soda diabase and keratophyres, the ore being subsequently localized along the contacts of the intrusive rocks. In addition to the petrological similarities between pyritic ore-fields, there are also structural features which are common to the pyrite deposits. Almost without exception the pyritic areas have been subjected at least to fairly intense folding and in some cases to extreme folding and shearing. (see references 24,26,29,30,31,33,34,35,63,76, 78,79,80). Some of the orefields are known to occur in geosynclinal-orogenic areas, (Urals, Sweden, Iberia) whilst others are likely to be similarly located. The orebodies may be associated with faulting, as in the Flin Flon area where the mineralization is closely related to north-south faults which are themselves subsidiary to a major east-west fault[79].

Within the Iberian pyritic belt the zone of mineral deposition may have been controlled by pressure gradients, according to the theory on sensitive pressure controls proposed in the preceding section. The position of this zone would depend primarily upon the depth below the Triassic (approx.) land surface at which pressures became favourable to deposition, and secondly upon the

superimposed effect of pressure inequalities due to oregenic forces acting upon a heterogenous belt of rocks. According to this theory pyrite deposits would not be expected to be found to-day below a certain horizon, which indeed may not be very deep. During the past 200 million years or so of erosion that has proceeded since mineralization took place there may have been some tilting of the land, especially during the Alpine orogeny when the Guadalquivir fault was formed, so that it does not follow that the base of the zone of pyrite orebodies will lie quite parallel to the present mean land surface.

Summary of the Controls of Mineral Localization.

(1) Orebodies may form on the contacts between competent and incompetent rocks along which couples have developed and differential movements have induced fracturing.

(2) Propitious zones of the above type are liable to develop where the contacts are at an angle to the regional trend and are believed to occur in the vicinity of a major structural disturbance such as a large scale warping of cleavage or a large fault.

(3) The ore solutions ascended through fractured competent rocks, generally porphyry, where they formed massive stockworks.

(4) The massive ores have principally formed by the replacement of slate.

(5) Pressure gradients were a major control which affected the size and shape of the massive orebodies and stockworks, and the depth at which they formed.

(6) Pyritic fields occur in areas where, as a generalization, sedimentary and spilitic volcanic formations have been strongly folded, intruded by soda-rich basic and acid dykes and finally faulted prior to mineralization.

CHAPTER 7.

THE GENESIS OF THE PYRITIC OREBODIES.

In the preceding chapters of this thesis many of the arguments presented have a direct bearing on the problems of the origin of these deposits. The more cogent points are listed below.

1. The combined evidence on the development of spherulites and colloform textures in wall rocks and their distribution through massive ore affords clear proof of the hydrothermal origin of the deposits (Chapters IV and V).

2. Experimental work and theoretical considerations lead to the conclusion that colloidal phenomena played a major role in the deposition of the ores. (Chapter IV).

3. The evidence of wall rock alteration and a consideration of the fields of formation of chlorite and sericite suggests that the hydrothermal fluids were either weakly alkaline, neutral or weakly acidic. (Chapter IV).

4. The pyrite geo-thermometer, supported by the evidence of ex-solution textures, indicates that the stockwork ores were deposited at temperatures mostly within the approximate range 350°C - 550°C. The massive ores were formed mostly between approximately 180°C and 330°C, though a small amount of richly cupriferous ore was deposited at up to 550°C. (Chapter V).

5. Pyritic deposits are typically associated with areas in which the sequence of events prior to mineralization

comprised spilitic vulcanicity in a geosynclinal environment, orogenic folding, intrusion of soda-rich acid and basic dykes or plutons, accompanied by continued pressure and faulting culminating in mineralization.

This resume shows that the major problems of genesis which remain to be discussed are the nature of the hydrothermal solutions, the mode of collection of the metals, and the reasons for the common regional associations of pyritic deposits. The jaspers and their field relationships provide a considerable insight into these problems.

Mineralization and its relationship to Jasperization.

The characteristic features of igneous rocks in pyritic ore fields are their richness in volatiles and spilitic affinities. It has already been pointed out that during the hydrothermal stages of cooling, the circulating solutions in these rocks were rich in alkalis and capable of carrying appreciable quantities of silica in solution (c.f., silica solubility experiments of Hitchen[82] and many others). These solutions tended to pick up Fe_2O_3, especially when circulating through basic and intermediate rocks rich in Fe_2O_3, and were later capable of creating the jaspers, hematized slates, adinoles, and siliceous margins so commonly found on the contacts of spilitic rocks. The not uncommon presence of sulphides disseminated in the jaspers is illuminating, for it proves that the transport of sulphides is compatible, on a small scale at least, with the processes of jasperization.

If it is accepted that jasperization on the margins of plutons can be caused by the segregation of deuteric solutions, and the writer claims there is a wealth of field evidence to show this, then one is prompted to consider the possibility of analagous processes acting in the parent magma chamber. One major difference between conditions within plutons and those within the deeper seated magma must be the confining pressure. Kania[81] has shown that in the presence of free CO_2 and H_2S, the ratio of H_2S to CO_2 will increase with pressure; he has also found that the stability of alkali double sulphide sols increases with H_2S content. Kirk[83] digested femic minerals with aqueous solution of H_2S in sealed tubes at 150°C and decomposed them to gelatinous silica and pyrite. Tolman and Clark[84] commented upon the efficiency of H_2S and alkaline metals in aiding the dispersion of metal sulphide sols, and Freeman[85] has shown that Na_2S will combine with iron, copper, zinc and lead sulphides between 500°C and 700°C to give fusions which are very easily broken down by water to form colloidal dispersions. Unfortunately, quantitative studies of the solubilities of metal sulphides in solutions of alkaline metals and H_2S at high pressures and temperatures have never been made, since the active attack of the solutions on the walls of the autoclaves interferes with the measurements. Nevertheless it seems reasonably certain that late stage hydrothermal solutions in deep seated magmas are powerful solvents of the metals, and if they are squeezed out of the

magma or otherwise migrate they are likely to become ore forming solutions. The process is analagous to local deuteric alteration and jasperization but because of the immense quantities of magma involved and the increased solvent power of the solutions, large quantities of material can be transported and deposited.

Origin of Jaspers associated with pyritic deposits. There is ample experimental work to show that alkaline metal solutions would be expected to transport barren silica in the early phases of migration and the microscopical evidence of pyrite disseminated within jaspers indicates that pyritization is later than silicification[18]. On a broader scale the relationship between pyrite and jasper is classically illustrated in the United Verde Mine[33], Arizona. The jasper, which is widely developed on the contacts of this very large pyritic mass, is generally fractured and cemented with pyrite but it sometimes shows the reverse relationship whilst in between these types there are gradational occurrences. Clearly the jasper has been formed as an early phase of mineralization, a conclusion also reached by D.Williams[18] from a study of similar, if less perfectly developed, occurrences at Rio Tinto. From considerations on the mechanisms of pyritic mineralization it seems likely that a siliceous phase precedes all ore formation. Large quantities of silica are carried in relatively stable colloidal form and experiments show[81] it is likely to travel much further than the ensuing sulphides. In view of this it is not in the least surprising that jaspers are often not

found near the pyritic masses in Iberia, for the covering rocks have undergone 200 million years of erosion.

Although it may be true that all pyrite deposits were accompanied by jaspers prior to erosion, it by no means follows that all jaspers are accompanied by ore. Sedimentary jaspers, hematized quartz, and local deuteric jaspers are all types unlikely to be connected with ore. Moreover, in small scale migrations of fluids from a portion of the magma chamber the mineralization process may never get beyond the jasper stage. This argument leads to the conclusion that perhaps only a small percentage of jaspers are indicative of ore, and the recognition of these jaspers is discussed in an appendix.

Composition of the hydrothermal solutions. The composition of modern juvenile water has been extensively studied, sometimes in elaborate investigations such as those in the Yellowstone Park described by Fenner[64]. The results of these studies together with the petrological and experimental evidence which has been described (Chapter III) leads to the conclusion that the solutions which collected the ore in the cooling magma were probably rich in soda, had a lesser amount of potassium, carried appreciable amounts of halogens, carbonates, carbon dioxide and H_2S, and small amounts of a variety of other elements. This conclusion is to some extent substantiated by a study of inclusions in ore minerals. Hartley and Ramogen[86] have shown spectro-

graphically that alkali metals commonly occur in pyrite, galena, sphalerite and other sulphides, and it appears likely from considerations of ionic radii that these elements are present as discrete inclusions rather than in solid solution. Buerger[87] has described fluid inclusions in pyrite and Newhouse[88] has stated that sodium chloride appears to be one of the most abundant and widespread substances in the solutions held in cavities in minerals, especially in or adjacent to sulphide ore deposits. The fact that NaCl occurs in such cavities may at first sight seem incompatible with the theories which have been suggested to account for the transport of metals as alkali double sulphides. This is not the case, however, because Na_2S will certainly become unstable (c.f., Kania, Freeman) inside an inclusion as cooling takes place and pressure falls. If the chloride radicle is present this will combine the sodium whilst S or possibly SO_4 is liberated. Newhouse has admitted that his tests were unable to reveal the presence of small quantities of S or SO_4.

During the principal phase of mineralization the solutions were probably fairly close to neutral, for experimental work has shown (e.g., Kania) that solutions do not usually remain strongly alkaline or acidic when passing through rocks. In bomb experiments F.G.Smith[90] recently found that water solutions evolved by a cooling magma are likely to be more alkaline than the parent silicate liquid, contrary to the theoretical deductions of

some geologists. From considerations of the fields of formation of marcasite and pyrite, the stability of colloidal sulphides, and Smith's experiments, it can be concluded that the ore solutions were weakly alkaline rather than weakly acid.

The late stage solutions which deposited sulphate apparently circulated during a period when orogenic pressures had slackened, for the sulphates have formed in some cases by the infilling of open fissures and have remained uncrushed since their deposition. It is not inconceivable that the acid stage may be accounted for by the relaxation of pressure. Williams's[6] suggestion that reactions may take place between water and sulphur to form sulphuric acid can be expressed as follows:

$$4S + 4H_2O \rightleftharpoons 3H_2S + H_2SO_4$$

According to Le Chatelier's Law this reaction tends to move to the right with decrease of pressure because of the increase of volume involved. Clearly then this type of reaction will tend to lower the pH as pressure is decreased. Any barium present in the solution would then be immediately precipitated as the highly insoluble sulphate and calcium would be deposited as gypsum.

The role of colloids in ore transport. The work on colloform structures and spherulites described in Chapters IV and V has shown that colloids played a major role at the site of deposition, but does not necessarily imply the

colloidal transport of sulphides in depth. There is no positive textural evidence of colloidal action in the stockworks, but this does not militate against colloidal transport, for much of the sulphide deposition in these 'tight' zones could have been due to replacement effected by the dispersion medium, which was a saturated ionic solution. In short, textural evidence in the stockworks is inconclusive regarding the nature of the ore solutions. Garrels[89] has said that dilute alkali salt solutions are extremely poor solvents for sulphides and he therefore favours colloidal transport. The present writer cannot agree with Garrels' argument when applied to the Iberian deposits, for there is no reason to presume that the ore solutions were dilute, and there is no evidence on the physical state of the liquid at the pressures and temperatures at which ore transport took place (350°C to 500°C +, 1000 Atm (?) +). It seems to the writer that for the present one can only say that existing experimental work indicates the feasibility of large scale ore transport in solutions of the type described, but it is mere speculation to talk of colloidal or ionic transport under deep seated conditions.

In the case of transport in and above the site of deposition there is little doubt that colloids must have played an important part. The existence of silica in colloidal form is probably the reason why it seldom travels far into the wall rocks during their alteration. Whilst K, for example, may advance into the wall rocks during the

early stages of hydrothermal attack on the ore zone, silica is likely to be leached out to travel up the ore channel as a colloid.

Reasons for the common regional association of massive pyritic deposits. According to theories propounded on ore genesis and on the controls of mineral localization it can be deduced that the fundamental requisites for the formation of massive pyritic deposits are as follows:

1. A large body of deep-seated magma exceptionally rich in volatiles.

2. Structures which tap the magma and provide channels for migrating solutions.

3. Probably, orogenic pressures to provide a 'filter press' action.

Clearly, the regional associations previously described provided these conditions. The spilitic suites were rich in the required volatiles, the intrusives which followed folding yielded structural discontinuities between competent and incompetent rocks, whilst the pressures which persisted during mineralization may have provided motive power for the ascending solutions by means of 'filter press' action.

Brief Summary of the Genesis of the Pyritic Orebodies of Southern Spain and Portugal.

The ores were deposited from hydrothermal solutions which rose from a deep-seated magma source rich

in volatiles. The metals were probably transported in solution in the form of alkali double sulphides, travelled along structural discontinuities such as the contacts between competent and incompetent rocks, and were deposited at a depth determined by the regional pressure gradient. Orebodies were localized at points where couples produced by orogenic pressures induced fracture systems in the rocks and possibly created 'pressure slacks'. The early phases of mineralization developed jaspers, some of which have been removed by erosion. Jaspers may have been formed in many ways and are by no means necessarily connected with mineralization. The principal phase of mineralization was colloidal replacement of slate to form fine-grained pyrite replete with colloform and spherulitic textures, whilst the stockworks were formed by replacement from ionic solutions. Temperatures of deposition varied from hypothermal in the stockworks to mesothermal in the massive ore. Chloritization of the wall rocks is intense and was due to alteration at comparatively high energy levels. Sericitization is mostly less intense and represents a lower grade of alteration. Ore solutions of the principal phase of mineralization were close to neutral in character, but the late phase was acidic, possibly due to the recession of orogenic pressures. Late stage hydrothermal fluids deposited sulphates and carried out limited sericitization, mostly along the ore contacts.

APPENDIX.

Search for Pyritic Orebodies.

Regional. It can be concluded from the results of the investigations presented in this thesis that all areas of spilitic vulcanicity which have been intensely folded and intruded by sodic plutons can be regarded as possible areas of pyritic mineralization. In such areas however, the vulcanicity may be represented by tuffs and steeply inclined lavas not always easy to recognise in the field (e.g., Spanish pyritic field), or the intrusive phase may be sheared almost beyond recognition. (e.g.,Mount Lyell, Tasmania, Malanas District, Sweden). It would be necessary therefore, in seeking areas of likely pyritic mineralization, to look for certain portents such as the association in strong folded areas of jaspers, occasional black slates, greywackes, and albitic acid and basic rocks carrying chlorite, epidote and carbonate. It is clear that a broad regional target of this type might be useful in a major programme of prospecting in helping to select particular areas for more detached geological, geochemical and geophysical exploration.

Exploration in Selected Regions.

Geological. In carrying out a geological reconnaissance the guides listed below are of particular importance:

(1) Iron staining in porphyry, which may be fairly

considerable over a concealed orebody (e.g., at La Zarza).

(II) Pyrite cubes or their limonite pseudomorphs, which are liable to occur in rocks above ore and may weather out in loose form.

(III) Black hydrothermally altered slates, which may occur on igneous contacts above ore.

(IV) Quartz-Carbonate veins, very commonly found in the wall rocks of orebodies and above concealed ore.

(V) Intense chloritization, sericitization or adinolization may be related to ore formation.

(VI) True hydrothermal jasper may be associated with ore, but should not be confused with hematized quartzite (easily recognised in the field and in thin section), or ferruginous cherts, (generally carrying radiolaria in deposits of Cambrian or later age.). Many hydrothermal jaspers may be related to barren mineralization or deuteric segregation, and further data diagnostic of these types might be obtained by geochemical investigations. Jaspers associated with ore may contain a different trace element assemblage from jaspers unrelated to ore. Jasperization immediately above ore at La Zarza (Los Silos) is accompanied by an unusual amount of iron oxides and the outcrop is midway in appearance between jasper and gossan; this type of cropping can probably be regarded as a particularly good sign.

(VII) Cleavage warps will only be recognised if cleavage trends are regularly noted during mapping, and a large-scale warp may indicate a propitious zone for mineralization.

(VIII) Faults may indicate deep seated disturbances and hence are potential loci or near loci of mineralization.

(IX) Contacts between igneous and sedimentary rocks which were not perpendicular to the resolved direction of applied pressure during mineralization (e.g., where cleavage abuts against an igneous contact, or where the contact is at an angle to the b direction of folding). Such contacts were potential zones of differential movements and hence may have been favourable to ore formation. Moreover, the differential effects induced at and near igneous contacts during cooling of the intrusions were likely to have yielded propitious loci for mineral deposition.

None of these features is particularly significant on its own but the occurrence of several of them together warrants further investigation.

During the course of mapping, basic rocks should be carefully plotted especially if magnetic or gravimetric surveys are to follow, since these rocks cause magnetic and gravimetric anomalies. Air photographs are recommended as an aid to both reconnaissance and detailed mapping.

Geophysical Prospecting. Gravimetric surveys can be carried out most efficiently with a Worden gravimeter for the instrument is sensitive enough to detect sizeable pyritic orebodies down to depths of many hundreds of metres. Gravimetric investigations should be conducted together with geological surveys since the distribution of basic

rocks must be known in order to interpret the gravimetric results. A knowledge of the geology is also necessary in selecting the most suitable anomalies for drilling and their order of priority.

Gravimetric surveys involve a major task of precise levelling, for the heights of all stations must be known accurately. Determining the levels of several thousand stakes in a limited field season is not easy, and must be commenced well before the start of gravimetric observations so that the results can be calculated immediately. If geophysical calculations proceed concomitantly with field work, observations made over anomalies can be doubly checked and the area subjected to detailed geological examination. On the other hand, if levelling lags behind, a great deal of the value of the field season is lost and much of the work may have to be repeated in the following season. The importance of the levelling organization can therefore hardly be overestimated.

Magnetic surveys may be useful in delineating basic rocks and in differentiating between gravimetric anomalies due to basic rock and those due to non-magnetic pyritic ore. Magnetic values are always comparatively low over sediments and porphyry, and are higher though variable over basic rocks. Spectacular anomalies sometimes occur on basic contacts, particularly where there is jasperization. The additional cost of following up a gravimetric survey with a magnetic survey based on the same stations would be

comparatively small. The writer used a Watts Vertical Variometer in carrying out surveys and found that the rate of working is comparable with that of the Worden Gravimeter, so that the two instruments could be used simultaneously during the same period in the field. It is believed that the joint use of a Worden Gravimeter and a vertical variometer would form a particularly valuable prospecting tool in poorly exposed terrain containing sediments, porphyries, basic rocks and suspected orebodies.

Geochemical Prospecting. An experimental soil sampling traverse has been made over the orebody at La Zarza at a point where it lies 120 metres below the surface (see La Zarza map). The samples were analysed for zinc and copper by the Dithozone technique[91] and gave poor results. No trace of a copper anomaly exists, whilst zinc shows a slight statistical anomaly. Fresh rock samples taken in a drainage gallery which lies 100 metres above the ore, do not show any anomalous trends in either zinc or copper.

It can be concluded from these results that it would probably be difficult to detect the La Zarza mass in the vicinity of the traverse by normal geochemical methods. The paucity of copper however in the La Zarza orebody naturally makes geochemical detection more difficult and geochemical prospecting for pyritic masses in general cannot be dismissed on the grounds of this preliminary work. Furthermore there is undoubtedly a strong pyrite dispersion

above the pyritic orebodies and research is required to find a geochemical method which utilizes this dispersion. In addition it has been suggested already that geochemical (spectrographic) studies of known barren jaspers and those associated with ore might reveal a prospecting guide. It is considered that a geochemical prospecting method could be most useful not only in its own right but as an aid in the interpretation of ambiguous geophysical anomalies. The development of a geochemical technique however remains a problem requiring additional study.

Note on Ore Microscopy applied to Mineral Dressing Studies.

Investigations of mill products have been carried out as part of the writer's research and techniques of preparation, mounting, and mineralogical and statistical examination have been evolved. These are not described here since they have been fully detailed in a paper published by the Institution of Mining and Metallurgy[67].

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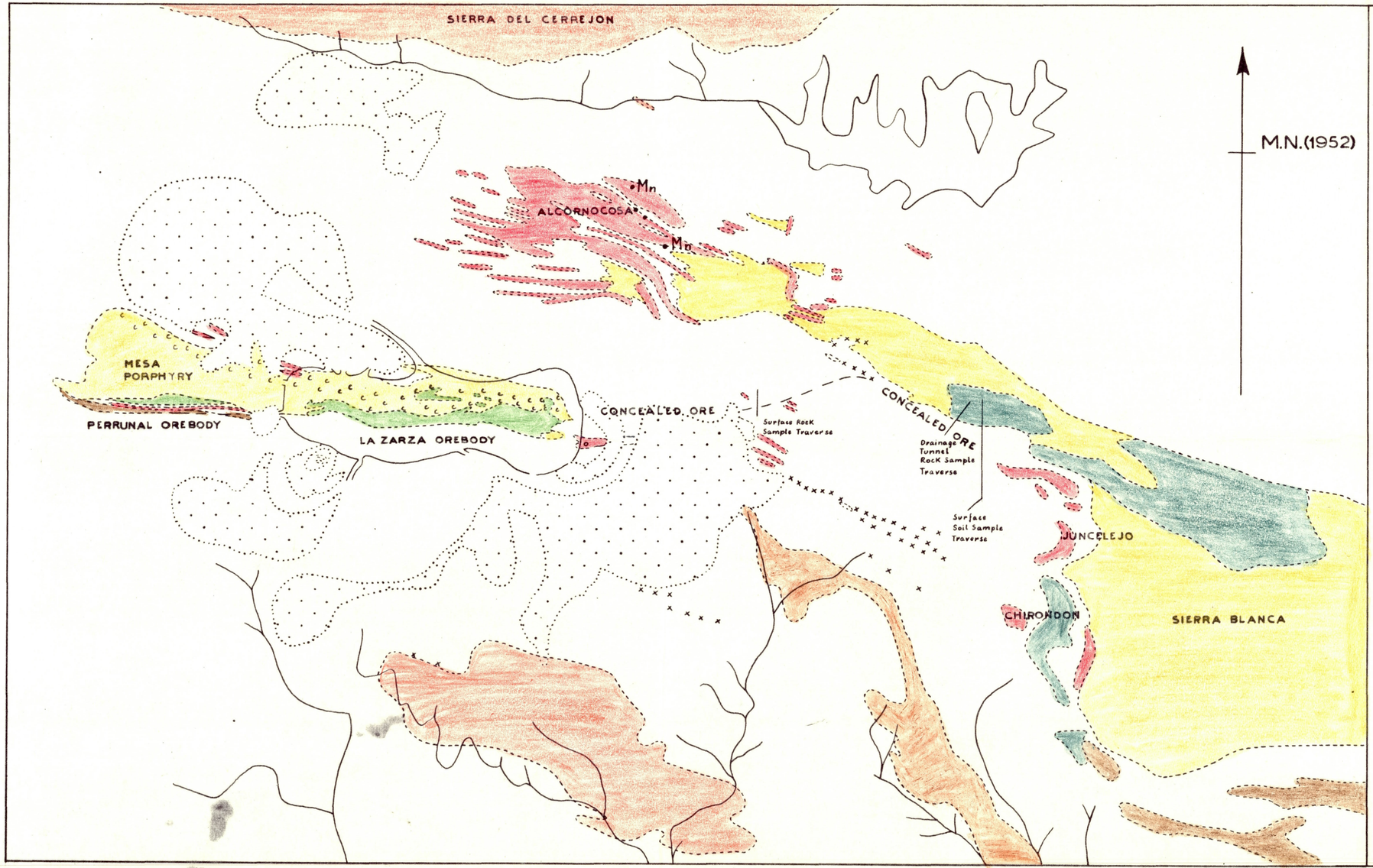
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GEOLOGICAL SKETCH MAP OF THE MINAS DE LA ZARZA AREA

APPROX. SCALE 1:10,000

500 0 500 METRES

LEGEND

- QUARTZ PORPHYRY
- MONZONITE PORPHYRY
- DIABASE
- AGGLOMERATE
- PYRITIC ORE
- SEDIMENTARY ROCK
- JASPER
- TRANSPORTED GOSSAN AND IRON STAINING
- INTENSE CHLORITIZATION
- ROCKS CONTAINING PYRITE CRYSTALS OR LIMONITE PSEUDOMORPHS AFTER PYRITE.
- Mn MANGANESE MINERALISATION

GEOCHEMICAL AND ALTERATION STUDY TRAVERSE MARKED.

SKETCH MAP BASED ON RECONNAISANCE SURVEY AMMENDMENTS TO EXISTING GEOLOGICAL MAPS MADE BY THE THARSIS SULPHUR COPPER COMPANY, LTD. AND GORDON WILLIAMS (1932).

GEOLOGICAL PLAN OF RIO TINTO AREA.

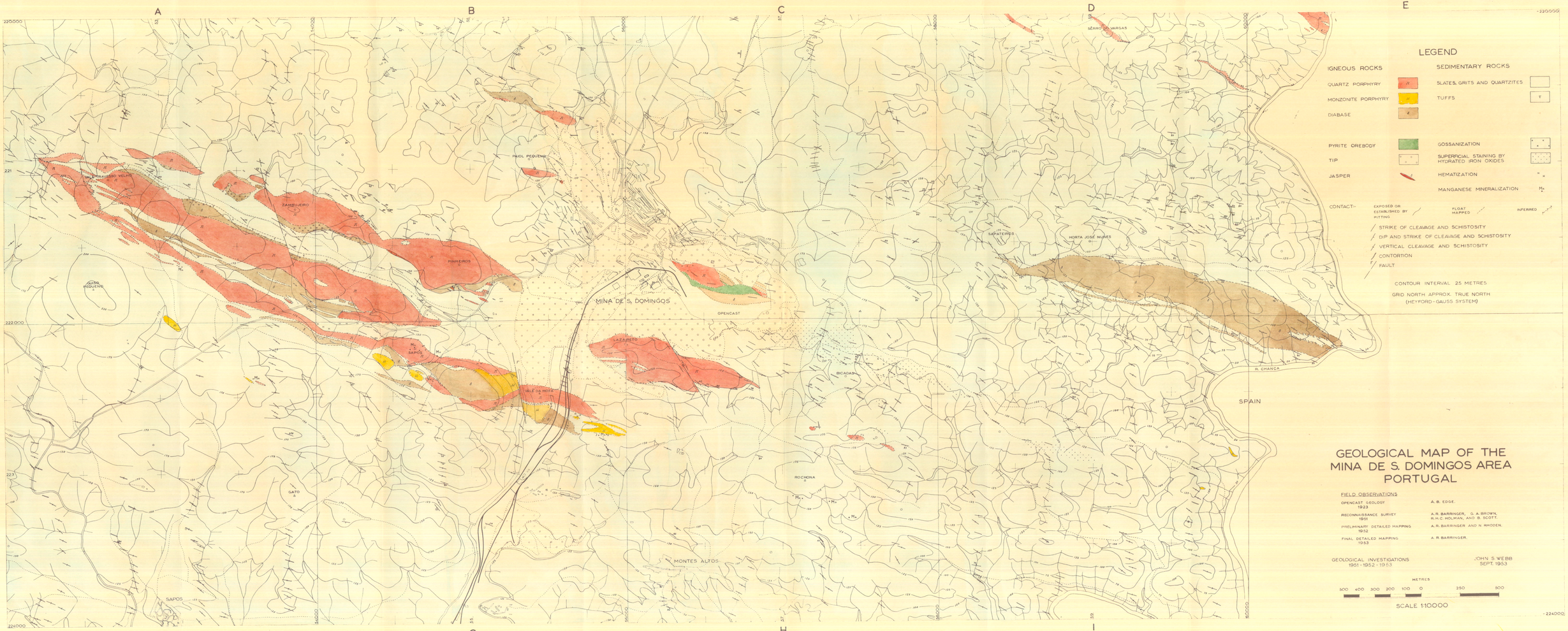
SCALE — Metres: 1000 800 600 400 200 0 — Kilometre: ½ 1

LEGEND

- Bog Iron ore.
- True Gossan.
- Gossanized Porphyry & Breccia.
- 'Dolerites'.
- Hornstone.
- Jasper.
- Metamorphosed Chloritic Rocks.
- Massive Sulphide Ore.
- Stockwork Ore.
- Stockwork Porphyry.
- 'Marginal Type' Porphyry.
- Porphyry.
- Slate Conglomerate.
- Slate.
- Fault.
- 75° Dip of Contact and Bedding.
- 79° Dip & Strike of Cleavage & Schistosity.
- Vertical Cleavage & Schistosity.
- 410 Metres above Huelva Station.

After D. Williams

MOJON LAS ALLANDAS
Rio Tintillo
Barranco de la Gangosa
Barranco Majaencina
NO. 4 TUNNEL
MOJON
ATALAYA
ATALAYA OPENCAST
12th Floor
SAN DIONISIO
NO. 3 TUNNEL
ALFREDO SHAFT
Eduardo
Victor
BELLA VISTA
VALLE
HOSPITAL
EL VALLE
MOJON HORNO DE LA TEJA
MOJON
DEHESA
Barranco Cagasa
Barranco de las Cuevas
MAL AÑO
DEHESA
CERRO COLORADO
SALOMON
MOJON SALOMON
LAGUNA
Outcrop of Conglomerate
ARGAMASILLA
PLANES
QUEBRANTAHUESOS
SOUTH LODE OPENCAST
RIO TINTO
MESA DE LOS PINOS
11th FLOOR TUNNEL
CERDA CEMENTATION HEAPS
MARISMILLA DAM
TALLERES
SOUTH DAM
NAVA TUNNEL
SMELTER CHIMNEYS


A
B
C
D
E
F
G
H
I
225000
224000
221
222000
223
MINA DE S. DOMINGOS
OPENCAST
LAZARETO
VALE DA MOTA
SAPOS
PAIOL PEQUENO
ZAMBUJEIRO
PINHEIROS
GUITO PEQUENO
GATO
ROCHONA
MONTES ALTOS
BICADAS
SÉRRO DE VARGAS
SAPATEIROS
HORTA JOSÉ NUNES
R. CHANCA
SPAIN
LEGEND
IGNEOUS ROCKS
QUARTZ PORPHYRY
MONZONITE PORPHYRY
DIABASE
PYRITE OREBODY
TIP
JASPER
SEDIMENTARY ROCKS
SLATES, GRITS AND QUARTZITES
TUFFS
GOSSANIZATION
SUPERFICIAL STAINING BY HYDRATED IRON OXIDES
HEMATIZATION
MANGANESE MINERALIZATION
CONTACT-
EXPOSED OR ESTABLISHED BY PITTING
FLOAT MAPPED
INFERRED
STRIKE OF CLEAVAGE AND SCHISTOSITY
DIP AND STRIKE OF CLEAVAGE AND SCHISTOSITY
VERTICAL CLEAVAGE AND SCHISTOSITY
CONTORTION
FAULT
CONTOUR INTERVAL 25 METRES
GRID NORTH APPROX. TRUE NORTH
(HEYFORD - GAUSS SYSTEM)
GEOLOGICAL MAP OF THE MINA DE S. DOMINGOS AREA PORTUGAL
FIELD OBSERVATIONS
OPENCAST GEOLOGY 1923 — A. B. EDGE.
RECONNAISSANCE SURVEY 1951 — A. R. BARRINGER, G. A. BROWN, R.H.C. HOLMAN, AND B. SCOTT.
PRELIMINARY DETAILED MAPPING 1952 — A. R. BARRINGER AND N. RHODEN.
FINAL DETAILED MAPPING 1953 — A. R. BARRINGER.
GEOLOGICAL INVESTIGATIONS 1951 - 1952 - 1953
JOHN S. WEBB SEPT. 1953
METRES
500 400 300 200 100 0 250 500
SCALE 1:10000