A

thesis

entitled

THE MINERALOGY, STRUCTURE AND ORIGIN OF THE LEAD-ZINC-COPPER RESIDUAL OREBODY AT TYNAGH, COUNTY GALWAY, IRELAND

submitted for the degree of

Doctor of Philosophy

in the Faculty of Science

of the University of London

by

CHRISTOPHER JOHN MORRISSEY

Department of Geology

Imperial College of Science and Technology

London

February 1970

Westward aerial view of the Tynagh open pit

ABSTRACT

This thesis describes the geology of a large body of metal-rich rubble and mud at Tynagh in the Republic of Ireland. The unconsolidated materials, which are worked for lead, zinc, copper and silver, are entrenched in Lower Carboniferous limestones underlying the Central Plain of Ireland. They originated by weathering of the upper part of a base metal sulphide orebody, the remainder of which is in limestones underlying the deposit. Weathering initiated from a Tertiary erosion level in which sulphides were being intensely oxidised caused widespread decalcification of mineralised limestones below the water table, but comparatively little alteration on the sulphides and barite they contained. Together with wood fragments and other introduced materials, the sulphide-rich residuum accumulated in a complex of waterlogged cavities, some of them partially roofed. The deposit has a complicated sedimentation history lasting into the glacial Pleistocene, and its structure has been continuously modified by weathering of the underlying limestones. Mechanical concentration of sulphides by weathering has apparently not taken place on a comparable scale elsewhere in the world.

Chemical weathering of the residual deposit has been in progress since it began to form, and its extensive resistate mineralogy has been augmented by numerous secondary minerals. Supergene galena is unusually abundant, and fossil wood has been partially replaced by supergene sulphides of zinc and cadmium. Supergene pyrite is known to have formed since mining began. Large quantities of lead, zinc and copper have been concentrated at the deposit's periphery by reaction between metal-charged groundwaters and the surrounding limestone. The residual orebody has been substantially enlarged in this way. It contains a fossil gossan that has been enriched in silver by weathering processes.

ACKNOWLEDGEMENTS

This research project arose largely from the far-sighted interest in scientific aspects of Irish mineralisation of Dr. D. R. Derry, consulting geologist to Irish Base Metals Ltd., to whom I am indebted for much advice and assistance. It was made possible by a grant from the Natural Environment Research Council, which is gratefully acknowledged. The field investigations were supported financially by Irish Base Metals Ltd. at the behest of Mr. P.J. Hughes, the chairman of the company, and were assisted in many ways by the management and staff of the Tynagh Mine. To them, and to many other people who helped to make my visits to Tynagh productive and enjoyable, I offer my sincere thanks. In this connection I should like to acknowledge the unfailing hospitality of Dr. R.W. Schultz, who made his expert knowledge of Irish ore geology available to me in many long discussions, and the helpfulness of Mr. N. Gillat, Mr. M. Pickard, Mr. D.H. FitzGerald, Mr. R. Oram and Mr. P. Connolly. The sustained cooperation of Mr. D. Whitehead, mine geologist at Tynagh, was expecially appreciated.

The laboratory investigations reported in this thesis were carried out in the Mining Geology Department of Imperial College, and were supervised by Dr. (now Professor) A.P. Millman. Working under the supervision of Professor Millman has been a rewarding privilege, and I am deeply indebted to him for counsel and criticism that have shaped this project.

I am grateful for assistance received in the course of the laboratory investigations and the preparation of this thesis from Professor G.R. Davis and other members of the staff of Imperial

College, and from fellow research students. In particular I should like to thank Mr. R. Curtis, Mr. J. McM. Moore, Mr. T. Kelly, Mr. G. Steed, Mr. J. Patterson, Mrs. E. Hill, Mrs. K. Irving and Mr. J. Gee.

My thanks are due to Dr. P. Williams (University of Dublin), Dr. P. Walsh (University of London), and Dr. M. Sweeting (University of Cambridge), and to Mr. J. van der Burgh (University of Utrecht), Professor W. Watts (University of Dublin), Dr. W. Chaloner and Mr. M. Boulter (both University of London) for guidance in matters relating to the palaeogeomorphology and palaeobotany of the British Isles. Dr. J. Jackson and Mr. D. Romer were valuable sources of information on many subjects relating to the geology of Ireland.

Finally I should like to thank my wife Jackie for her help in preparing photographs and diagrams, and for her infectious patience.

CONTENTS

		Page
ABSTRACT		i
ACKNOWLEDGEMENTS		ii
	PART I	
CHAPTER 1	INTRODUCTION	1
	1.1 Foreword	1
	1.2 Location and ownership of the Tynagh deposit	2
	1.3 Geography	2
	1.4 Previous geological work	3
	1.5 The present investigation	4
CHAPTER 2	REGIONAL GEOLOGY	6
	2.1 Stratigraphy and lithology	6
	2.2 Structure	6
	2.3 Igneous activity	11
	2.4 Mineralisation	12
CHAPTER 3	GEOLOGY OF THE TYNAGH MINE AREA	17
	3.1 Stratigraphy and lithology	17
	3.2 Structure	41
CHAPTER 4	PRIMARY MINERALISATION OF THE TYNAGH MINE AREA	51
	4.1 Introduction	51
	4.2 Distribution	53
	4.3 Mineralogy of the Main Orebody	61
	4.4 The mineralisation sequence	62
	4.5 Metal zoning	84
	4.6 Deformation	87
	4.7 Origin	90

Page

PART II

Introduction 93

Nomenclature 95

CHAPTER 5 COMPOSITION OF THE RESIDUUM 97

5.1 Theoretical decalcification products of rocks of the Tynagh area 97

5.2 Composition of the residuum 104

5.3 Summary and conclusions 117

CHAPTER 6 STRUCTURE OF THE RESIDUAL DEPOSIT 119

6.1 Structure of the western block 119

6.2 Structure of the eastern block 139

6.3 Structure of the central block 153

6.4 Superficial deposits 162

6.5 Summary and conclusions 171

CHAPTER 7 DESCRIPTIVE MINERALOGY 175

7.1 Mineralogy of lead 175

7.2 Mineralogy of zinc and cadmium 204

7.3 Mineralogy of copper 225

7.4 Mineralogy of silver 239

7.5 Principal gangue minerals 244

7.6 Minor gangue minerals 262

Page

CHAPTER 8 CHEMICAL WEATHERING OF THE RESIDUUM 269

8.1 Alteration of primary minerals 269

8.2 Relative weathering rates of primary minerals 284

8.3 Distribution of weathering effects 291

8.4 Weathering of rocks bounding the residual deposit 333

8.5 Summary of weathering history 335

CHAPTER 9 ORIGIN AND AGE OF THE RESIDUAL DEPOSIT 337

9.1 Relative solubility of calcite and sulphides 337

9.2 Controls of residuum formation 341

9.3 Age of the residual deposit 349

9.4 Survival of the residual deposit 358

9.5 Comparison with other residual deposits 363

SUMMARY OF CONCLUSIONS 372

PRACTICAL APPLICATIONS AND IMPLICATIONS OF RESEARCH RESULTS 377

REFERENCES 380

APPENDIX - Sources of illustrated material 397

LIST OF PLATES

Plate		Page
Frontispiece - Aerial view of the Tynagh open pit		
3.1	Diagenetic pyrite in Lower Muddy Limestone	25
3.2	Calp ironstone drillhole cores	36
4.1	Textures in veinlet mineralisation	65
4.2	Corroded dolomite rhomb in sulphides	65
4.3	Colloform-banded pyrite	
4.4	Marcasite euhedra overgrown by pyrite	69
4.5	Replacement of colloform pyrite by sphalerite	71
4.6	Sphalerite cavity-lining	71
4.7	Crystalline aggregate of barite	76
4.8	Guided replacement of sphalerite by galena	76
4.9	Atoll-shaped replacement relics of sphalerite	77
4.10	Framboidal pyrite in tennantite matrix	77
4.11	Galena replacement idioblast in limestone	80
4.12	Galena replacement idioblasts in sphalerite	80
4.13	Galena idioblasts in pyrite	81
4.14	Bournonite inclusions in galena	82
4.15	Jordanite segregation(?) at galena grain margin	82
4.16	Enargite-bournonite intergrowth	83
5.1	Crustified residual sulphide-barite block	109
5.2	Chalcopyrite inclusions in sphalerite	109
5.3	Fossil wood fragment	116
6.1	Transported gossan	125
6.2	Gossan fragments in Calp mud	125
6.3	General view of the Collapse Breccia	128
6.4	Detail of the Collapse Breccia	128
6.5	Margin of the Collapse Breccia	129

Plate		Page
6.6	Calp mud intrusive into disaggregated limestone	138
6.7	Solution subsidence structure	140
6.8	Solution subsidence structure	140
6.9	Detail of resedimented Calp mud	143
6.10	Exposure of the North Tynagh Fault plane	146
6.11	"Draped" Calp ironstone residuum	149
6.12	Contorted relict bedding in ironstone residuum	149
6.13	Subsidence in thin-bedded Calp	150
6.14	Calp/Calp mud contact	150
6.15	Tight fold in partially decomposed Calp	151
6.16	Overlap of Calp mud onto Fossil Gossan	157
6.17	Lower contact of the Gossan Talus	157
6.18	Flexures in Black Calp exposed in the open pit	161
6.19	Subsidence sag in Calp mud	161
6.20	Reworked residuum underlying glacial till	164
6.21	Decomposed off-bank limestones and cave fill	164
6.22	Galway Granite glacial erratic	168
6.23	Peat bog in post-glacial subsidence structure	168
7.1	Drusy galena encrusted by pyrite	187
7.2	Replacement rims of supergene galena on sphalerite	187
7.3	Sphalerite encrusted by supergene galena crystals	188
7.4	Malachite-cerussite intergrowth	202
7.5	Mimetite encrusting malachite	202
7.6	Supergene sphalerite in fossil wood	215
7.7	Microspheroidal supergene sphalerite	216
7.8	Cuprian smithsonite	222
7.9	Supergene chalcopyrite replacing bornite	233
7.10	Barite breccia cemented by malachite and azurite	237
7.11	Malachite veined by cerussite and azurite	237

Plate		Page
7.12	Supergene native silver in tennantite	242
7.13	Supergene barite crystals	248
7.14	Supergene barite crystals	249
7.15	Crystalline marcasite	256
7.16	Pyrite microcrystallites and framboidal aggregates	256
7.17	Diagenetic and epigenetic forms of pyrite	257
8.1	Cleavage-guided alteration of galena	272
8.2	Grain boundary-guided alteration of galena	272
8.3	Patchy alteration of galena	273
8.4	Galena relics in cerussite	273
8.5	Replacement of galena by anglesite	274
8.6	Replacement of galena by chalcocite	274
8.7	Secondary copper sulphide replacements of galena, sphalerite and chalcopyrite	275
8.8	Partially dissolved sphalerite grains	276
8.9	Chalcocite rim on chalcopyrite	280
8.10	Covellite rims on chalcopyrite	280
8.11	Alteration of chalcopyrite to chalcocite and limonite	281
8.12	Cleavage-guided dissolution of barite	283
8.13	Selective alteration of galena	285
8.14	Selective alteration of galena	285
8.15	Alteration of chalcopyrite and tennantite	288
8.16	Dissolution of dolomite	288
8.17	Cerussite overgrowth on supergene galena	295
8.18	Mineralised newt carcase	299
8.19	Pyrite mineralisation in newt carcase	299
8.20	Smithsonite pseudomorph of limestone	312
8.21	Granular aggregate of smithsonite	312
8.22	Limonite replacement of framboidal pyrite	322

LIST OF FIGURES

Fig. No.		Page
	Location map and geological map of the neighbourhood of the Slieve Aughty Mountains	Pocket Map 1
2.1	Simplified surface geology of Ireland	7
2.2	Lead-zinc-copper occurrences in Ireland	13
3.1	Stratigraphic column of the Tynagh area	18
3.2	Geological cross-section of the Tynagh Mine area	19
3.3	Geological map of the Tynagh Mine area	20
3.4	Plan and section of the Tynagh Iron Formation	32
4.1	Main Orebody cross-sections on 94W, 84W and 77W	54
4.2	Metal distribution in the Main Orebody	55
5.1	Structure and lithology of rocks bounding the residual deposit	Pocket Map 2
5.2	Metal distribution in rocks bounding the residual deposit	103
6.1	Borehole location plan	120
6.2	Schematic cross-sections of the residual deposit	Pocket Map 3
6.3	Residual deposit bench maps, 5180 and 5160	Pocket Map 4
6.4	Structure of the residual deposit in horizontal sections 5140, 5120, 5100, 5080, 5060, 5040, 5020, 5000, 4980 and 4960	Pocket Map 5
6.5a	Lead and silver distribution in the residual deposit	121
6.5b	Copper and zinc distribution in the residual deposit	122
6.6	Contour map of the base of the gossan talus	159

Fig. No.		Page
6.7	Superficial deposits of the Tynagh mine area	167
7.1a	Lead:silver relationships in the Main Orebody and residuum	181
7.1b	Heavy metal relationships in sulphide concentrates	182
7.2	Silver content of hydrothermally synthesised PbS	184
8.1	Distribution of some supergene minerals in the residual deposit	293
8.2	Spatial variation in the relative abundances of sulphides and non-sulphides of lead and zinc, 5160 bench	Pocket Map 6
8.3	Assay profiles through the zone of lead and copper carbonate enrichment	309
8.4	Assay profiles through the zone of zinc carbonate enrichment	311
8.5	Stability fields of some lead and copper minerals	315
9.1	Calcite solubility curves	339
9.2	Eh/pH characteristics of some natural waters	340
9.3	Tertiary and Pleistocene-interglacial deposits in central Ireland	353

LIST OF TABLES

Table No.		Page
2.1	Stratigraphic succession of west-central Ireland	8
5.1	Chemical composition of Lower Carboniferous rocks bounding the residual deposit	100
5.2	Main non-carbonate constituents of Lower Carboniferous rocks bounding the residual deposit	101
5.3	Chemical composition of mineralised Calp mud	106

Table No.		Page
6.1	Typical grades of residual ore types	123
7.1	Mineralogy of the residual deposit	176
7.2	Spectrographic analyses of galena	179
7.3	Reflected light optics of some lead sulphosalts	192
7.4	X-ray powder data for geocronite	193
7.5	Qualitative x-ray fluorescence analyses of some secondary minerals	196
7.6	X-ray powder data for beudantite	200
7.7	X-ray powder data for bayldonite	205
7.8	Spectrographic analyses of sphalerite	210
7.9	Assays of fossil wood	214
7.10	X-ray powder data for zinc and cadmium sulphides	218
7.11	X-ray powder data for aurichalcite	224
7.12	Spectrographic analyses of tennantite	228
7.13	X-ray powder data for mercurian silver	243
7.14	Chemical analyses of barite concentrates	246
8.1	Solubilities of some sulphides and chlorides in water at approximately 25°C, 1atm.	290
8.2	Solubilities of some sulphates and carbonates in water at approximately 25°C, 1atm.	318
9.1	Stages of the British Pleistocene	352

CHAPTER ONE

INTRODUCTION

1.1 FOREWORD

Late in 1961, drill holes put down to investigate a geochemical anomoly in soils near the village of Tynagh in County Galway encountered, immediately below the glacial till, a considerable thickness of gritty black mud. The mud was at first disregarded as a potential ore material, but when samples were sent for assay, extremely high lead values were obtained. Further drilling defined a five million ton body of rubble and mud rich in lead, zinc, copper and silver, and showed in addition that the underlying limestones were strongly mineralised by base metal sulphides and barite.

The Tynagh mineralisation proved to be the first virgin base metal deposit of major economic importance to be found in the British Isles for over a century. Its discovery gave impetus to a surge of interest in the mineral resources of Ireland that has since resulted in the discovery of several other orebodies.

This thesis is mainly concerned with the unconsolidated ore deposit at Tynagh (Part II), which it describes in detail for the first time. The solid rock geology of the Tynagh area (Part I) is described at a length dictated by the circumstances of the deposit's formation. Descriptive mineralogy has been consolidated in a chapter (Chapter 7) that is intended to complement an account of the weathering history of the deposit in the following chapter. Otherwise the layout of the thesis needs no explanation.

1.2 LOCATION AND OWNERSHIP OF THE TYNAGH DEPOSIT

The Tynagh base metal deposit lies about a mile to the north of the village of Tynagh, County Galway, which is 36 road miles east of the port of Galway, 40 air miles north-east of Shannon international airport, and 90 air miles west of Dublin (Fig. 1.1). The nearest railhead is Loughrea, about nine miles to the west, from which the mine is approached by all-weather tarmac roads.

The map location of the mine area (53°10'N, 8°23'W) is included in Ordnance Survey One-inch Sheet 116, and straddles the junction of Six-inch Sheets GALWAY 106, 107, 116 and 117.

The deposit is owned by the Irish State and is worked under a lease agreement by Irish Base Metals Limited, a wholly-owned subsidiary of Northgate Exploration Limited of Toronto, Canada.

1.3 GEOGRAPHY

The country around Tynagh is mainly pasture and arable land of low relief, with thin developments of peat bog in local depressions. North and east of the mine, which lies at about 200 ft. above Irish Ordnance Datum*, stretches a gently undulating plain floored by Carboniferous Limestone. Local relief, rarely exceeding 25 ft., is provided by eskers, kames and other accumulations of the glacial drift that generally mantles bedrock in this part of Ireland. To the south a broad, shallow valley lies between the mine area and a rolling highland of pre-Carboniferous rocks, the Slieve Aughty Mountains, in which elevations reach 1314 I.O.D. Low limestone hills are the main topographic feature of the country between Tynagh and Loughrea.

The mean annual rainfall of the district is about 50 in. Rain tends to be an almost daily occurrence for weeks at a time,

---

*Irish Ordnance Datum (I.O.D.) is about 8 ft. below mean sea level around Ireland and the same distance below English Ordnance Datum (O.D.).

irrespective of the season of the year. Drainage of the country within a three-mile radius of the mine is largely sub-surface, though a few small tributaries of two rivers that ultimately discharge into Lough Derg near Portumna rise in the area. The mean annual air temperature is about 10°C.

1.4 PREVIOUS GEOLOGICAL WORK

The geology of the country around Tynagh was first mapped and described just over a hundred years ago by G.H. Kinahan (1865). The One-inch Geological Survey map of the district has not subsequently been revised, though minor additions have been made to the Survey's Six-inch manuscript maps.

During the past eight years, geologists of Irish Base Metals Ltd. have re-mapped the company's original 17-square mile licence area centred on the Tynagh deposit on a scale of six inches to a mile, logged the cores of 300 or so boreholes sunk to depths of over 1,700 ft. (most of them in the immediate vicinity of the deposit), and made various geological investigations for ore exploration and proving purposes. Mapping and limited drilling programmes have been carried out by other companies with prospecting interests in the district. Since exploitation of the Tynagh deposit started, much additional information about the geology of the ores and their environment has been accumulated by the geological staff of Irish Base Metals Ltd.

A general account of the geology of the Tynagh deposit by Derry, Clark and Gillat was published in 1965. In 1966 Schultz described a cherty ironstone formation in the Lower Carboniferous rocks of the mine area. Both papers were based largely on drill-hole information, though the authors of the first did base their description of the mud and rubble ores partly on exposures in three 20 ft. trenches that had been excavated across the orebody

after stripping of the overburden. There was subsequently published a brief exchange of views between Derry (1966) and Schultz (1966) on the possibility of a genetic relationship between the sulphide-barite mineralisation and the thin ironstones and tuffs in the Lower Carboniferous succession of the mine area.

Donovan (1965) carried out geochemical prospecting research work in the Tynagh area between 1963 and 1965, and Lees (1964) studied limestones west of Tynagh as part of a regional investigation of Waulsortian bank limestone facies. In 1965 the writer described the deposit in an undergraduate dissertation.

The most recent and detailed account of the solid-rock geology of the Tynagh area is contained in a doctoral thesis submitted in 1968 to the University of Dublin by Schultz. Schultz described the rubble and mud deposit that is the subject of this thesis in a 2,000-word appendix based largely on information provided by the writer.

1.5 THE PRESENT INVESTIGATION

The main objectives of the present investigation were:

(a) to elucidate the structure and mineralogy of the deposit of metalliferous mud and rubble known as the Tynagh residual orebody;
(b) to establish the provenance of its constituents; and
(c) to determine the manner, controls and time of the deposit's formation.

Other aims related to these were to establish the genetic relationship between the orebody and so-called sink-fill deposits of various kinds elsewhere in the British Isles and other parts of the world; and to assess the geomorphological implications of the orebody's formation and preservation in a part of Ireland

that contains little material evidence of the course of geological events between the Carboniferous and the Pleistocene.

The writer's field work at Tynagh was begun in the summer of 1964, when he spent two months at the mine preparing an undergraduate dissertation on the geology of the deposit as a whole. Since then he has visited the mine on eight separate occasions and spent a total of about seven months there, mainly mapping mining faces, logging drill core, and collecting study material. Some complementary fieldwork was carried out in other parts of Ireland, in England, and in Sardinia. Laboratory work at the Royal School of Mines, London, included microscopic examination of polished sections, thin sections and hand specimens, x-ray diffraction studies and electron probe microanalyser investigations. Partial spectrographic analyses were made of a few samples of the main sulphide ore minerals in the deposit, but variations in the trace element composition of particular species were not investigated systematically.

An integral part of the investigation was a study of the mineralogy, chemistry and structure of the rocks surrounding the residual body, and of the nature and distribution of mineralisation in those rocks. This has involved some duplication of the research work of Schultz, but there is no overlap in the objectives of the two investigations. It has yielded information relevant to the present study about some aspects of the primary mineralisation of the Tynagh deposit, such as the mineralogy of minor phases and the trace element composition of major phases, that Schultz did not have facilities to investigate.

CHAPTER TWO

REGIONAL GEOLOGY

Tynagh is situated in a part of Ireland, termed geographically the Central Plain, that is extensively underlain by gently flexed Lower Carboniferous limestones (Figs. 1.1, 2.1). Framed by the Carboniferous sediments are large and small tectonic inliers of Devonian and Lower Palaeozoic rocks, many of them elongated on a NE-SW or ENE-WSW axis. The main faults of the region have the same trend. The region contains no known Permian, Mesozoic or Tertiary rocks. Pleistocene glacial deposits are very extensive, and in the drift-mantled lowlands underlain by Carboniferous limestone bedrock exposures are generally scarce. For this reason the stratigraphy and structure of large areas are known only in outline. The main topographic relief of the region is provided by the larger inliers of pre-Carboniferous rocks.

2.1 STRATIGRAPHY AND LITHOLOGY

The generalised stratigraphic succession of the region, and the lithologies of the various stratigraphic elements, are summarised in Table 2.1.

2.2 STRUCTURE

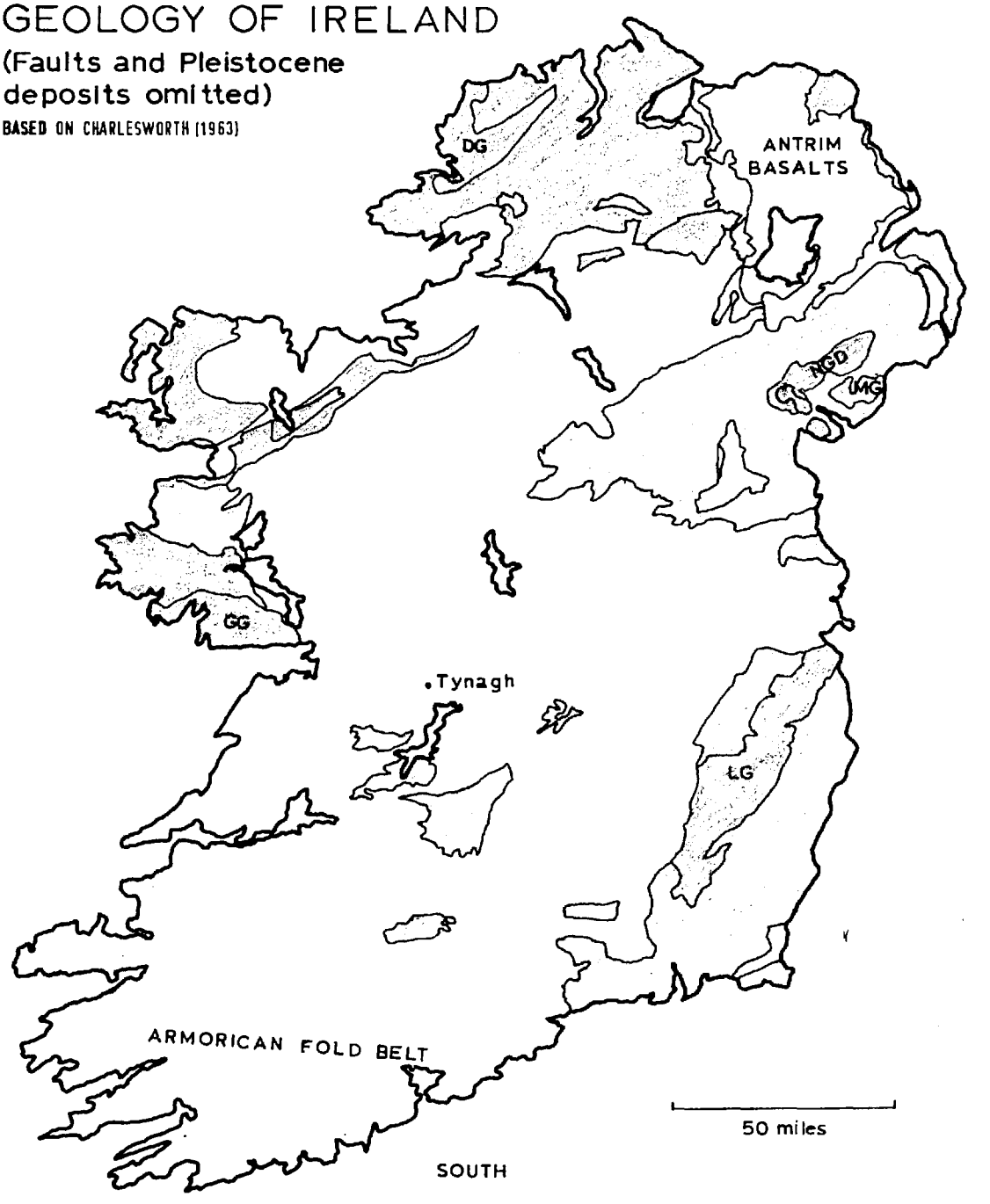
Lower Palaeozoic rocks exposed in inliers are generally steep-dipping and folded about ENE-WSW axes. Strong concentric folding and associated reverse and wrench faulting have been described in the Lower Palaeozoic rocks of Slieve Bernagh and the Cratloe Hills by Weir (1962). These structures, attributed to Caledonian compression, are displaced by faults striking E-W to ENE-WSW that are considered by Weir to be due to release of

SIMPLIFIED SURFACE GEOLOGY OF IRELAND

Fig. 2.1

(Faults and Pleistocene deposits omitted)

BASED ON CHARLESWORTH (1963)



Tertiary

Mesozoic

Upper Palaeozoic

Lower Palaeozoic

Moinean and Dalradian

Post-Carboniferous Plutons

MG - Mourne Granite (Tertiary)

Pre-Carboniferous Plutons

NGD - Newry Granodiorite (Devonian)

DG, GG, LG - Donegal, Galway and Leinster Granites (Lower Palaeozoic)

C.J.M. 1969

Table 2.1 Generalised stratigraphic succession of west-central Ireland (after Schultz, 1968)

		Formation	Thickness (feet)	Lithology
LOWER CARBONIFEROUS	Visean	Upper Limestone	up to about 1,900	Bioclastic limestones, in part oolitic or cherty. Subordinate interbedded shales.
		Middle Limestone	up to about 1,500	Bank facies (Waulsortian): Pale micritic-skeletal limestones with small amounts of terrigenous material; biomicrite/crinoidal limestone cover developed locally. (0-900 ft.) Basin facies (Calp): Dark medium- to fine-grained limestones, moderately fossiliferous in part, with interbedded shales. Commonly argillaceous and carbonaceous. Very cherty in places. (0-1,500 ft.)
	Tournaisean	Lower Limestone	700-1,000	Upper part: Dark argillaceous micrites and bioclastic limestones. Nodular chert towards the top locally. Lower part: Dark bioclastic limestones with small amounts of argillaceous material as whispy partings and thin shale interbeds.
		Lower Limestone Shale	175-200	Sandstones, siltstones and thin fossiliferous limestones grading up into argillaceous limestones and fossiliferous shales. Includes 10-15 ft. laminated non-calcarous siltstone/shale (Ballyvergin Shale).
UPPER DEVONIAN		Old Red Sandstone	500-1,200	Fluviatile sandstones (feldspathic to arkosic), in part conglomeratic; flaggy siltstones, shales and marlstones. Thin limestones towards the top.
Angular Unconformity				
LOWER PALAEOZOIC			unknown	Silurian shales, siltstones and minor conglomerates. Ordovician greywackes with subordinate shales and chert beds; andesitic volcanics and minor intrusives locally.

Proto-Armorican (pre-Upper Devonian) compression. Schultz (1968) attributes them to release of Caledonian compression.

The main tectonic structures in the Devonian and Carboniferous rocks of the region are:-

i) extensive dome-shaped and periclinal structures that bring pre-Carboniferous rocks to surface in the Slieve Aughty, Slieve Bernagh, Slieve Bloom and Silvermines Mountains, and many small structures of the same type in the cores of which Devonian, and in some cases Lower Palaeozoic, rocks are exposed. The axis of elongation of most of the periclines is approximately NE-SW.

ii) broad, gentle folds about axes striking NE-SW to ENE-WSW in the Devonian rocks of the larger inliers. The plunge of these folds in the Slieve Aughty inlier is westward on the western flanks of the inlier, and eastwards on the eastern flanks, and the folds apparently die out rapidly in the surrounding Lower Carboniferous. The axis of the broad westward-plunging East Clare Syncline trends ENE-WSW, and gentle folds elsewhere in the Lower Carboniferous of the region have similar axial trends.

iii) normal faults, some with maximum displacements of well over 1,000 ft., striking approximately ENE-WSW and dipping north or, less commonly, south. Faults with this trend can be traced for distances of many miles in and at the tectonic boundaries of pre-Carboniferous inliers. In most cases they are presumed to die out rapidly when they pass into the Lower Carboniferous rocks. In the Silvermines district, County Tipperary, ENE-WSW gravity faulting was accompanied by subsidiary N-S and ESE-WNW fracturing (Rhoden, 1958). The main ENE-WSW fault at

Keel, County Longford, is displaced by faults striking approximately N-S (Morrissey et al, 1969), and faults trending at high angles to the main E-W fault are indicated at Tynagh. In Counties Clare and Galway mineral veins that may have been localised faults in Lower Carboniferous rocks strike in various directions. Old mining records suggest that most of the exploited veins are alligned N-S, NW-SE or NE-SW.

The age of these structures in the Upper Palaeozoic rocks of the region is uncertain. They are generally considered to have resulted from Permo-Carboniferous (Armorican) earth movements that caused strong deformation of Devonian and Carboniferous rocks in the south-western part of the country, and to have been influenced by NE-SW structures in the Caledonian foundation of the Central Plain (Morrissey et al, 1969). Gill (1962) considers that Armorican compression directed approximately northwards had a far-reaching effect on the Upper Palaeozoic rocks of Ireland. He divides the region to the north of the belt of strongest folding into a southern part in which the main effects of lateral compression were isoclinal folding and reverse faulting, and a northern part including the Tynagh area in which it resulted in broad, open folding and normal faulting. Schultz (1968) has suggested that some of the major folds and faults in the Slieve Aughty Mountains and neighbouring areas, including those of the Tynagh area, resulted not from the imposition and release of lateral compression but from vertical uplift at local centres. This may have resulted from deep-seated magmatic activity. He considers that uplift took place largely during Permo-Carboniferous times, but that it may have been initiated at some centres before or during the late Devonian. Sedimentary non-sequences and local slumping in the Carboniferous rocks of the region are possibly

manifestations of minor disturbances in early Visean and post-Visean pre-Dinantian times that presaged the main Permo-Carboniferous earth movements. Powerful tectonic uplift of the Leinster Massif 70 miles south-east of Tynagh probably took place in mid-Visean times (Charlesworth, 1963).

As the region contains no post-Carboniferous rocks in which to observe the effect of the structures described above, it must be allowed that some of them may have been initiated since Permo-Carboniferous times. There is growing evidence that Mesozoic and Tertiary earth movements caused widespread reactivation of Caledonian and Armorican structures in Ireland (Dewey and McKerrow, 1963; Blundell et al, 1968).

2.3 IGNEOUS ACTIVITY

Ordovician volcanics and associated minor intrusives are exposed in the Slieve Aughty Mountains and other inliers. Petrographically similar rocks have been penetrated by drill holes at Tynagh. The only plutonic rocks that outcrop in the region are those of the Connemara granite complex. The youngest element of the complex is the composite Galway Granite (Fig.2.1), which is early Devonian in age (Leggo et al, 1966). At its eastern margin, which is some 25 miles to the west of Tynagh, the Galway Granite is transgressed by Lower Carboniferous sediments. No intrusives or extrusives have been recognised in the Silurian or Devonian rocks of the region.

Spasmodic vulcanicity occurred at local centres in the region during the Lower Carboniferous. The main centre of activity seems to have been 40 miles south of Tynagh, where lava flows, pyroclastics and minor intrusives of early Visean and mid-Visean age, and ranging in composition from basic (olivine-basaltic) to intermediate (trachytic), form the Pallas Hills near Limerick (Fig.2.2). Another centre was at Edenderry 50 miles north-east of Tynagh, where a vent of basaltic agglomerates, breccias and lapilli tuffs

cuts through Lower Visean limestones, and associated pyroclastics are interbedded with Calp and Upper Limestone. Pyroclastics of early and mid-Visean age occur at many places in Counties Clare, Limerick and Cork. At Tynagh thin beds of reworked trachytic tuff are interbedded with Lower Visean cherty ironstones and bioclastic limestones. All these pyroclastics may be the products of the Limerick volcanic centre, though there may have been other centres of activity that have not yet been located. If vulcanicity occurred in the Tournaisean its products have not yet been recognised.

The main centres of Tertiary magmatism were in north and north-east Ireland, well outside the region under consideration. The nearest Tertiary intrusives to Tynagh are teschenite and dolerite dykes about 70 miles away to the north-west. There are unconfirmed reports that dykes presumed to be Tertiary in age have lately been intersected in boreholes through Lower Carboniferous limestones about the same distance to the north-east of Tynagh (Jackson, pers. comm.).

2.4 MINERALISATION

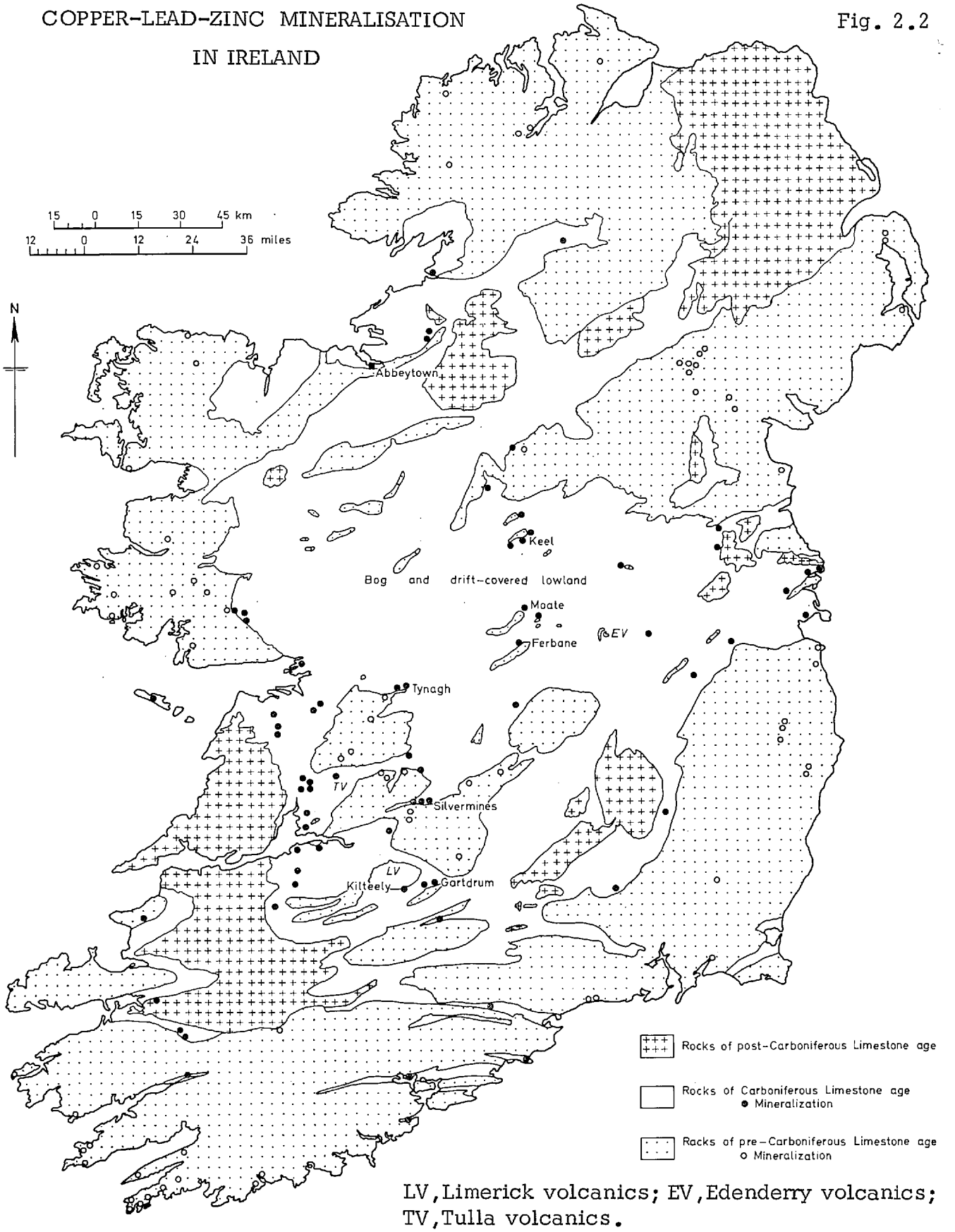
Four major base metal deposits with proved ore reserves at the present time ranging between five and fifteen million tons are situated in the Central Plain (Fig. 2.2). Numerous other occurrences of base metal sulphides are known in the region.

The most widely distributed economic minerals are galena, sphalerite, chalcopyrite and members of the tetrahedrite-tennantite series. Minor associates of these that have been reported from several deposits include enargite, bournonite, boulangerite, geocronite and jordanite. Calcite and barite are the commonest gangue minerals, and pyrite and dolomite are

COPPER-LEAD-ZINC MINERALISATION

IN IRELAND

Fig. 2.2



LV, Limerick volcanics; EV, Edenderry volcanics; TV, Tulla volcanics.

From Morrissey et al., 1969

major gangue constituents in some places. Mineralisation in a number of the deposits contains economically significant amounts of silver, which is variously associated with galena, tetrahedrite-tennantite and sphalerite.

Most of the deposits are in Lower Carboniferous limestones, but host rocks range in age from Ordovician to Upper Carboniferous, and their lithologies include sandstone, conglomerate, shale and grit as well as various types of limestone. The style of mineralisation is similarly variable, ranging from discordant veins and massive replacements to, at one deposit, an extensive stratiform sulphide body that is apparently concordant with the enclosing sediments.

The four major deposits and their main ore metals are Gortdrum (Cu, Hg), Silvermines (Zn, Pb), Tynagh (Pb, Zn, Cu) and Keel (Zn). The Silvermines mineralisation complex includes a massive barite body worked for that mineral alone, and barite concentrates are a by-product of base metal mining at Tynagh. At Silvermines, too, occurs a large replacement body of secondary zinc minerals, mainly smithsonite and hemimorphite, that has been sporadically mined.

All the major deposits occur in deformed Lower Carboniferous rocks on the flanks of tectonic inliers of Devonian sandstones and, at Silvermines, Silurian shales. In each case there is evidence of tectonic control of the distribution of mineralisation. The main faults at all four localities strike approximately ENE-WSW.

A comparable uniformity in structural setting is not apparent in the minor base metal sulphide occurrences of the region. Some of the occurrences in E. Clare seem to have resulted from the impounding of upward-moving mineralising fluids by shale or

chert horizons (Charlesworth, 1963; Halloff et al, 1962).

Whether all the mineralisation in Upper Palaeozoic rocks is of essentially the same age and origin is not known. Charlesworth (1963) postulated an Armorican age and a hydrothermal origin for all the mineralisation in the region that had been discovered up to 1959. He related it genetically to veins and irregular bodies of chalcopyrite and other copper minerals in quartz gangue, and veins of barite and hematite, in Devonian and Lower Carboniferous rocks in the Armorican fold belt of S.W. Ireland.

Holmes-Houterman model ages of galenas from seven deposits in E. Clare determined by Pockley (1961) have an arithmetic mean of 289 $\pm$ 40 m.y., which encompasses much of the Permian, all the Upper Carboniferous, and part of the Lower Carboniferous. Hydrothermal activity, perhaps during the Triassic or early Jurassic, was considered by Rhoden (1958) to have been the cause of the mineralisation in the Silvermines district that was known in 1958.

Geological study of the important mineralisation discovered since 1959 is still at an early stage, and only the primary mineralisation at Tynagh has been described in detail. The origin of the Tynagh mineralisation is discussed elsewhere in this thesis.

The mineralisation at Gortdrum which includes primary chalcocite, cinnabar and other minerals that have not been reported from any of the other deposits, appears on field evidence to be epigenetic (Thompson, 1967). The Silvermines "G" Zone mineralisation, which apparently differs in certain major respects from the mineralisation described by Rhoden, has textural features and field relationships that suggest an Upper

Tournaisean or Lower Visean synsedimentary origin for the upper orebody (concordant stratiform, fine-grained and mineralogically simple) and an epigenetic-hydrothermal origin, perhaps followed by stress remobilization locally, for the rest (Gordon-Smith, pers. comm.).

CHAPTER THREE

GEOLOGY OF THE TYNAGH MINE AREA

3.1 STRATIGRAPHY AND LITHOLOGY

The stratigraphic succession of the Tynagh mine area is shown in Fig. 3.1. Most of the contacts indicated are lithologically gradational over as much as 50 ft. and are positioned according to arbitrary criteria. The conformable contact between the Carboniferous and the Devonian, for instance, has been placed at the level at which fossils of marine fauna first become apparent in hand specimen. The junction between the Tournaisean and the Visean is arbitrarily drawn at the upper contact of the Lower Limestone. The main lithological variations in the Visean of the area are between sediments of different facies.

A. Lower Palaeozoic

Lower Palaeozoic rocks do not outcrop in the area, but greywackes, greywacke conglomerates and shales assigned by Schultz (1968) to the Ordovician because of their lithological similarity to rocks of that age exposed in the Slieve Aughty inlier have been intersected at depths of 400 ft. or more below surface in four boreholes into the North Tynagh Fault footwall block (Fig. 3.2). A lamprophyre intrusive, presumed by Schultz to be a dyke related genetically to Ordovician volcanic activity that is manifest in the composition of the greywacke conglomerates, was intersected in one borehole.

B. Upper Devonian

Devonian rocks form few natural outcrops in the area, and the bounds of the Tynagh Devonian inlier (Fig. 3.3) have been

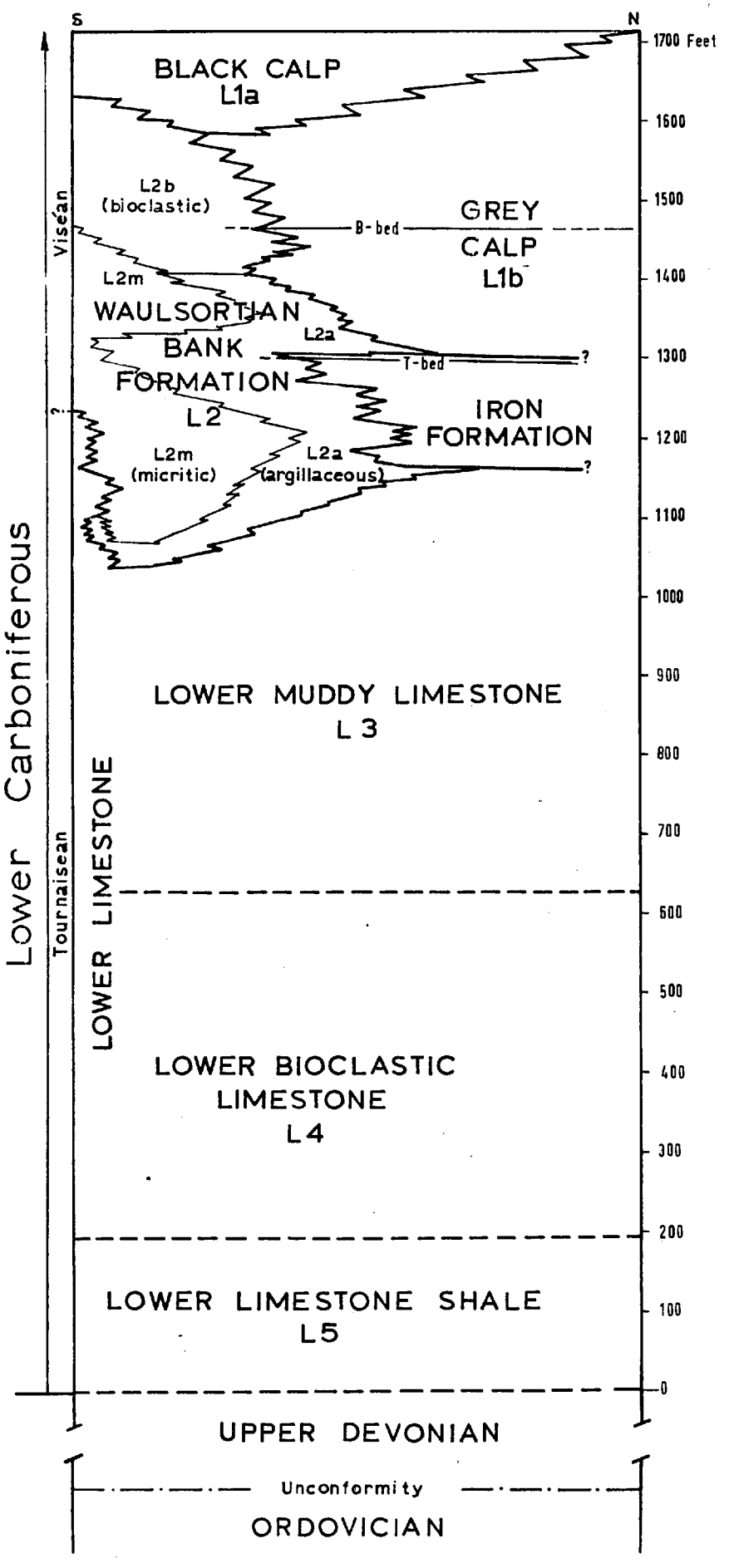
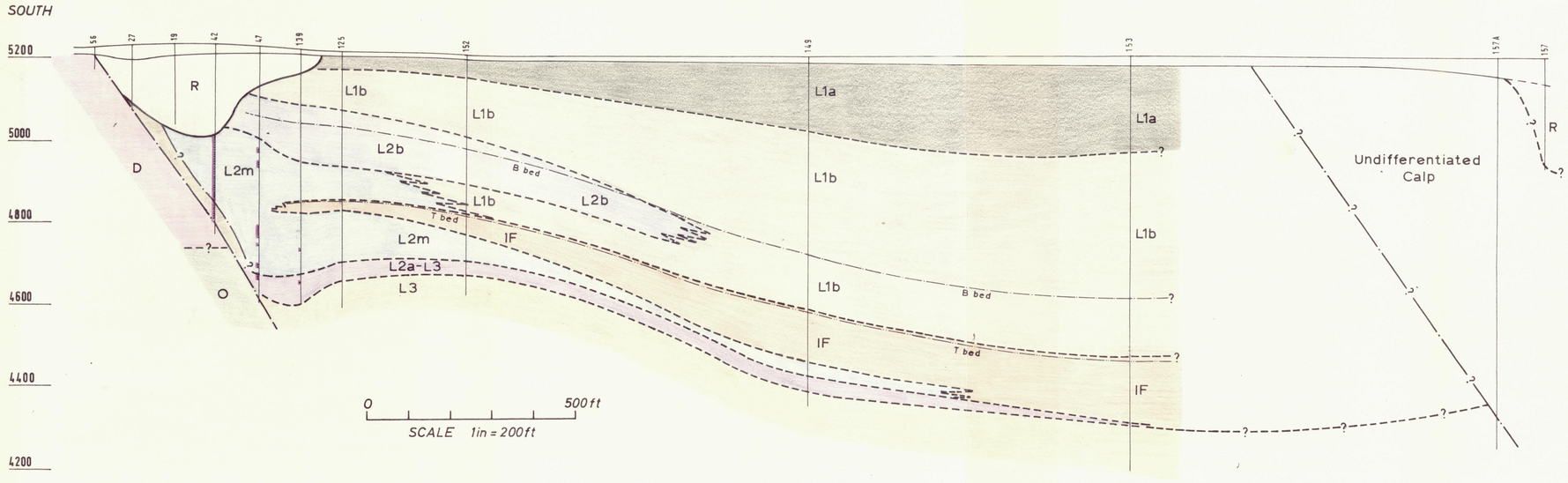


Fig. 3.1

Generalised stratigraphic succession of the Tynagh Mine area

AFTER SCHULTZ (1968)

Fig. 3.2



EXPLANATION

- Till
- R — Residuum
- L1a — Black Calp
- L1b — Grey Calp

Calp

- L2a — Argillaceous limestones
- L2b — Bioclastic limestones
- L2m — Micritic limestones
- IF — Iron Formation
- L3 — Lower Muddy Limestone

Waulsortian Bank Formation

LOWER CARBONIFEROUS

- D — UPPER DEVONIAN
- O — ?ORDOVICIAN

Fault

Ore-grade primary mineralisation

Elevations above Mine Datum (-5000 I.O.D.)

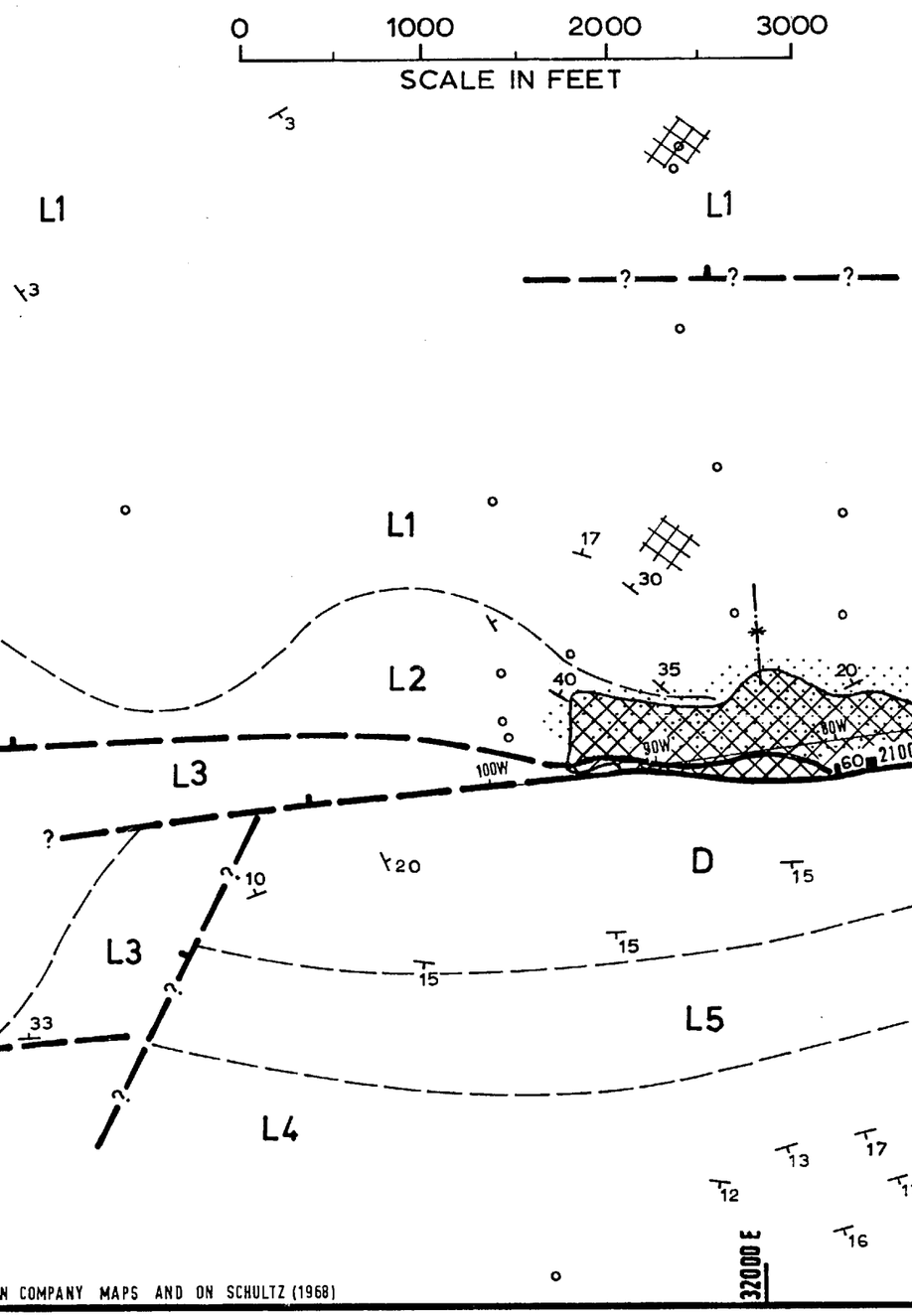
GEOLOGICAL SECTION OF THE TYNAGH MINE AREA AT 85W.

C.J.M. 1969

BASED ON COMPANY DATA AND SCHULTZ (1968)

Fig. 3.3

GEOLOGICAL MAP OF THE TYNAGH MINE AREA



mapped largely on the distribution of sandstone blocks in drift, and on topographic criteria. The conformable contact between Lower Carboniferous and Devonian sediments in the hanging wall block of the North Tynagh Fault has been penetrated by a few boreholes. Devonian rocks in the footwall block have been penetrated by numerous boreholes, and are well exposed in the south wall of the open pit. Borehole intersections leave some uncertainty as to whether or not the Devonian has a faulted contact with the Ordovician: if not, or if the fault cuts out little of the Devonian succession, the total thickness of the latter in the Tynagh area is probably about 750 ft.

The rocks of the Devonian succession are predominantly sandstones, with subordinate siltstones, shales and marlstones. Those exposed in the mine area are well-bedded in 1-5 ft. units. Individual beds tend to be irregular in thickness or slightly lensoid.

The sandstones are medium to coarse grained, and mainly pale grey or greenish grey in an unweathered condition. Constituent grains are generally sub-rounded to sub-angular, $\frac{1}{4}$-1 mm. in size and fairly well sorted. Strained quartz comprises 70-90% of the grains of typical sandstone, and other constituents are vein quartz, microcline, perthite, orthoclase, sodic plagioclase and muscovite. The silica cement, and to a lesser extent the clastics, are often partially replaced by calcite, which is probably a late-diagenetic feature in the main.

The basal few inches of certain sandstone beds exposed in the open pit are conglomeratic, and gritty and pebbly phases are common at other levels in the Upper Devonian succession. Pebbles comprise vein quartz, metamorphic quartzite and occasionally schist that, with fragments of grey and black shale that the

sandstones also contain, are presumed to have been derived from denuded prominences of Lower Palaeozoic rocks in the floodplains in which the sediments accumulated. Cross-bedding and sparse remains of terrestrial flora in sandstones are evidence that the sediments were deposited in an estuarine-fluviatile environment.

The grain composition of the siltstones and shales differs little from that of the sandstones. Muscovite is more abundant, and in some beds the clay minerals of the matrix are interspersed with hematite or chlorite that colours the sediments red or green respectively. Calcite occurs as a matrix constituent and as irregular clots and veinlets. The shales grade petrologically into calciferous shales and marlstones.

C. Lower Carboniferous

i) Lower Limestone Shale

The basal member of the Lower Carboniferous represents a sedimentological link between the estuarine-fluviatile sediments of the Upper Devonian and calcareous marine sediments deposited in the northwards-transgressing Carboniferous sea. It comprises a 175-200 ft. thick alternating sequence of sandstones and siltstones that are indistinguishable in hand specimen from equivalent Devonian sediments, interbedded with shales and bioclastic limestones that become thicker, less sandy and more argillaceous towards the top of the sequence.

The Lower Limestone Shale has a narrow sub-outcrop below till on the unfaulted margins of the Tynagh Devonian inlier (Fig. 3.3). It is not known to form bedrock elsewhere in the area.

ii) Lower Limestone

The Lower Limestone includes the Lower Bioclastic Limestone, which is about 400 ft. thick in the mine area, and the overlying Lower Muddy Limestone, which is about 800 ft. thick. The Lower Limestone is exposed in small outcrops at a few places in the neighbourhood of the mine. Its upper division is well exposed in the open pit in a narrow fault slice in the immediate hanging wall of the North Tynagh Fault, and has been intersected in numerous boreholes.

The limestones of the lower divisions are predominantly grey, moderately well-bedded calcarenites and calcirudites that consist mainly of grain-supported brachiopod, crinoid, bryozoa and coral debris. Matrix materials include fine organic debris, sparry calcite, and micritic and argillaceous materials coloured dark grey to black by finely dispersed carbonaceous matter. Shale, silty shale and occasionally siltstone occur as thin interbeds. Well-preserved brachiopods and rugose corals, especially spiriferid and zaphrentid types respectively, are fairly common. Colonies of the tabulate coral Syringopora are sometimes found.

The sediments of the upper division are similar to those of the lower division, comprising calcarenites and calcirudites interstratified with black shales and occasional thin silty shales and siltstones. Overall, however, they are very much more argillaceous and carbonaceous. Typical shaley material contains about 25% (by weight: see footnote) silica, partly as detrital and authigenic quartz and partly as microscopic chert replacements of calcareous fossils.

Footnote: Except where otherwise stated, weight percentages will be used throughout this thesis.

As a whole, the Lower Muddy Limestone probably contains about 1% by volume of diagenetic pyrite. Individual shaley phases contain several times that amount. The pyrite occurs mainly as dispersions and clusters of micro-euhedra, framboidal and other microspheroidal aggregates, and anhedral grains (Plate 3.1). Replacements of calcareous fossils, carbonaceous matter and detrital quartz grains by diagenetic pyrite are fairly common.

Scattered idioblastic rhombs and crystalline aggregates of diagenetic ferroan dolomite constitutes a percent or so of typical Lower Muddy Limestone, and diagenetic replacement of sedimentary calcite by ankeritic carbonate is commonly seen in thin section. Disseminated 1-2 mm. crystals of arsenopyrite that are occasionally found in Lower Muddy Limestone, in some cases well beyond zones of known epigenetic mineralisation, may also be of diagenetic origin.

A textural characteristic of the Lower Muddy Limestone is the presence, in large parts of the sequence, of irregular clots, lenticles and roundish lumps of bioclastic limestone enclosed in flow-structured argillaceous materials, giving the whole a turbid appearance in hand specimen. These structures are thought to have resulted from gravitational creep of partly lithified sediments down a gently inclined bottom slope, causing distortion and disruption of plastic carbonate layers and flow of muddy sediments into pinched areas and gaps.

Plate 3.1 - Diagenetic pyrite and carbonaceous matter (c) in Lower Muddy Limestone. Polished section.

The sources of illustrated materials are given in Appendix 1.

iii) Waulsortian Bank Formation[1]

The Waulsortian limestones of the Tynagh mine area constitute a bank-like structure elongated parallel to and partly abutting a major fault - the North Tynagh Fault - that forms the southern limit of the primary and the residual orebodies (Figs. 3.2, 3.3).

The lithology and structure of the Waulsortian bank limestones of west-central Ireland have been described by Lees (1961, 1964), who concludes that they formed by accumulation of chemically precipitated carbonate mud and the debris of shallow shelf-sea organisms. The organic debris was originally held in place by non-skeletal organisms. In this respect the banks differ from true reefs, which characteristically have, at the acme of their development, a rigid organic framework capable of being preserved in fossil form. Lateral and vertical growth of the banks in various modifications of a basic knoll pattern took place by successive deposition of overlapping carbonate sheets. The largest of the sedimentary structures so formed were elongated banks that may not have risen more than 50 ft. above the local sea floor. Lateral growth of individual banks led to the formation of aggregate complexes of considerable extent.

The Tynagh bank evidently represents the fault-truncated local forefront of a complex of Upper Tournaisean-Lower Visean carbonate mudbanks that extends over much of west-central and south-west Ireland. To the north and east of this complex Waulsortian limestones form less extensive complexes, and scattered knolls and banks surrounded by sediments of lagoonal facies.

---

[1] The term Waulsortian is applied in this thesis, following the usage of Schultz (1968), to sediments of autochthonous and allochthonous bank facies, bank-cover facies and off-bank facies. Lees (1961, 1964) restricts his use of the term to sediments of bank facies.

Because the Tynagh bank is marginal to an aggregate complex, the Visean stratigraphy of the area is characterised by facies changes. The main facies and their representative lithologies are:

Facies	Symbol	Reference name	Lithology
Bank and Bank-margin	L2m	Micrite	Mainly micritic-skeletal limestones; bryozoan beds; micritic slump deposits.
Off-Bank	L2a	Slump Breccias and calcirudites	Sedimentary breccias and conglomerates of bank-derived materials, other calcirudites.
Bank Cover	L2b	Crinoidal Biomicrites	Encrinites, micritic-skeletal limestones; shale interbeds.

Stratigraphic relationships between sediments of different facies are shown diagrammatically in Fig. 3.1. These relationships, and patterns of lithological variation within particular units, are at present known mainly from borehole information. Certain aspects of the distribution of rock types in the lower and marginal parts of the bank structure are still problematical. Where the upper parts of the bank formation are concerned, interpretations of borehole information have largely been confirmed by recent large-scale exposures of Waulsortian sediments in the open pit.

a) Micrite (L2m)

Chemically pure micritic-skeletal limestone - carbonate mudstone.. with a mean grain size of less than 30μ mixed in varying proportions with skeletal debris - is the main rock type of the Waulsortian bank facies. Over 400 ft. of limestone of bank facies is present in the hanging wall of the North Tynagh Fault at the western end of the mine area, and an estimated 50-100 ft. has been removed by erosion. Eastwards along the main fault the micritic

bank limestones thin to less than 200 ft. and northwards they thin and pass laterally into sediments of off-bank and basin facies that include the Tynagh Iron Formation (Figs. 3.1, 3.2).

Bank micrites contain over 90% of the known primary ore mineralisation in the Tynagh area, and many of the economic constituents of the residual orebody, which is widely underlain by micrites, are the weathering products of Waulsortian limestones of this type.

Micritic-skeletal limestones (hereafter referred to as micrites) are usually mottled in appearance, due mainly to variations in carbonate grain size and uneven distribution of organic debris. They are generally pale grey in colour. Typical material contains over 95% calcium carbonate, the remainder comprising detrital and authigenic forms of silica, diagenetic dolomite, authigenic pyrite, clay minerals (predominantly illite), and traces of feldspar, rutile, ilmenite, and sometimes hematite and/or chlorite. A dark grey colour is occasionally imparted to bank limestones by dispersed carbonaceous substances.

The structure of micrites on a hand specimen and microscopic scale reflects a complex history of deposition and early diagenesis. Their formation initially involved the accumulation of quasi-flocculated lumps of carbonate mud and the contemporaneous deposition of a true sediment of the same material. Gentle settling of the resulting more or less plastic mass was accompanied by deposition of geopetal carbonate sediments in small voids (stromatactis cavities) formed in the process. Lining and infilling of voids by drusy and sparry calcite also took place during early diagenesis.

In addition to the scattered and more or less finely comminuted debris of bryozoa and shelly organisms, limestones of

bank facies also contain occasional beds of fenestellid bryozoan fronds varying in thickness from a few inches to a few feet but apparently of little extent in the Tynagh bank. Scattered individuals and small pockets of well preserved brachiopods (mainly Spiriferids and Productids), molluscs (including pelecypods, gastropods and goniatitic ammonoids), and partially disarticulated crinoid stems are common.

Schultz (1968) distinguishes a bank-margin facies of disturbed mottled micrite containing small-scale slump structures. Laminated micrite was deposited as an infill sediment between slumped boulders and lumps of micrite and in crevices in bank-margin and autochthonous bank limestones. Sedimentary conglomerates comprising irregular lumps of micrite in a matrix of micritic and skeletal sediment are assigned to the facies. These materials have essentially the same bulk composition and weathering characteristics as the autochthonous bank limestones.

Extensive recrystallisation of the bank micrites followed their lithification, and small amounts of calcite were redistributed in solution. Typical products of these processes are mosaics of anhedral calcite in fine and coarse grain sizes that sometime have drusy surfaces in small voids, roundish and irregular patches of fibrous calcite, and veinlets of sparry calcite. Of enigmatic origin are bands and "veins" of fibrous calcite up to six inches across, some of which may have formed under the stress of deep burial or tectonic loading.

b) Slump Breccias and Calcirudites (L2a)

The upward and lateral growth of the bank was accompanied by movements of carbonate sediments in various states of plasticity down gentle submarine slopes. Movements are thought to have been caused mainly by the over-steepening of bank margins resulting from

the greater rate of sedimentation and lithification of bank sediments compared with sediments of off-bank and basin facies. It is possible that earth tremors may have been responsible for some of them, though Schultz (1968) discounts the possibility that the North Tynagh Fault was active at this time. Slump deposits and associated bioclastic limestones and shales occur in northward-thinning units of up to 50 ft. intertonguing micrites at several levels in the bank structure. The eastern parts of the bank widely have a 20-150 ft. basal division that includes breccias and conglomerates of bank-derived materials in muddy matrices.

c) Crinoidal Biomicrite (L2b)

This litho-stratigraphic unit comprises an alternating sequence of grain-supported crinoidal limestones (encrinites) containing small amounts of interstitial sparry calcite and micrite, and limestones in which crinoid and brachiopod debris occur more or less abundantly in a micrite matrix. The disarticulated crinoid stems that are the main bioclastic components of these limestones represent in situ and reworked debris of a forest of crinoids that covered the bank in the later stages of its development. Crinoid stems have axial diameters of up to half and inch. Limestones consisting of well-winnowed stem fragments cemented by sparry calcite are the coarsest in grain size that occur in the area. "Spirit level" fossils are fairly common.

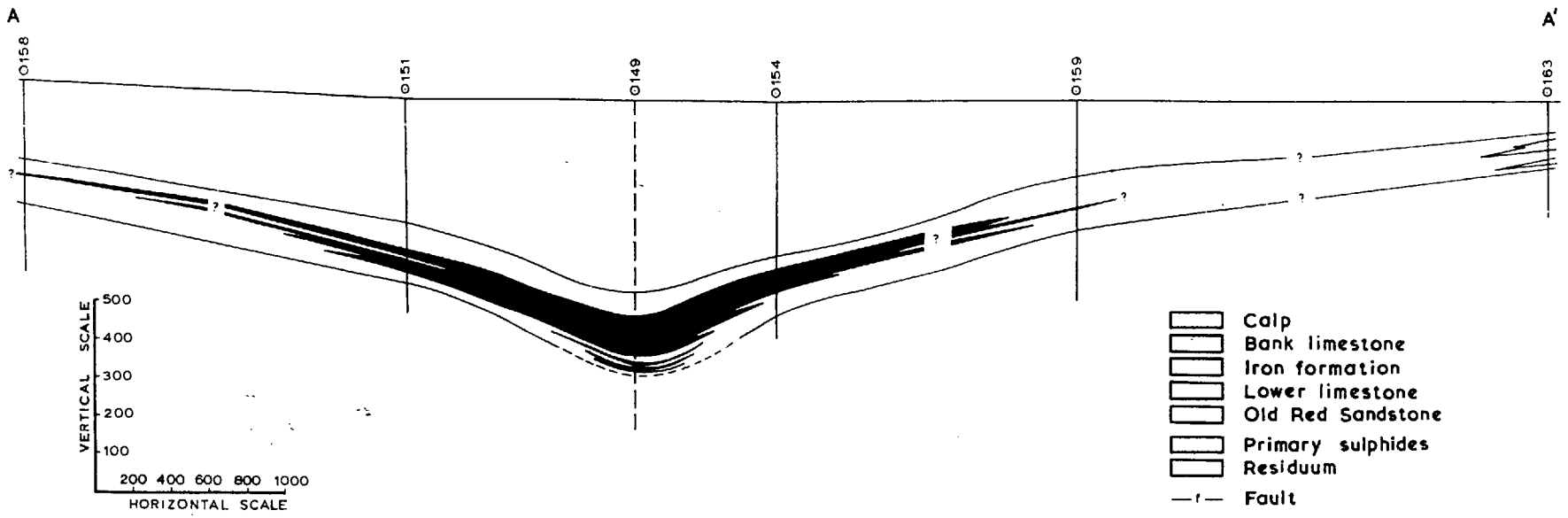
Constituent sedimentary units of the Crinoidal Biomicrite are sheets and extensive lenses separated by thin partings and interbeds of shale that become thicker and more numerous towards the top of the sequence. The maximum thickness of sheets exposed

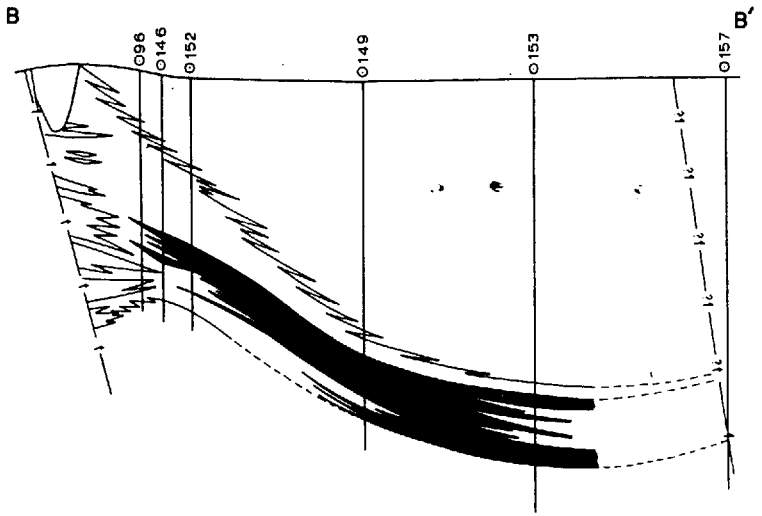
in the open pit is about 5 ft., and of the shale interbeds about 3 in. The aggregate thickness of the sequence in the mine area decreases irregularly westwards from an average of 130 ft. on Traverses 86 to 90W to an average of 100 ft. on Traverses 79 to 80W (Fig.3.3). The sequence feathers out between 79W and 77W. Except on Traverses 81, 83 and 86W, the sequence thins southwards, i.e. towards the North Tynagh Fault.

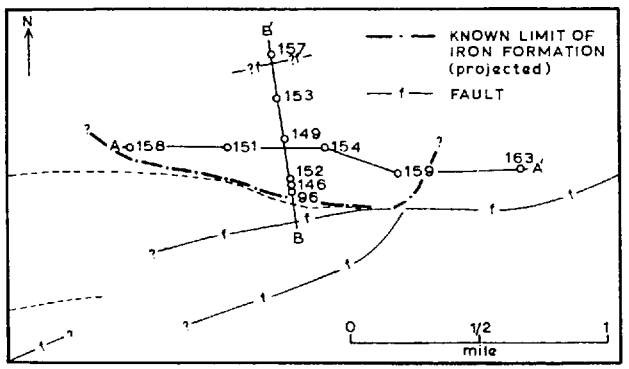
iv) The Iron Formation

To the north of the Waulsortian bank, graded calcirudites and subordinate shales of off-bank facies are interstratified and intertongue with thin beds of hematite, jasper and chert in a sedimentary sequence up to 200 ft. thick known as the Tynagh Iron Formation (Figs. 3.2, 3.4). The petrology and possible origin of the Iron Formation have been described in some detail by Schultz (1966a,1966b). Limestones, some of them coloured shades of red or green by dispersions of hematite or chlorite respectively, comprise about 60% of the Iron Formation. Tinted limestones persist into the outcrop area of the residual deposit and are locally exposed in the open pit, but the main development of the Iron Formation is to the north of the deposit. The Formation has not been fully delimited, but its N-S extent is known to be over 4,000 ft. Constituent limestone beds tend to wedge out, and ironstone beds to become more numerous and attain individual thicknesses of several feet, in a northerly direction.

Hematite and chert are the most abundant constituents of ironstone beds, which also contain small amounts of chlorite, magnetite, pyrite, stilpnomelane and minnesotaite. The last two minerals are thought to be of late diagenetic origin, and chlorite, magnetite and pyrite of early diagenetic origin.







Surface Geology

Tynagh Iron Formation

(after Schultz, 1966)

C.J. MORRISSEY, 1965

Fig. 3.4

The original sediment is considered by Schultz to have consisted of colloidal ferric hydroxide and silica, accompanied in places by carbonate mud (now diagenetic dolomite) that may have been precipitated by algae. Thin layers of colloform braunite and psilomelane - presumably representing a manganese facies of sedimentation - were intersected in a five-foot section of a borehole near the presumed northern limit of the Iron Formation.

A significant feature of the ironstones is their low content of lead, zinc, copper and barium. Schultz reports the following values for 10 ft. of ironstone containing 52% total iron and 14% silica:

Ba	470 ppm
Pb	100 ppm
Zn	50 ppm
Cu	not detected
S	trace

Towards the top of the Iron Formation occur several beds of well-graded pyroclastic material, mainly trachytic tuff. One, designated the T-bed in Fig. 3.2, is sufficiently persistent and petrologically distinctive to be used as a marker bed. Individually, beds of recogniseable tuff are usually less than 3 ft. thick. They and associated green shale beds that may represent chloritised accumulations of volcanic dust constitute less than 10% of the thickness of the Iron Formation.

Schultz considers that the pyroclastics were wind-borne into the Tynagh area from an indeterminate but probably distant centre of early Visean vulcanicity, and sees no direct genetic connection between them and the iron-silica sediments. Hematite and chert, he believes, were formed by chemical precipitation from the well-oxygenated waters of a restricted marine basin of iron and silica

derived by intense chemical weathering of Lower Carboniferous and perhaps Devonian sediments uplifted by minor earth movements. Derry et al (1965) and Derry (1966), while agreeing that the hematite and chert are primary chemical sediments, consider that the iron and silica were introduced in solutions of volcanic origin that emanated from submarine fissures related to the North Tynagh Fault during the formation of the Waulsortian bank. Further thoughts on this subject will be found in the next section.

v) Calp

At stratigraphic levels above the Tynagh Iron Formation, sediments of Waulsortian off-bank facies tongue northwards into a thick succession of basin-lain limestones and shales known collectively as Calp (Figs. 3.2, 3.3). The origin of the name, which has been applied by Irish geologists to dark compact Lower Carboniferous limestones since at least the early part of the last century, is unknown.

The Calp is sub-divided into a lower division (Grey Calp, L1b) that is 100-150 ft. thick, and an upper division (Black Calp, L1a) that is not preserved in full anywhere in the Tynagh district. The original thickness of the Calp in the mine area is therefore uncertain, but on the evidence of boreholes collared four miles SE and $2\frac{1}{2}$ miles NE of the open pit, which respectively passed through 1,400 ft. and 1,250 ft. of Calp and then into Lower Limestone, it was probably at least 1,000 ft.

In open pit exposures and for some distance to the north, the lower subdivision is represented by medium to dark grey calcilutites in beds up to 2 ft. thick interstratified with bioclastic and biomicrite-conglomeratic calcirudites, and argillaceous limestones grading to fossiliferous black shales. The silica content

of Grey Calp beds normally ranges between 5 and 10%. Most of the silica takes the form of silt-sized detrital quartz grains and microscopic chert. Illite is the main clay mineral in both varieties of Calp, and both contain carbonaceous matter as cryptogranular dispersions and as microscopic whisps and angular fragments of partially graphitised hydrocarbon (macerals). A particularly carbonaceous shale bank (the B-bed) that transgresses from the Grey Calp basin facies into the Waulsortian off-bank facies is used as a marker bed (Fig. 3.2).

The darker colour of the well-bedded and laminated calcarenites, calcilutites and shales that comprise typical Black Calp seems to be due largely to their higher average content of carbonaceous matter. Compared with its paler counterpart, the Black Calp also contains more silica (generally 10-35%), mostly as microgranular detrital quartz, microscopic chert replacements of bryozoa, and siliceous sponge spicules. Nodules and thin beds of black chert are relatively common in Black Calp.

A peculiarity of near-bank Calp of both divisions is that it contains, in addition to virtually ubiquitous disseminations of fine-grained diagenetic pyrite, substantial stratiform concentrations of iron minerals. Towards the base of the Calp, and transgressive into limestones of Waulsortian off-bank facies, there occurs a thin (up to about 5 ft. thick) hematite-chert sequence that closely resembles the non-calcareous elements of the Tynagh Iron Formation (Plate 3.2). One difference is that the silica-iron sediments are in places interstratified with pyrite-rich sediments. Close to the Calp/Waulsortian facies contact they grade laterally into a facies-equivalent dominated by black chert and pyrite. Near-bank Black Calp contains lenses and stratiform bands of iron sulphide up to 3 in. thick at many

Plate 3.2 - Drill core sections of cherty hematite iron-stone horizon in Calp. The actual diameter of the cores is 1.25in.

levels. Some of the sulphide bands exposed in open pit walls are individually traceable over distances of 100 ft. or more. Granular pyrite is by far the most abundant sulphide in bands, but some small sulphide lenses consist largely of euhedral marcasite. Both sulphides appear to have formed mainly by replacement of sediment - pyrite pseudomorphs of sponge spicules and other organic debris are commonly seen in polished section - and are considered to be of diagenetic origin.

The distribution of stratiform concentrations of iron oxides and sulphides in off-bank and basin sediments can be explained in terms of such closely related factors as water depth, current rate, and the activity of bacteria in bottom sediments. These jointly play an important part in controlling the oxygen partial pressure and the activity of dissolved carbonate and sulphur ionic species above and below the sediment/water interface, and hence the mineralogy of sedimentary and diagenetic iron precipitates (Hallimond et al, 1951; James, 1954; Borchert,1960; Curtis and Spears, 1968).

In most parts of the Tynagh area, the waters of the shallow Waulsortian sea probably circulated freely and contained free oxygen to the sediment interface. Dissolved iron was therefore precipitated most widely as f rric iron compounds. The main sedimentary precipitate is likely to have been goethite, of which the existing hematite is seen as a diagenetic alteration product.

Within normal sediments, decomposition of organic remains by sulphate-reducing bacteria set up an environment favourable to the formation of small amounts of diagnetic iron sulphide. This probably took place by a complex series of reactions that can be expressed in summary as indirect sulphidation of goethite.

At some places tentatively equated with topographic depressions in the seaward margin of the bank structure, and at intervals elsewhere, a combination of severely restricted circulation and high rates of bacterial activity in bottom muds brought about the complete sulphidation of original ferric iron precipitates. This was normally effected in alkaline solutions and yielded pyrite. Locally, perhaps where the rate of production of ammonia by decomposition of nitrogenous organic substances was particularly slow, marcasite was precipitated from more acid pore waters. Bacterial and inorganic reduction of seawater sulphate inhibited the formation of siderite, which takes place most readily in solutions with zero sulphide ion activity. At places where the redox potential of depositional or pore waters was too high for pyrite to form and too low for goethite, ferrous and ferric iron were precipitated together as chlorite.

There remains the problem of the source of the iron and of the presumably cogenetic silica concentrated in the sediments under consideration. Without being able to substantiate it fully, the writer holds the view that both are remobilized constituents of the normal argillaceous sediments of the area, probably of sediments that lay to the south of the position of the North Tynagh Fault. It is envisaged that remobilization resulted from transfer of the sediments into a submarine zone in which partial oxidation of organic matter substantially increased the bicarbonate ion activity of solutions and caused iron to be redissolved as $Fe(HCO_3)_2$. This mechanism of iron mobilization has been discussed at some length by Borchert (1960). Transfer could have resulted at Tynagh either from tectonic uplift of iron-bearing sediments, or from changes in the pattern of sea-water circulation due to variations in climate or sea-floor topography. Recognition in the Tynagh area of widespread non-sequences in argillaceous facies-equivalents of the Waulsortian bank limestones would tend to support this notional

scheme of remobilization.

An alternative possibility that the iron and silica, in common common with lead, zinc and other metals concentrated in primary ore mineralisation, were introduced in solutions of volcanic origin will be discussed in the next chapter.

D. Post-Carboniferous

The Tynagh area contains no post-Visean igneous or sedimentary rocks. A large deposit of rubble and mud entrenched in Lower Carboniferous sediments adjacent to the North Tynagh Fault is thought to be late Tertiary in age, and rock consisting largely of smithsonite has been formed in some quantity at its margin by Tertiary and Quaternary weathering. These materials, in common with most of the bedrock of the Tynagh area, lie under up to 50 ft. of Pleistocene glacial till. The Tertiary and Quaternary deposits of the area are the main subject of the succeeding chapters.

E. Rocks of Unknown Age

i) Epigenetic sulphide-barite rock

The Tynagh area contains large quantities of sulphide-barite rock formed, largely by metasomatic alteration of Waulsortian bank limestones, at some unknown time(s) during and/or since the Lower Carboniferous. This rock type is the subject of the next chapter.

ii) Epigenetic dolomite

Schultz (1968) distinguished three types of dolomite in the rocks of the Tynagh area: (a) "diagenetic dolomite", which occurs disseminated in small amounts through most of the Lower Carboniferous limestones and has been referred to several times in the preceeding pages; (b) "alteration dolomite", which is spatially

and genetically related to the sulphide-barite mineralisation and will be dealt with in the next chapter; (c) "epigenetic dolomite". Since the last constitutes a rock type not preferentially associated with mineralisation and apparently formed at a different but unknown time, it seems appropriate to describe it here.

Epigenetic dolomite (to adopt Schultz's nomenclature) has been intersected in boreholes at a number of places in the Tynagh area, as is locally exposed in the open pit. It occurs in zones of uncertain shape and size that appear to be irregular in shape and very variable in size. The vertical intersection width of the majority ranges from a few feet to a few tens of feet, while their indicated horizontal continuity is generally less than 200 ft.

Dolomite zones of this kind are particularly common in limestones of the Waulsortian Bank Formation, but are also known in most of the Lower Carboniferous litho-stratigraphic units of the area. The largest is in Waulsortian limestones adjacent to the North Tynagh Fault and immediately to the east of the open pit. It extends from outcrop to depths of up to 350 ft. and has an E-W continuity of about 600 ft.

The dolomite in this zone (which is the only one of importance where the residual deposit is concerned) is for the most part pale pink to pale grey, and consists of interlocking anhedral grains and euhedral rhombs up to about 3 mm on edge. Small drusy cavities lined by dolomite, sometimes overgrown by small crystals of pyrite, are common. Stain tests show that most of the dolomite has a low ferrous iron content, in which respect it differs from relatively iron-rich epigenetic dolomite that occurs in more argillaceous limestones.

Petrographic studies leave no doubt that the dolomite in this zone formed by metasomatic alteration of normal Waulsortian

limestone: it is, for instance, quite common for partially altered material to contain crude dolomite pseudomorphs of calcite bioclasts. The distribution of dolomite zones and features observed in drill cores strongly suggest that dolomitization was to a large extent localised by tectonic fractures, especially the North Tynagh Fault. Further to that it need only be said that the fact that dolomite zones in well-mineralised limestones tend to contain low concentrations of ore minerals formed mainly by replacement of dolomite indicates that dolomitization pre-dated mineralisation, while recent investigations of the conditions of formation of dolomite (Friedman and Sanders, 1967) suggest that the alteration agency was probably a magnesium-rich brine. As Schultz has pointed out, similar dolomitization effects are of region-wide distribution, which is consistent with his proposition that "the dolomitizing fluids were connate brines that had been trapped in certain reservoir rocks of wide lateral extent and which were eventually released and migrated along many fractures that had intersected the strata-bound reservoirs". The probable denudation history of the area is such that a post-Carboniferous marine cover is unlikely to have been the source of the fluids (see Chapter 9).

3.2 STRUCTURE

The dominant tectonic structure of the Tynagh area is a northward-dipping normal fault, the North Tynagh Fault[1] (Fig. 3.3). The fault has an estimated maximum dip-slip displacement of about 2,000 ft. and an indicated ENE-WSW continuity of at least six miles.

---

[1] So called to differentiate it from a fault of uncertain existence shown on current Geological Survey maps as branching south-westwards into the footwall of the North Tynagh Fault from a point 2½ miles east of the main Tynagh deposit.

The main related structures are an elongated half-dome in the footwall block, and sub-parallel faulting and pronounced local folds in the hanging wall block. Some of the rocks are strongly jointed.

All the structures to be described were in existence long before the residual deposit began to form. More attention will be paid to their distribution and geometry, which had a direct bearing on residuum formation, than to their origin.

A. Faults

i) The North Tynagh Fault

In the mine area the North Tynagh Fault is a somewhat undulating structure striking approximately E-W. To depths below surface of at least 600 ft. it dips northwards at $60 \pm 15^{\circ}$. At greater depths a steepening of its dip to $70 \pm 10^{\circ}$ is indicated by three vertical (non-deflecting) boreholes drilled to 1,400-1,700 ft. Such variations in dip and strike are common in major normal faults: they do not necessarily signify buckling of the fault plane by later movements.

On the assumption that the average dip of the fault is 70° and that 350 ft. of Devonian have been removed from the footwall block by erosion, it is estimated that the throw of the fault in the mine area is about 2,100 ft. Eastwards and westwards from the mine area the throw apparently diminishes, but throws of over 1,000 ft. have been indicated by drilling at points several miles distant from the mine in both directions.

Slickensiding on areas of fault plane exposed in the open pit indicates that movement took place several times and in senses that differed by 20° or more, but in the absence of evidence to the contrary it is assumed that the main displacement was essentially dip-slip. There is no evidence that the fault movement had a large horizontal component.

The position of the fault is generally marked by a dark clayey gouge up to 10 ft. thick. The gouge is veined by calcite and contains, in some places, angular fragments of sandstone, bioclastic and argillaceous limestone, and primary mineralisation. It largely consists of the argillaceous and carbonaceous residue of tectonised Tournaisean sediments.

Micritic limestones in the hanging wall of the main fault have been affected, to a varying degree and over varying distances, by brittle fracture. This effect will be described in more detail in the next section, as it has played an important part in localising epigenetic mineralisation. Post-mineralisation movements have caused marked deformation of mineralised micrites in a zone up to 20 ft. wide in the immediate hanging wall of the fault. Despite these repeated movements, it is not uncommon for boreholes to core virtually undeformed micrite from this position.

The argillaceous limestones that underlie the Waulsortian micrites have been affected by shearing and drag over a distance of at least 300 ft. from the main fault. Devonian sediments in the footwall block are locally sheared in a zone a few feet wide immediately adjacent to the fault.

The North Tynagh Fault is one of many major structures with mean strikes between ENE-WSW and NE-SW in the Palaeozoic rocks of Ireland. The age and origin of these structures was discussed in a previous chapter. To reiterate briefly, major normal faults with this trend in central Ireland are thought to have been caused either by vertical major stresses of local effect arising from cryptomagmatism and/or block jostling of the Caledonian basement, or by a horizontal major stress of regional effect directed approximately N-S. The North Tynagh Fault may be related to a more ancient tectonic structure in the Caledonian basement, and

have a long history of activity extending from mid-Carboniferous or earlier to the mid-Tertiary. Alternatively, it may have been initiated in Upper Palaeozoic rocks during the Permo-Carboniferous, and been active only at that time.

ii) Faulting sub-parallel to the North Tynagh Fault

In the mine area, and for indeterminate distances eastwards and westwards, movement on the North Tynagh Fault had the effect of interposing between the Waulsortian Bank Formation and the Devonian a narrow wedge of Lower Limestone (largely, but perhaps not exclusively, Lower Muddy Limestone)(Fig. 3.3). In parts of the open pit area this fault slice is so attenuated and deformed that it is best described as a gouge retaining vestiges of original sedimentary structures. Elsewhere it has, at present mining levels, a width in plan of up to 150 ft., and sedimentary structures have been strongly deformed only at its margins.

The fault slice is bounded to the north by a zone of shearing that dips generally northwards at 70-85°, and merges with the North Tynagh Fault at depths below surface of up to 300 ft. The shape of the slice in plan is complicated by undulations of the bounding structures, and by at least one cross-fault (see below). Exposures at the eastern end of the open pit area suggest that the northern boundary of the slice is, in places, a reverse fault, but this is one of many details of the structure of the area that still have to be resolved.

Lithologies represented in the fault slice include muddy bioclastic limestones, fossiliferous shales, and argillaceous slump deposits. Near the centre of the open pit area, mining in the upper levels of the residual deposit has shown that the argillaceous sediments are interstratified with pale biomicrites that may represent the zone of facies transition at the base of the Waulsortian Bank Formation.

iii) Faulting oblique to the North Tynagh Fault

Over the 2,500 ft. of strike exposed in the open pit area only two faults trending at 45° or more to the North Tynagh Fault have been located (Fig.5.1). These are: (a) a high-angle normal fault with an apparent strike of NNE-SSW and a westward down-throw of about 5 ft. in Devonian sediments walling the open pit at 32200E; and (b) a fault of unknown throw, with a highly variable (35-80°) eastward dip that strikes NW through the Lower Muddy Limestone fault slice. The latter seems to have no effect on adjacent Devonian rocks, and in neither case is there convincing evidence that the fault persists far in depth or on strike.

In the open pit area, therefore, it seems that movement on the North Tynagh Fault was accompanied by little subsidiary oblique faulting of the Waulsortian limestones. This may be because the main movement was well lubricated by clayey gouge, and because concommitant stresses on Waulsortian limestones were absorbed by zones of brittle fracture.

iv) Other faults

The following faults and shear zones of which the geometric details are not known have been indicated or proved by drilling in the neighbourhood of the Tynagh mine. No conclusions can be drawn about their relationship to the North Tynagh Fault system, but it is not considered likely that they resulted from a separate phase of tectonic activity.

a) A strong gouge intersected in a borehole collared 3,400 ft. north of the North Tynagh Fault on Traverse 85W (Fig. 3.2). The absence from the hole of the Tynagh Iron Formation or rocks definitely correlatable with it suggests that the gouge represents a major fault, perhaps a parallel of the North Tynagh Fault.

b) A few narrow shear zones in footwall Devonian sandstones and in Waulsortian and Calp limestones at various distances into the hanging wall of the North Tynagh Fault. Minor movements in hanging wall limestones are also evidenced by slickensiding on sheated calcite excavated from an unknown locality in Calp several hundred feet north of the open pit.

c) Strong shearing and gouge zones in Lower Limestone about 6,000 ft. ESE of the open pit, i.e. in the vicinity of the Old Tynagh Mine..

In addition, Schultz (1968) has suggested that the western end of the Tynagh Devonian inlier is truncated by a westward-dipping normal fault that has the effect of displacing the North Tynagh Fault about 1,200 ft. to the south (Fig.3.3). Recent drilling has confirmed the existence of such a fault, but it is not yet clear what its orientation is and whether or not it displaces the Lower Muddy Limestone fault slice.

B. Folds

In the neighbourhood of the mine, the footwall block of the North Tynagh Fault is gently folded into a half-dome elongated roughly E-W and truncated parallel to its long axis by the North Tynagh Fault (Fig.3.3). Boreholes into the footwall block and exposures in the open pit and in rare natural outcrops suggest that the structure is a fairly simple one. The folded beds dip generally southwards at angles of less than 20°, though low-angle northward dips have been recorded in sandstone beds immediately adjacent to the North Tynagh Fault. Here and elsewhere the Devonian sediments are gently flexed about axes of which it has not been possible to measure the strike.

Doming of the footwall block is a common concommitant of normal faulting (De Sitter, 1956), and the fold that has given rise to the Devonian inlier at Tynagh is thought to have developed at the same time as the main movement on the North Tynagh Fault.

Another comparatively major fold in the mine area is a shallow asymmetrical trough with monoclinal limbs in the hanging wall block (Fig. 3.3). Contouring of two facies-transgressive marker beds referred to earlier shows that the axis of the trough strikes approximately N10W. Calculated dips on the western limb of the trough attain 22° to the NE, and on the western limb 14° to the NW.

As neither marker bed persists southwards to the North Tynagh Fault (Fig.3.2), whether the fold affects limestones close to the fault cannot be guaged in this way. North-eastward dips of 40-45° in well-bedded crinoidal limestones walling the western end of the open pit suggest that it does. Its monoclinal limbs may steepen towards the fault, though since the measured dips of 40-45° presumably include depositional and differential compaction components as well as a tectonic component, this is not certain.

The fold is thought to have resulted from the wedging effect of the Lower Limestone fault slice on its hanging wall during the main fault movement. Alternatively, it may have resulted from a horizontal major force applied some time after the main fault movement.

C. Jointing

Numerous steep quasi-planar fractures without displacement cut the rocks of the mine area and the surrounding country. They can be described collectively as joints. Joint formation postdated mineralisation.

To judge from good (but not extensive) exposures in the open pit and more limited ones elsewhere, joints are most closely spaced and best organised in Calp. Three sets are present:

i) a dominant vertical set striking $350\pm10^{\circ}$

ii) a steep northward or southward dipping set, only slightly less well-developed than the first, striking $270\pm10^{\circ}$

iii) a minor set striking $235\pm10^{\circ}$ and generally with steep northward to vertical dips.

More widely spaced joints of the first two sets are well-developed in Devonian sandstones of the mine area. Joints in sandstones are generally unfilled, whereas major joints of the first two sets in Calp commonly have a filling of sparry calcite, sometimes accompanied by quartz and by traces of fluorite. Slickensiding of the fillings and surfaces of joints in Calp, and rare cases of offsetting of calcite-filled joints on shale interbeds, indicate that minor movements have taken place since the development of all three joint sets.

Joints in off-bank and bank-cover limestones are considerably less numerous and well-organised than those in Calp. Measurements on 85 such joints exposed in 1,500 ft. of pit wall showed them to have two fairly pronounced directions of preferred strike, namely $240\pm10^{\circ}$ and, subordinately, $335\pm10^{\circ}$. Non-vertical joints with approximately the same strike in limestones of this type dip steeply in a non-uniform direction.

Up to the time of writing, massive Waulsortian micrites of bank facies had been too poorly exposed in the mine area for the pattern of jointing within them to be established. Such joints as had been exposed were widely spaced planar and slightly curved structures with no clear grouping in sets.

Interpretation of joint geometry should be based on measurements far more numerous than exposures in the Tynagh area have so far allowed. Even so, it is reasonably certain that the dominant joint set in the Calp and in Devonian rocks formed in response to a regional rather than a local stress system. Joints striking approximately N-S are of region-wide distribution, and are generally considered to be tension fractures arising from N-S Armorican compression (O'Brien, 1969). Joints striking $290 \pm 10^{\circ}$ are also of region-wide distribution, but those with approximately this trend ($270 \pm 10^{\circ}$) in the mine area were probably caused by local rather than regional stresses. They and the joints striking $235/240 \pm 10^{\circ}$ may be pinnate tension or shear joints arising from the vertical major stress that gave rise to the North Tynagh Fault. The poor development of N-S and E-W jointing in Waulsortian limestones generally, and the apparently random orientation of joints in massive micrites, are hard to explain. It is possible that tectonic stresses on rocks of the Waulsortian Bank Formation were partly taken up by movement on joints developed during lithification of the bank limestones.

D. Minor structures

i) Tension gashes and cleavage

Steep calcite-filled tension gashes, some of them arranged in en echelon sets, parallel the N-S jointing in Calp. They are thought to have formed in response to a near-horizontal major stress applied N-S. It is not clear whether the tension gashes formed at the same time as the N-S jointing or at a different time.

Other sets of tension gashes occur in crinoidal limestones and biomicrites on the limbs of the main hanging wall fold. Poorly developed cleavage can sometimes be seen in interbedded argillaceous limestones and shales. The tension gashes and the

cleavage have various orientations and seem to have developed in response to local stress systems set up by the folding.

ii) Fractures

Some of the primary sulphide-barite mineralisation of the area takes the form of open space fillings and replacements guided by fractures. Products of pre-mineralisation fracturing include at the one extreme breccias consisting of rotated blocks, and at the other simple and branching fissures. Little is known about the distribution and orientation of the fractures, except that they are most numerous in micritic limestones and are widely variable in attitude. Some of the steep mineralised fractures exposed in open pit walls are organised into groups striking approximately E-W, but the majority seem to have no preferred orientation.

Fracturing of brittle limestones was probably a complementary effect of the application to the hanging wall block of the compressive stresses that caused the compound fold structure described in the previous section. The limestones most affected were those without shale interbeds on which interstratal gliding could take place.

CHAPTER FOUR

PRIMARY MINERALISATION OF THE TYNAGH AREA

4.1 INTRODUCTION

The earliest written record of the occurrence of minerals of economic interest in the Tynagh area is a reference by G.H. Kinahan in a Memoir of the Geological Survey of Ireland dated 1865 to a long-abandoned lead mine a mile and a half NE of Tynagh village. There is a tradition that native silver was found at this locality (Kinahan, 1878). The exact position of the workings, referred to hereafter as the Old Tynagh Mine, is not known.

In the 1865 Memoir, Kinahan mentioned the occurrence of copper-stained sandstone float in the Tynagh area, and in 1953 and 1956 members of the Geological Survey of Ireland visited the area and found several pieces. Their suspected source was the small inlier of Devonian sandstone described in the previous chapter, which was known to be bounded on its northern side by a major fault. Experience elsewhere had shown that the faulted margins of pre-Carboniferous inliers were a favourable situation for ore, and the then Director of the Geological Survey of Ireland, Mr. M.V. O'Brien, recommended the Tynagh area for further investigation.

In 1960 strongly anomalous heavy metal values were found in soils in the vicinity of the Old Tynagh Mine by a geochemical exploration team of Irish Base Metals Ltd. The following year, systematic geochemical soil testing outlined a strong and extensive lead anomaly with high associated zinc and copper values a mile to the west of the old mine, and several pieces of heavily mineralised float consisting largely of galena and barite were found in stone-walls and ditches. Electromagnetic and induced polarisation

surveys indicated a metallic body at shallow depth coincident with the main geochemical anomaly.

Drilling and pitting of the anomaly in 1961 and 1962 showed that immediately below the glacial drift was a boat-shaped body of mud and rubble some 2,000 ft. long and up to 250 ft. thick. The unconsolidated materials, which became known as the residual deposit, contained base metal sulphides and barite in extraordinary abundance, and rich sulphide-barite mineralisation was intersected in the underlying limestones. As drilling continued, a belt of mineralised limestone over 10,000 ft. long was outlined. The main economic minerals present were galena, sphalerite, tennantite-tetrahedrite and chalcopyrite. They were usually accompanied by barite, pyrite and epigenetic calcite.

Subsequent exploration has defined two main zones of mineralisation with a combined strike length of about 4,300 ft. (Fig. 3.3). These are known as the Main Orebody and the East Extension Orebody. Their calculated contents of economically mineable material at the end of 1967 were:

	Short tons	Pb%	Zn%	Cu%	Ag oz/ton
Main Orebody	6,199,000	3.0	3.2	0.3	1.3
East Extension	3,218,120	3.0	3.1	0.2	0.5

Neither orebody outcrops, and up to the time of writing only the easternmost fringe of the Main Orebody had been exposed in the open pit. Most of what follows is therefore based on a study of borehole cores. The Main Orebody is at present being developed for production in 1971. Development of the East Extension Orebody is not scheduled to begin until 1972. The underground exploration that has just started will certainly give new insights into detailed aspects of the mineralisation, and may provide answers to certain questions that are now best left open.

4.2 DISTRIBUTION

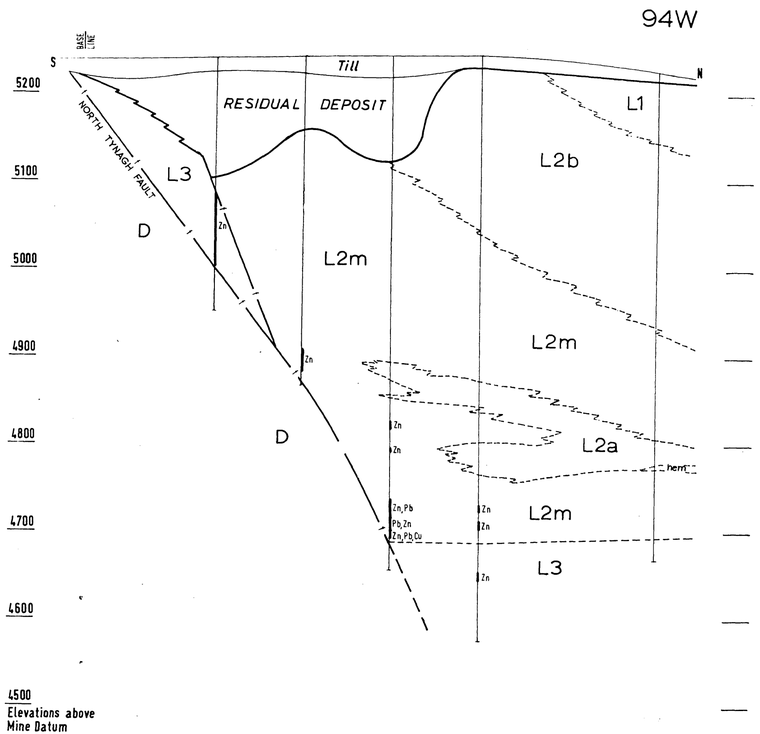
A. The Main Orebody

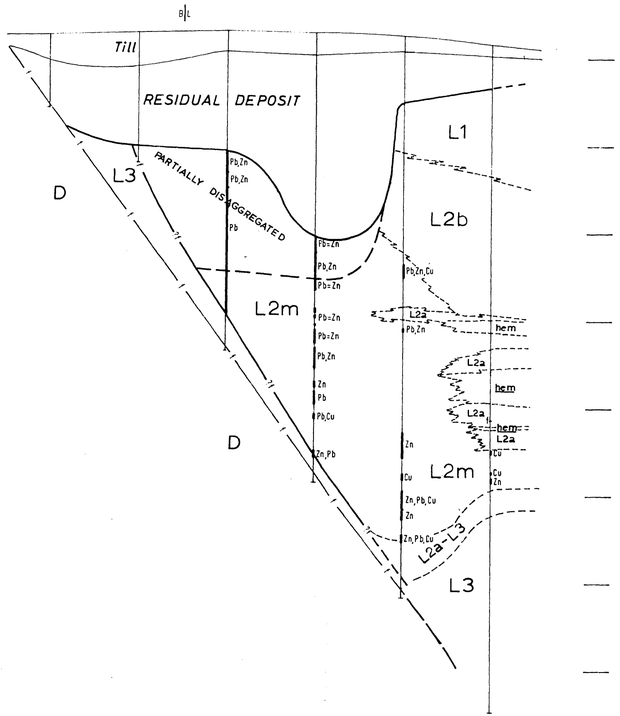
The Main Orebody can be regarded as lying directly below the residual deposit. Why this statement has to be a qualified one will become apparent in later chapters. Projected vertically to surface, the bounds of the ore zone somewhat transgress those of the residual deposit on its northern, eastern and western sides (Fig. 3.3). Mineralisation as such extends over a much larger area.

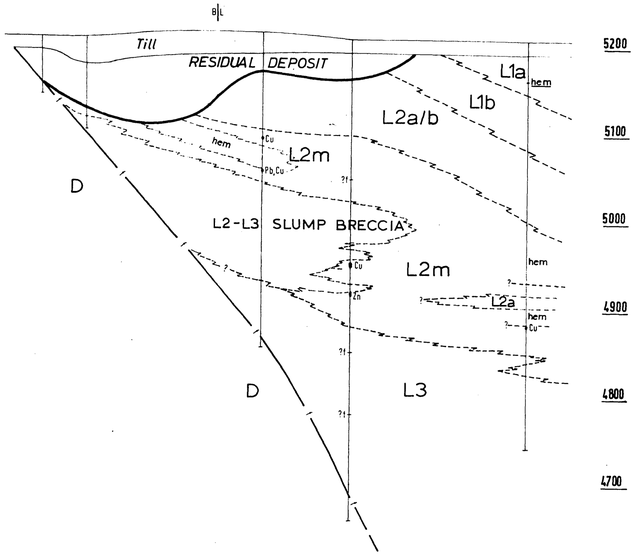
Mineralisation is strongly concentrated in Waulsortian micrites in the hanging wall of the North Tynagh Fault (Fig. 4.1). An estimated 10% of the known mineralisation occurs in other lithologies of the Waulsortian Bank Formation and in Lower Muddy Limestone conformably underlying the Waulsortian and faulted into position between it and the Devonian. Minor amounts are present in Calp and in Devonian rocks of the footwall block. Traces of mineralisation have been intersected by boreholes at distances of 600 ft. to the north of the plane of the main fault.

Most of the mineralisation in micritic limestones apparently takes the form of massive, patchy and disseminated replacements of limestone and dolomitised limestone; linings and fillings of solution-enlarged fractures and irregular solution cavities; and ramifying veinlets. (Uncertainty about the precise range of mineralisation styles is due to the fact that the latter are often hard to determine from the appearance of mineralisation in small-diameter core.) Open space fillings are considerably rarer in impure and crinoidal limestones, which otherwise contain the same styles of mineralisation. In places, richly crinoidal limestones have suffered selective replacement of the matrix of bioclasts by sulphides and barite.

Fig. 4.1







LOWER CARBONIFEROUS

L1 Undifferentiated Calp

L1a Black Calp

L1b Grey Calp

L2 Waulsortian Bank Formation

- L2a Slump breccias, argillaceous calcarenites, shales
- L2b Crinoidal limestones
- L2m Micritic limestones

L3 Lower Muddy Limestone

D Devonian and pre-Devonian

hem Limestones coloured by hematite

hem Section contains cherty ironstone

Pb+Zn > 5.0% and/or Cu > 0.5%

ORDER OF ORE METAL ABUNDANCE INDICATED FOR Pb>5%, Zn>5%, Cu>0.5%

TYNAGH MINE

GEOLOGICAL SECTIONS

C.J.M. 1969

Fig. 4.2

5000 Upper contact L2m (massive micrite)
o control point

4700 Upper contact L3 (Lower Muddy Limestone)
· control point

0 300
FEET

N

NORTH TYNAGH FAULT PLANE (SIMPLIFIED) assuming constant dip of 65°

4600
4700
4800
4900
5000
5100
5200

I<50

I>400

I>50<400

OUTLINE OF RESIDUAL DEPOSIT AT 5200

NORTH TYNAGH FAULT AT 5200

Footwall block I<50

$$\text{INTENSITY OF BEDROCK MINERALISATION (I)} = \frac{100(\%\,Pb + \%Zn + 2(\%Cu)) \times \text{rock footage assayed}}{\text{Length of hole in bedrock}}$$

Pb, Zn, Cu WEIGHTED AVERAGE ASSAY Pb≥5%, Zn≥5%, Cu≥1%

Ba BaO x footage assayed > 1000

C J M. 1969

Metal values in excess of 5% Pb/Zn or 0.5% Cu are largely restricted to a zone with a strike length of about 2,400 ft. that is bounded to the south by the plane of the North Tynagh Fault. Measured horizontally from the fault, the northward extent of the ore zone decreases westwards from about 350 ft. to 150-200 ft. (Fig. 4.2). Sparse mineralisation persists for unknown distances to the north and west. Eastwards, the Main Orebody is separated from the East Extension by about 600 ft. of low-grade mineralisation in strongly dolomitised Waulsortian limestones.

The lower limit of the Main Orebody is geometrically related to, but not coincident with, the lithological contact between predominantly micritic limestones of the Waulsortian Bank Formation and predominantly argillaceous sediments of Lower Muddy Limestone type. The facies contact between the two types of sediment is shallowest in the south-eastern part of the mine area. Here the ore zone has a limited sub-till outcrop and a large area of contact with the residual deposit. Ore-grade mineralisation occurs partly in the upper 20 ft. or so of a large argillaceous slump deposit underlying the micrites, but similar slump deposits and associated red (hematitic) limestones interbedded with the micrites are in general conspicuously unmineralised.

In western and north-central parts of the area the ore zone can be described as a sub-horizontal wedge that thickens southwards to about 200 ft. Mineralisation is in Waulsortian micrites, in the purer phases of a sequence of calcirudites of lower off-bank facies, and in the upper 10-20 ft. of the Lower Muddy Limestone. The latter's upper facies contact is undulating and lies at 500-600 ft. below surface.

In the south-central part of the area the ore zone changes attitude abruptly as it nears the North Tynagh Fault, and extends

up the dip of the fault as a lenticular body of massive mineralisation that is in places over 200 ft. wide (Fig. 4.1). The steepening of the ore zone is accompanied by a marked upward displacement of the drill-indicated elevation of the lithological contact between pure and impure limestones. Whether this is a depositional or a tectonic feature, or a combination of both, is not known. Mineralisation in the steep south-central part of the ore zone formed partly at the expense of argillaceous sediments of the fault slice.

A noteworthy concentration of mineralisation in upfaulted Lower Muddy Limestone occurs between 91W and 94W, where the fault slice wedges out well above the zone of mineralisation that is spatially related to the L2/L3 facies contact (Fig. 4.1). Between 87W and 94W, furthermore, limestones in the upper part of the Waulsortian Bank Formation contain what can reasonably be described as a persistent zone of low-grade mineralisation. It will be shown, by reference to the structure of the residual deposit, that these are relics of a large body of mineralisation in the upper part of the Waulsortian Bank Formation that was probably a high-level westward extension of the steep central portion of the Main Orebody.

Another interesting feature of base metal distribution is the occurrence of mineralisation in Calp immediately to the north of the central part of the residual deposit. Other than in this area, where it has been downwarped and fractured on the axis of the main hanging wall fold, the Calp is virtually unmineralised.

The distribution of mineralisation within the zone of its greatest concentration is in most places far from regular, and for ore reserve calculation purposes is considered by Irish Base Metals to be concentrated in two large, steeply-inclined irregular

prisms or lenses in the western and central parts of the area, and in a number of flat-lying, fairly extensive lenticular bodies in the eastern part

It remains to be seen whether underground mining will confirm this interpretation of borehole information. To date it apparently has: a decline now being driven westwards through the Main Orebody from the eastern end of the open pit is reported to have passed through a number of flat tabular or lensoid ore concentrations. These could have resulted from selective replacement of sheets of sediment with some favourable characteristic of texture or composition, or from impounding of metal-bearing solutions by relatively impermeable sedimentary units. For reasons that will be given later, it is improbable that their geometry reflects essentially contemporaneous deposition of ore mineralisation and the host limestones.

B. East Extension Orebody

A second major zone of mineralisation in hanging wall limestones adjacent to the North Tynagh Fault extends eastwards for about 2,000 ft. from 66W (Fig. 3.3). Proving of this zone is still in progress. The mineralisation is similar in many respects to that of the Main Orebody, and although it has yet to be studied scientifically, it is almost certainly of the same age and origin.

Mineralisation is concentrated in Waulsortian micrites within 200 ft. of the North Tynagh Fault, but is also present in local quantity in other lithologies of the Bank Formation and in the upper 20 ft. or so of the underlying Lower Muddy Limestone. A narrow sub-outcropping fault slice of Lower Muddy Limestone is largely unmineralised. Some mineralisation has been intersected in Calp, where it is apparently localised in fracture zones of unknown distribution.

Galena and sphalerite, accompanied in places by tetrahedrite-tennantite and chalcopyrite, are the main economic minerals, and barite their main non-carbonate associate.. Other mineralogical details are not available, though it is apparent from assay values that the tetrahedrite-tennantite is argentiferous but (like the galena) probably less so on average than in the Main Orebody.

A feature of the ore zone that is particularly pertinent to the subject of this thesis is that over most of its strike length the micritic limestones that are the main hosts of mineralisation do not outcrop below the till, being generally overlain against the main fault by up to 300 ft. of Calp. The average depth below surface of the uppermost assay section in 39 boreholes drilled in the area to date was 190 ft. Only four of the holes encountered mineralisation worth assaying at a depth of less than 100 ft.

C. Mineralisation in Devonian and Lower Palaeozoic Rocks

For the most part, the Devonian sediments of the North Tynagh Fault footwall block are unmineralised, but in some places they contain, in addition to the local concentrations of pyrite and arsenopyrite referred to earlier, small amounts of sphalerite, galena, tennantite, chalcopyrite and barite. These minerals usually occur as disseminations formed by replacement of the silica and carbonate matrix of sandstones. Occasionally they fill steep discontinuous fractures, up to 3 in. or so across in rare cases, that appear, from ephemeral exposures in the wall of the open pit, to be sub-parallel to the North Tynagh Fault. In polished section they are seen to be later than pyrite and arsenopyrite, and their paragenetic relationships to each other to be the same as they usually are in Lower Carboniferous rocks.

Mineralisation of this kind has only been seen in situ in upfaulted Devonian rocks immediately adjacent to the North Tynagh

Fault. No mineralisation was present in Devonian sediments intersected by two deep boreholes in the fault's hanging wall block.

Small amounts of epigenetic mineralisation were noted by Schultz (1968) in two drill-core sections of Ordovician greywacke from the footwall block. The greywackes contain fairly abundant disseminated pyrite in places. Barite occurred as patchy replacements and, with calcite and pyrite, lining small cavities. Thin stringers of chalcopyrite were found in strongly sheared material, and coarsely crystalline pyrite and arsenopyrite were also present in shear zones. According to Schultz, the mineralised shears are sub-parallel to the North Tynagh Fault.

D. The Old Tynagh Mine Area

The general location of the Old Tynagh Mine is 6,000 to 7,000 ft. SSE of the present open pit (Fig. 3.3), but the exact location of the workings is not known. From old records and what is known of the geology of the area, it seems that they were pits and shallow shafts in Lower Limestone, and produced a pyritiferous galena ore that was probably high enough in grade and silver content to be worth hand cobbing and desilverising. There is no evidence that any of the ore was residual or detrital in origin.

Exploratory drill holes in the general area of the Old Tynagh Mine have located narrow sections of mineralisation - galena accompanied by lesser amounts of sphalerite and a little chalcopyrite - along a strong shear zone that apparently strikes approximately E-W. The old workings probably exploited the surface expression of this mineralisation, which takes the form of veinlets and fracture-controlled replacements of dark bioclastic limestones with shaley phases. The area contains a fairly extensive geochemical anomaly, especially in lead, but recent drilling suggests that

bedrock mineralisation is comparatively localised, and it is likely that the spread of the anomaly is partly due to glacial dispersion and partly to former mining activities.

E. Other mineralisation

Small amounts of mineralisation have been found by drilling within a four-mile radius of the Tynagh mine at several places remote from the North Tynagh Fault. Specifically, disseminated chalcopyrite in Devonian sandstone was intersected in several boreholes four miles SW of the mine in the NE corner of the Slieve Aughty inlier, and minor sphalerite-galena mineralisation in a borehole $2\frac{1}{2}$ miles NNE of the mine.

Donovon (1965) concluded from geochemical investigations around Tynagh that there may be two base metal ($Zn^{+}Pb$) sources in the area other than the known orebodies and mineralisation in the vicinity of the Old Tynagh Mine. The geochemical soil anomalies attributed to them lie about half a mile to the west and a quarter of a mile to the south-west of the open pit, respectively. It cannot be said that the existence of mineralisation in either of the two areas concerned has been disproved, but it is unlikely that any mineralisation that is present has a sub-till outcrop of any extent.

4.3 MINERALOGY OF THE MAIN OREBODY

The most abundant and widespread primary minerals are galena, sphalerite, barite and pyrite. With these are usually associated lesser amounts of tennantite-tetrahedrite, bournonite, jordanite-geocronite, arsenopyrite and marcasite. Chalcopyrite is a common

associate of tennantite[1] in copper-rich material, in which also occur small quantities of enargite and rare grains of primary covellite.

A small proportion of the pyrite is distinctly nickeliferous, and siegenite is present in very small amounts.

Common non-opaque associates of the sulphides and sulphosalts are epigenetic dolomite and calcite. Quartz, chlorite and several types of feldspar are minor associates of the main non-opaque minerals. Fluorite is present but very rare.

A solid hydrocarbon is a minor but fairly widespread constituent of primary mineralisation.

All these minerals occur in the residual deposit, and details of their mineralogy are therefore given in a later chapter.

4.4. THE MINERALISATION SEQUENCE

Application of the paragenetic criteria of Bastin et al (1931), Edwards (1954) and others to textures in over 200 polished and thin sections of primary mineralisation shows that the sulphides and sulphosalts comprise three paragenetic assemblages. In their usual order of deposition, from earliest to latest, there are:

i) sulphides of iron and zinc
ii) chalcopyrite and copper sulphosalts
iii) galena and lead sulphosalts.

---

(1) For convenience, the members of the tetrahedrite-tennantite series that occur at Tynagh will be referred to as tennantite in most parts of this thesis, since they generally have a higher atomic content of arsenic than antimony (see Chapter 7). Similarly, members of the jordanite-geocronite series will be referred to as jordanite, since they usually contain little or no antimony.

The order of deposition of the minerals in each group is somewhat variable from place to place, and there is some textural evidence that lead and copper minerals were in some places deposited simultaneously or in the reverse order to that given above. Small amounts of iron and zinc sulphide were precipitated penecontemporaneously with copper and lead minerals.

Arsenopyrite and siegenite generally appear to be paragenetically related to iron sulphides of the main generation, but they have been too infrequently seen for it to be certain that they have a unique position in the crystallisation sequence.

The non-opaque minerals - barite, dolomite, calcite, quartz and chlorite - cannot be similarly subdivided into paragenetic assemblages. They formed in greatest quantity during the early stages of mineralisation, and were deposited during the later stages of sulphide formation and after it had ceased.

a) The wallrock alteration stage

The first chemical effect of the mineralising process was widespread leaching of limestone by solutions that were guided to some extent by tectonic structures. Leaching of micrites was particularly intense, and caused the formation within them of numerous small, irregular cavities, and the enlargement of fractures, stylolites and other structural discontinuities. Open pit exposures show that fractures enlarged by solution to an inch or two in width developed at intervals into cavities several feet wide, probably because of subtle variations in wallrock lithology. It is likely that some of the mineralised cavities in unexposed micritic limestones, which are up to at least 5 ft. in vertical intersection width, are also closely related to fractures.

Cavities in comparable sizes and profusion did not form in crinoidal or argillaceous limestones or in Calp, though in all these rock types pre-existing fractures were enlarged by solution, and small-scale cavity formation took place.

Most of the dissolved calcium carbonate was evidently carried out of the system, but a small proportion was rapidly reprecipitated as fibrous and drusy linings of solution cavities. Non-carbonate rock constituents - mainly clays, quartz, feldspar and pyrite - tended to be concentrated at the reaction forefront between limestone and the attacking solutions (Plate 4.1), and some re-sedimentation in the lower parts of solution cavities took place. Small collapse breccias of limestone fragments in an argillaceous matrix were formed at a few places.

An essentially contemporaneous event was widespread replacement of limestone by ferroan dolomite. The dolomite that formed at this time largely occurs as 10-50 μ euhedra. and euhedral aggregates in an alteration halo up to 2 cm. wide marginal to mineralised fractures and solution cavities in limestones of all types, and as corroded euhedra in later epigenetic minerals (Plate 4.2). A small amount was precipitated as a sandy chemical sediment on the floors of such cavities. In some cavities, alternating deposition of pyrite and sandy dolomite apparently took place.

Subsequent replacement processes probably destroyed most of the dolomite formed at this time, but the occurrence of numerous dolomite relics in massive sulphide-barite rock indicates that in some places continuous vertical sections of limestone tens of feet in length were dolomitised during the early stages of mineralisation.

Other minerals that commonly occur as small euhedra replacing limestone in the alteration haloes around subsequently filled

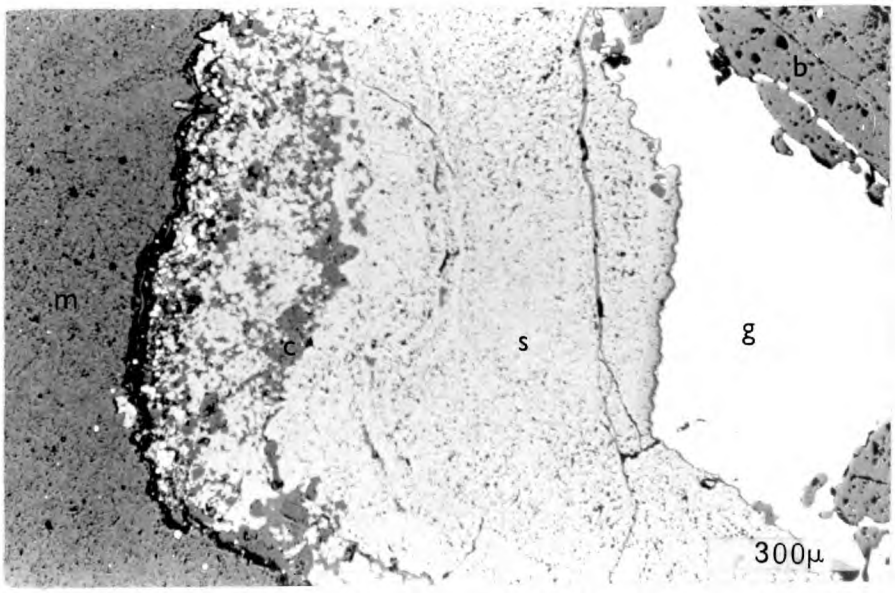


Plate 4.1 - Edge of sulphide-barite veinlet in micritic limestone (m). The inferred crystallisation sequence of the main epigenetic minerals was: sphalerite (s) (earliest) - barite (b) - galena (g). Calcite (c), probably of several generations, has replaced sphalerite preferentially. The veinlet has a narrow selvage of clay minerals and microcrystalline pyrite that represents an insoluble residue of the limestone. Polished section.

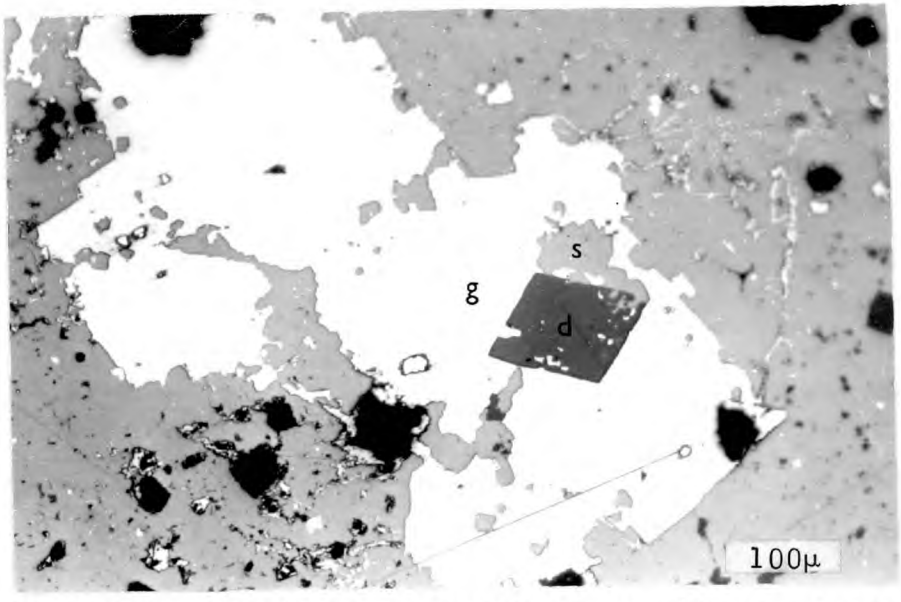


Plate 4.2 - Rhomb of epigenetic dolomite (d) corroded by sphalerite (s) and galena (g). Polished section.

solution cavities are feldspar, arsenopyrite, pyrite and marcasite. Ambiguous replacement relationships between these minerals suggest that they were deposited penecontemporaneously. Small mineralised cavities in impure limestones commonly have narrow rims of quartz, with which are occasionally intergrown tiny flakes of chlorite or sericite.

The types of feldspar most commonly found in close association with sulphide-barite mineralisation are orthoclase (which typically occurs in the pseudo-orthorhombic habit attributed to adularia) and albite. The first gives a strong potassium reaction with sodium cobaltinitrite, the latter no potassium reaction. Extinction angles measured on twinned albite indicate that it generally contains less than 5% anorthite molecule. Schultz (1968) found small zoned crystals of plagioclase, tentatively identified as oligoclase, as a replacement of micrite in the alteration halo around one mineralised solution cavity.

Potassium-rich orthoclase in the adularia habit, and essentially pure albite, are typical feldspars of diagenetic formation (Baskin, 1956), and the latter is widespread in very small amounts in unmineralised limestones at Tynagh. Nevertheless, it is clear that both were formed by the mineralising processes. The significance of this vis-a-vis the temperature of the solutions responsible for wallrock alteration is uncertain, since both feldspars are evidently capable of forming under a fairly wide range of temperature conditions. Orthoclase of the adularia variety is a typical constituent of vein mineralisation of the Alpine type, and is a minor epigenetic associate of base metal sulphides in mineralisation of the Mississippi Valley type (Lindgren, 1933; Ohle, 1959). Both types of mineralisation are generally classified as epithermal to low mesothermal.

The alteration effects described so far are thought to have resulted from reaction of the affected rocks with solutions containing dissolved potassium, sodium, magnesium and iron. These elements are all present in the indigenous constituents of Waulsortian limestones, but it is probable that they were derived in greater quantity from other sources. Certain features of sulphide distribution that are described elsewhere suggest that the main direction of movement of mineralising solutions was upwards, and there is no reason to believe that radical changes in their direction of flow took place at any time. A possible source of most of the elements introduced into the zone of mineralisation during the early phases of chemical activity was the Lower Carboniferous sediments underlying the Waulsortian bank, in particular the Lower Muddy Limestone.

In some places the solutions circulating during the stage of wallrock alteration were sufficiently rich in reduced sulphur species for pyrite and arsenopyrite to be deposited in local quantity. Formation of the two minerals as disseminated and aggregated euhedra up to 5 mm. across in Lower Muddy Limestone of the fault slice and in Devonian sediments in the immediate footwall of the North Tynagh Fault is thought to have taken place at this time.

A similar distribution of pyrite and arsenopyrite has been reported by Rhoden (1958) at Silvermines, County Tipperary, where Devonian sediments for a considerable distance from the main fault zone are unusually pale and pyritic. Rhoden attributed the formation of pyrite and subordinate arsenopyrite at Silvermines to sulphidation of compounds of iron and arsenic indigenous to the sediments during the phase of wallrock alteration. Reconstitution of sedimentary constituents by early sulphur-rich

solutions introduced along faults may also have occurred at Tynagh. The Lower Muddy Limestone and the Devonian sediments both contain indigenous hematite, and the background arsenic content of the rocks of the area is 30 ppm (Donovon, 1965). A similar process may have been responsible for the formation of the small amounts of early-formed siegenite that are occasionally found as corroded relics in later sulphides.

Another effect tentatively attributed to an early phase of reaction between sulphur-rich solutions and indigenous minerals was partial pyritization of thin hematite-jasper bands in Black Calp. This effect is only marked in ironstone bands exposed in the open pit, i.e. within 300 ft. of the North Tynagh Fault.

b) The iron and zinc sulphide stage

The first of the existing sulphides to form in quantity over a wide area were pyrite and marcasite, which crystallised in a multiplicity of habits (see Chapter 7) on the walls of solution cavities and, less abundantly, as replacements of limestone. Many cavities were lined by minutely crustified iron sulphides containing microspheroidal aggregates of tiny pyrite crystals (framboids). Some cavities were almost entirely filled by iron sulphides in nodular, botryoidal and arborescent aggregates with a fibrous internal structure.

Textures observed in polished sections, particularly sections of cavity linings, record a complicated history of deposition and post-depositional recrystallisation of iron sulphides. It is arguable from textural features exemplified by Plate 4.3 that much of the pyrite in the deposit is an alteration product of marcasite, and that in many cavity linings pyrite and marcasite were deposited alternately. In some crustified aggregates the external

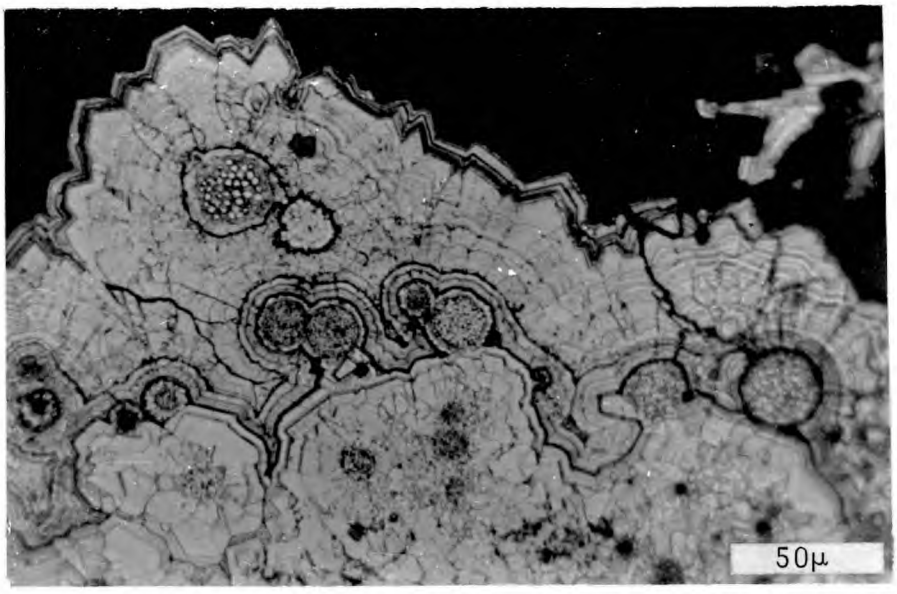


Plate 4.3 - Colloform banding and recrystallisation in pyrite. The oldest material illustrated (lower part of the photograph) is in an advanced state of grain-growth recrystallisation. It is overgown by bands of colloform pyrite that incorporate framboidal aggregates of pyrite. The younger bands have crystallised in structural continuity with drusy crystals of pyrite that appear to be an inversion product of marcasite. Polished section. Etched.

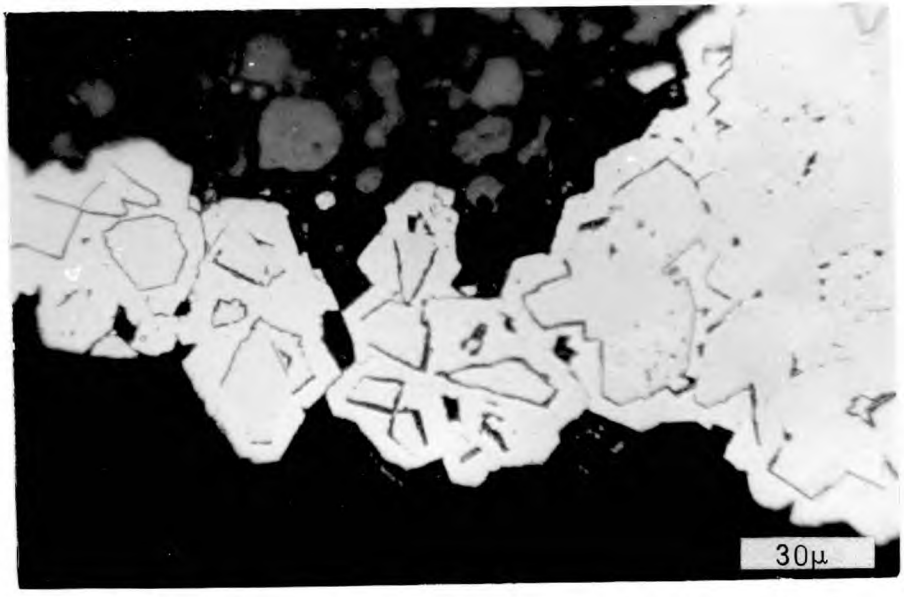


Plate 4.4 - Marcasite euhedra overgrown by pyrite. Polished section.

crust is original pyrite, in others pyrite pseudomorphous after marcasite, in a few original marcasite (Plates 4.3, 4.4). The "older" parts of crustified aggregates commonly show advanced grain-growth recrystallisation of an original iron sulphide of indeterminate structure to a medium-grained aggregate of subhedral or anhedral pyrite.

Alternating deposition of pyrite and marcasite may have arisen from periodic variations in the pH of the mineralising solutions, since it has been shown that formation of marcasite is favoured by (though it does not demand) acid conditions (Allen et al, 1914; Rickard, 1968, 1969). It has also be found experimentally that marcasite tends to form preferentially from low temperature solutions. Marcasite is probably less stable than pyrite under virtually all natural conditions, but since all the factors that control the rate of its monotropic transformation to pyrite have not been established, no firm conclusion can be drawn from the fact that the transformation has gone to completion in some specimens of Tynagh protore and is only partial in others. The degree of transformation does not seem to be related to the distance of sample sites from the North Tynagh Fault.

Lining of cavities, and complete infilling of smaller ones, was continued by zinc sulphide, which also formed in abundance as a replacement of limestone and of pre-existing iron sulphides (Plates 4.5, 4.6). Deposition of zinc sulphide largely postdated that of iron sulphide, but there was clearly some overlap in time between the main generations of the two. Crustified pyrite, sometimes containing small globular bodies of sphalerite on junctions between growth zones, was locally deposited on an initial cavity lining of sphalerite, and small euhedra of pyrite formed in places on drusy sphalerite. Replacement of sphalerite

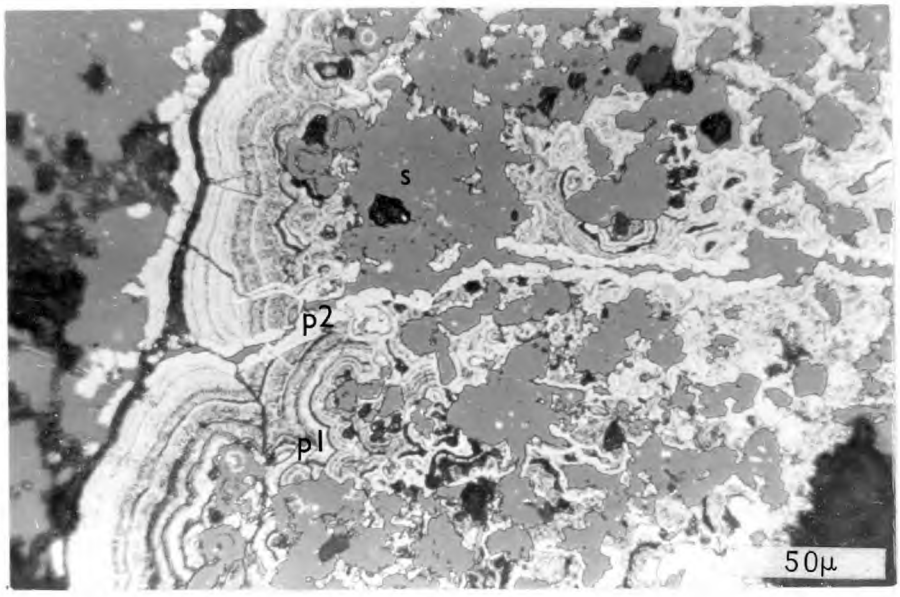


Plate 4.5 - Fractured colloform pyrite (p1) partially healed by pyrite (p2) and replaced by sphalerite (s). Polished section. Etched.

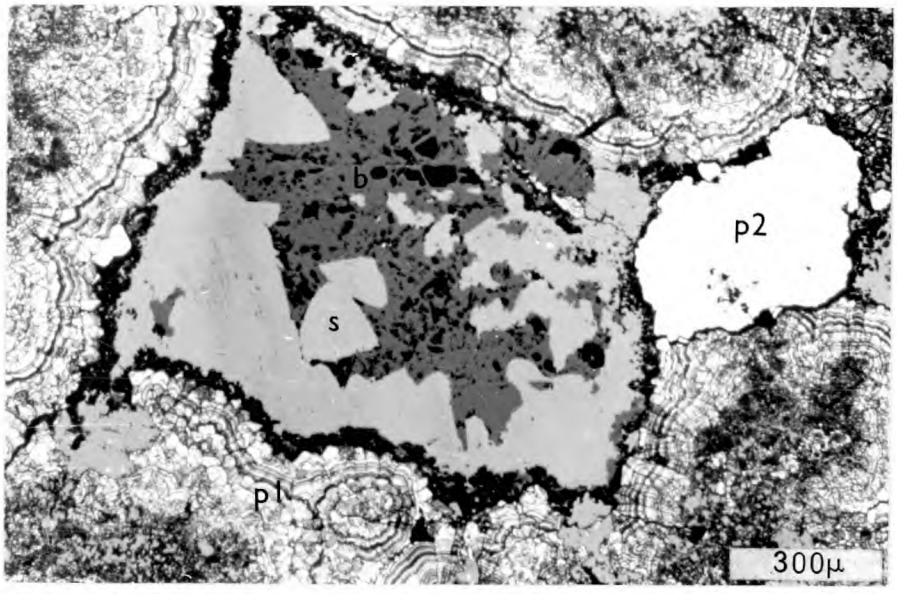


Plate 4.6 - Colloform pyrite (p1) overgrown and partially replaced by later pyrite (p2) with greater etch resistance, and by sphalerite (s). The central cavity was infilled by coarsely crystalline barite (b). At a later stage, solutions moving along the junction between colloform pyrite and the central sphalerite-barite intergrowth dissolved sphalerite and precipitated barite and pyrite. Polished section. Etched.

by pyrite and marcasite are occasionally seen, and aggregates of apparently co-deposited sphalerite and pyrite are not uncommon.

Much cavity-lining sphalerite, and some formed by replacement of limestone, occurs in colour-banded microgranular aggregates that are often overgrown by coarser crystalline material. The latter is generally paler in colour than the darkest of the colour-banded material, which tends to be concentrated in narrow, closely-spaced zones in the "older" parts of aggregates. Relatively pale granular sphalerite occurs as microscopic veinlets cutting crustified sphalerite aggregates. The colour of the sphalerite in thin section ranges from deep reddish brown to very pale yellow.

These relationships, which are described in greater detail in Chapter 7, may indicate that the character of the solutions from which zinc sulphide was deposited changed with time from colloidal to ionic, and tended to become progressively depleted in iron. As discussed elsewhere, however, the colour of sphalerite may not always be a reliable indication of the mineral's iron content, and it has recently been shown by Roedder (1968) that many textures hitherto regarded as indicative of colloidal deposition can result from crystallisation from ionic solutions, especially when precipitation is rapid. Present evidence on both points is therefore inconclusive.

Schultz (1968) states that small quantities of sphalerite in the Main Orebody occur in radiating fibrous and bladed habits, and may be an inversion product of the hexagonal ZnS dimorph, wurtzite. Original wurtzite has not been observed in the deposit, and its former presence cannot be proved on textural grounds. The range of conditions under which wurtzite forms in preference to sphalerite is uncertain (see Chapter 8) but they are thought to include conditions analogous to those that favour the formation

of marcasite rather than pyrite (see above). As deposition of sphalerite at Tynagh probably overlapped that of marcasite, Schultz's conjecture may be correct.

Coarse grained primary sphalerite at Tynagh occasionally contains tiny vacuoles that appear to have a fluid filling. The composition and homogenisation temperature of their contents have not been investigated and could well provide valuable information about the nature and the temperature of the ore-forming fluids during this stage of mineralisation. The trace element content of Tynagh sphalerite is probably not a function of the mineral's crystallisation temperature: in particular, since it cannot be demonstrated that sphalerite formed contemporaneously with an iron-rich phase, the sphalerite geothermometer cannot validly be applied to the deposit.

During the phase of mineralisation now being considered, small amounts of a hydrocarbon that was presumably introduced into the system of cavities as a viscous derivative of organic substances in impure limestones solidified as thin crusts on pyrite and occasionally on sphalerite. In some specimens the hydrocarbon appears to have encrusted pyrite before the deposition of sphalerite, in others to have encrusted both sulphides.

Most of the voids that remained when deposition of iron and zinc sulphides had largely ceased were filled by coarsely crystalline barite and calcite (Plate 4.6). The two minerals crystallised together in some cavities, while in others barite replaced calcite or vice versa. Variations in the iron content of calcite revealed by staining show that some cavity-filling calcite in anhedral mosaics was originally deposited as crystalline crusts on cavity walls. Small amounts of pyrite, arsenopyrite and hydrocarbon were deposited with the calcite.

Barite was also deposited abundantly as a replacement of limestone and dolomite, generally forming as radiating, reticulated or disordered aggregates of small bladed crystals (Plate 4.7). Textural evidence as to the order of deposition of barite and of sulphides (particularly those of iron and zinc) is frequently ambiguous. In particular it is sometimes impossible to verify texturally that barite that appears in hand specimen to be a final filling of a void previously lined by sulphides did not crystallise before the latter, perhaps in a cavity of which an original calcite lining subsequently suffered selective replacement by sulphides.

A characteristic of the barite is that it is littered with inclusions, most of them too small to be resolved by optical methods of microscopy. Two analyses given in Chapter 7 strongly suggest that the included substances include halides (dominantly or exclusively chlorides), and it is conjectured that the fluid inclusions in sphalerite referred to above would also be found to contain halides. Chlorine-rich solutions have been found as inclusions in sphalerite at the Keel zinc deposit, Co. Longford (Morrissey et al, 1969).

Small-scale effects that were probably related in time to the period of cavity infilling included widespread replacement of sphalerite by ferroan dolomite as poikilitic areas and euhedra, and zonal and uncontrolled replacements of sphalerite by calcite. Tiny euhedra of feldspar included in sphalerite may also have formed at this time, though most were probably inherited by the sulphide from replaced limestone. A recurrent dilemma in determining the crystallisation sequence of minerals in Tynagh protore is whether euhedral inclusions of one mineral in another crystallised before, contemporaneously with, or after their host. In interpreting ambiguous relationships of this sort the writer has usually assigned the minerals concerned to their

major generations, though in doing so he may have over-simplified the paragenetic sequence.

Rare marginal replacements of disseminated sphalerite grains in impure limestone by chlorite or by mixtures of chlorite, feldspar and quartz may (by analogy with similar replacements noted by Rhoden (1958) at Silvermines) have occurred at this stage in the mineralisation history, but this is not certain. These replacements are thought to have resulted from chemical equilibration of newly-deposited sphalerite with the enclosing sediments in the presence of residual solutions of mineralisation.

c) The copper and lead sulphide stage

The succeeding phase of mineralisation resulted in the simultaneous and sequential deposition of sulphides and sulphosalts of copper and lead. To a large extent this took place at the expense of pre-existing epigenetic minerals, and was sometimes strongly influenced by compositional and structural inhomogeneities in the latter (Plates 4.8, 4.9). Tennantite and galena, for instance, sometimes formed by selective replacement of early sulphide linings of barite-filled cavities, producing a crustification effect that in hand specimen gives a misleading impression of the crystallisation sequence.

The first copper mineral to crystallise was generally tennantite, accompanied locally by subordinate amounts of enargite (Plate 4.10). In the usual granular aggregates with each other, the two sulphosalts typically have mutually interpenetrating junctions, and occasionally occur in each other as smooth-sided microveinlets with non-matching walls. They are thought to have been essentially co-depositional.

Plate 4.7 - Radiating bundles of barite crystals in a sulphide-barite aggregate. Thin section.

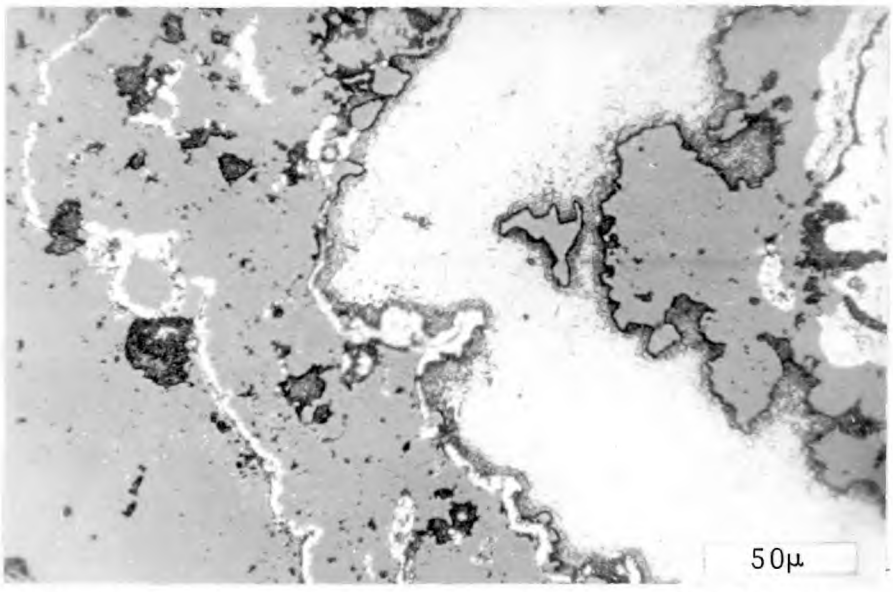


Plate 4.8 - Guided replacement by galena (white, low relief) of sphalerite (grey) containing relics of colloform-banded pyrite. Polished section.

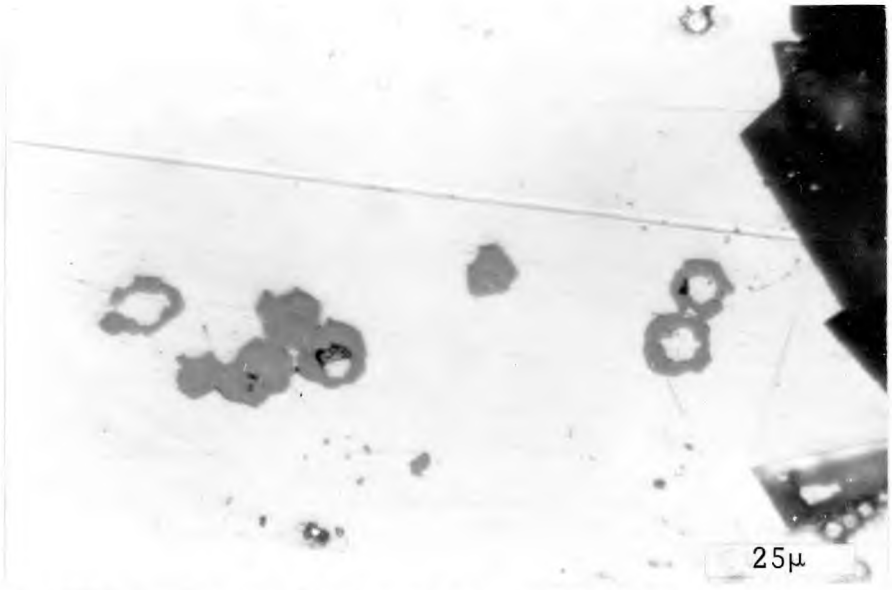


Plate 4.9 - Atoll-shaped replacement relics of microgranular sphalerite (medium grey) in galena (white). Polished section.

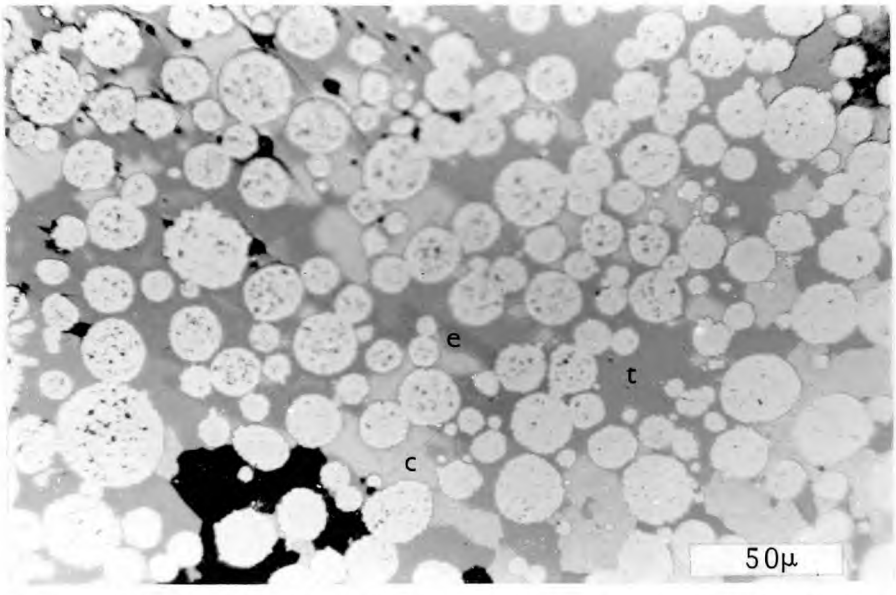


Plate 4.10 - Framboidal pyrite aggregates in a matrix of tennantite (t) and enargite (e). The sulphosalts have been preferentially replaced by chalcopyrite (c). Polished section.

Where tennantite is accompanied by chalcopyrite, replacement textures generally indicate that the sulphosalt crystallised first, but occasionally tennantite appears to have replaced chalcopyrite, or the two minerals have intergrowth relationships similar to those of tennantite and enargite.

Both chalcopyrite and tennantite sometimes have mutual grain boundaries with galena, indicating some co-deposition of the three minerals. This may be a local effect, as such textures have so far only been seen in material from close to the North Tynagh Fault. Veinlets of galena cross-cut by veinlets of primary copper minerals have been seen in the walls of the open pit by Whitehead (pers. comm.), but textural relationships in polished section usually show that galena crystallised after chalcopyrite and tennantite.

Galena had a strong tendency to form by idioblastic replacement, especially of fine-grained pyrite and sphalerite, sometimes of fine-grained limestone. This tendency is illustrated by Plates 4.11, 4.12 and 4.13. Textures closely resembling those shown in Plate 4.12 were observed by Beales and Jackson (1966) in mineralisation from the Pine Point orefield, N.W. Canada, and by Boyle and Jambor (1966) in the Magnet Cove deposit, Newfoundland. Boyle and Jambor concluded that the galena euhedra at Magnet Cove resulted from replacement of sphalerite by a lead sulphide colloid which, on aging, slowly crystallised. Roedder (1968) has recently suggested that simultaneous crystallisation of galena and sphalerite from ionic solutions could produce euhedra of the first that transect colloform banding in the second. It is possible that some encrustations of euhedral galena by colloform pyrite in Tynagh primary mineralisation resulted in this way, but more likely that all textures of the kind exemplified by Plates 4.12 and 4.13 resulted from replacement

of early sulphides by a later generation of galena. In some specimens, there is textural evidence that grain-growth recrystallisation of pyrite was well advanced by the time that galena began to be deposited.

Characteristically associated with galena are small amounts of bournonite and jordanite, which sometimes occur as 5-30 μ blebs elongated in galena cleavage directions, but more commonly as randomly distributed irregular or roundish inclusions with approximately the same size range, or as larger grains at the margins of galena areas (Plates 4.14, 4.15).

Occasionally bournonite and jordanite occur other than as intergrowths with galena. Jordanite has been found as tiny idioblastic euhedra replacing granular pyrite, and bournonite in a simplectic intergrowth with enargite apparently formed by replacement of tennantite (Plate 4.16). An unusual assemblage found in a veinlet of sparry calcite comprised discrete grains of bournonite with microscopic euhedra of enargite, covellite, and pyrite. Although the material was not typical, and simultaneous deposition of covellite and pyrite could not be proved, it is worth noting that these two minerals do not, in the presence of a sulphur-rich liquid and a vapour phase, form a stable assemblage in the Cu-Fe-S system above 434°C (Roseboom and Kellerud, 1958).

In all their associations, bournonite and jordanite may have formed as a result of the reaction of lead-rich solutions with pre-existing tennantite. Silver derived from tennantite may have been reprecipitated as a constituent of minerals deposited from these solutions, including galena, jordanite and bournonite. It will be shown in Chapter 7, by reference to silver:lead ratios in copper-poor mineralisation, that in some parts of the

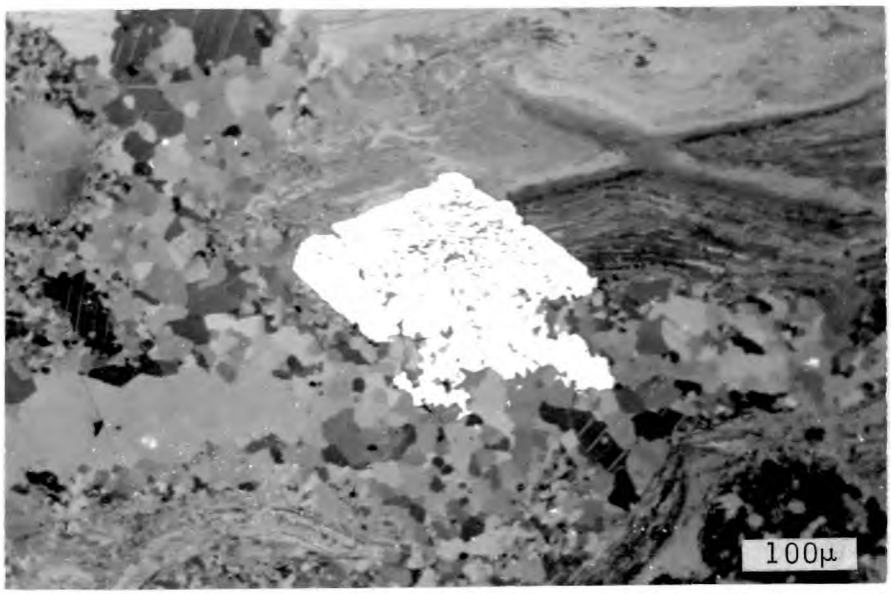


Plate 4.11 - Idioblastic replacement of limestone (biomicrite) by galena. Polished section.

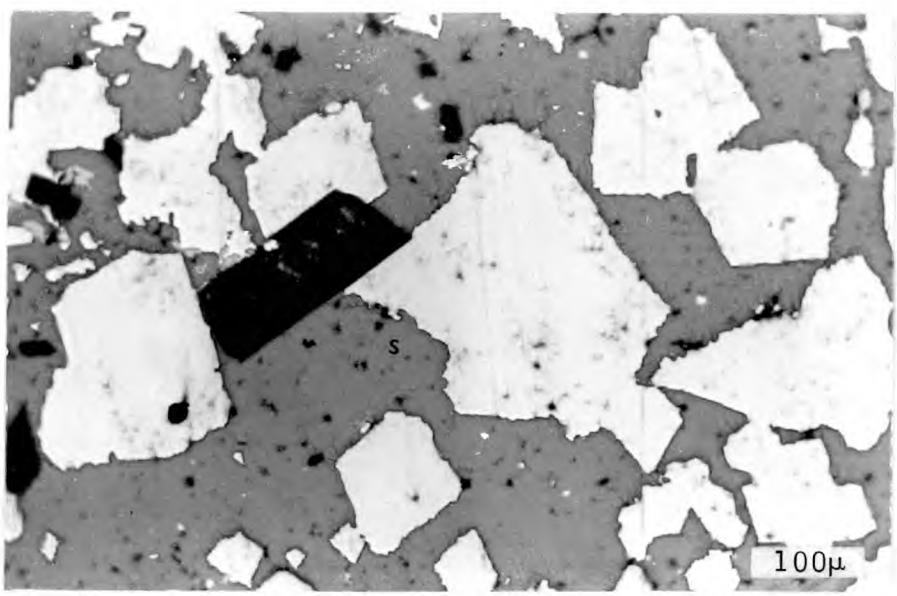


Plate 4.12 - Idioblastic replacement of sphalerite (s) by galena. The poorly reflecting tabular crystal is albite. Polished section.

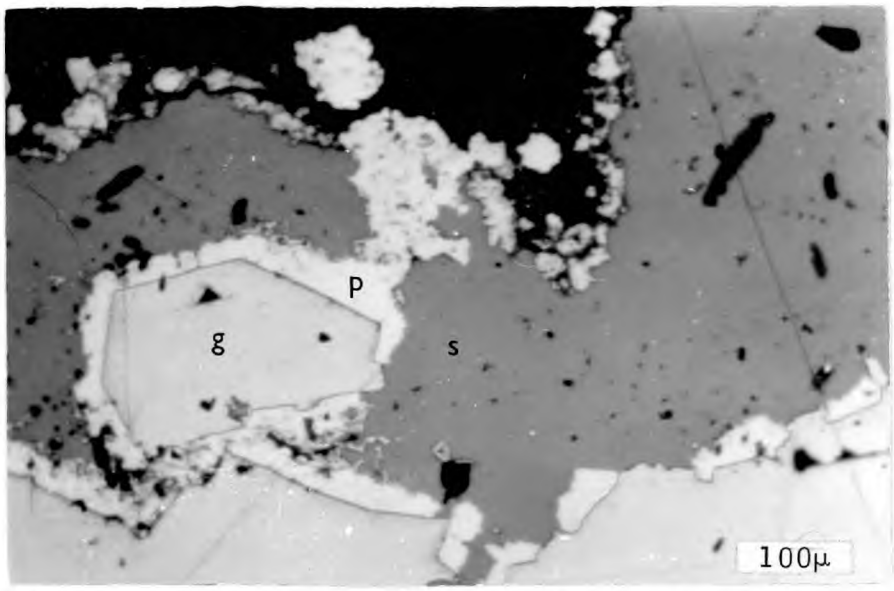


Plate 4.13a - Sphalerite (s) containing euhedral areas of galena (g) partially rimmed by pyrite (p). The galena seems to have formed by idioblastic replacement of the other sulphides. Polished section.

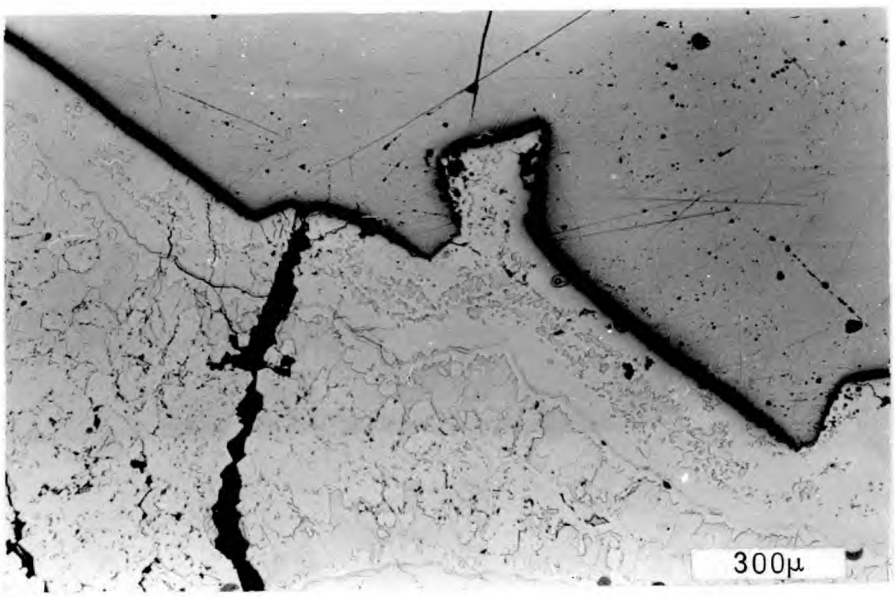


Plate 4.13b - Colloform pyrite rimming euhedral galena (low relief). Textural evidence of the crystallisation sequence of the two sulphides is ambiguous. The black areas are voids. Polished section.

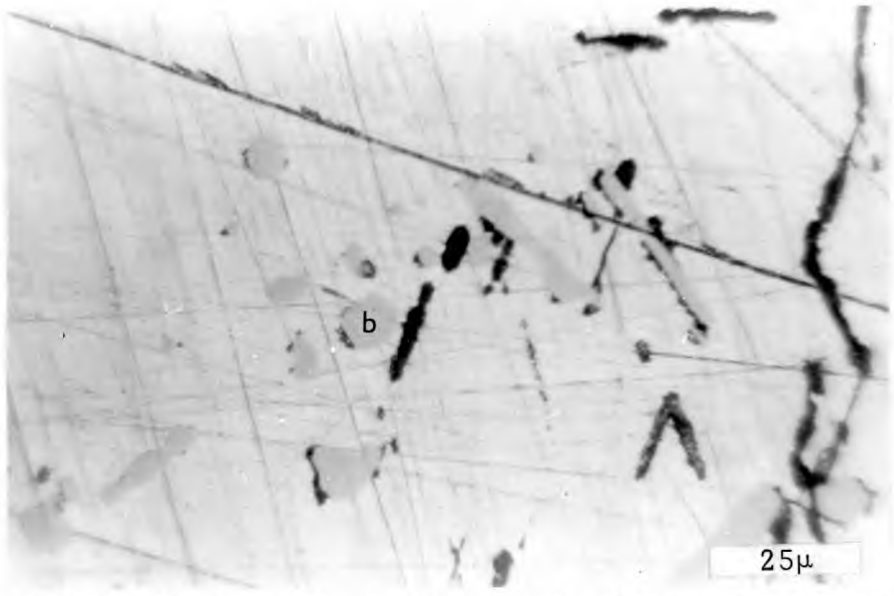


Plate 4.14 - Inclusions of bournonite (b) in galena. Some bournonite blebs are elongated in galena cleavage directions, which have been emphasised by light etching. Polished section.

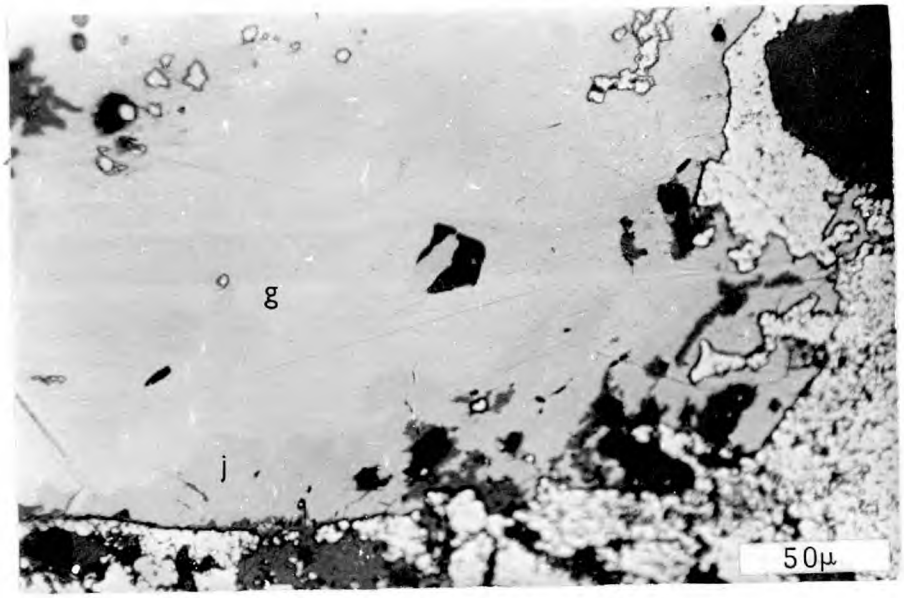


Plate 4.15 - Jordanite (j) marginal to galena (g), from which it may have exsolved. Polished section.

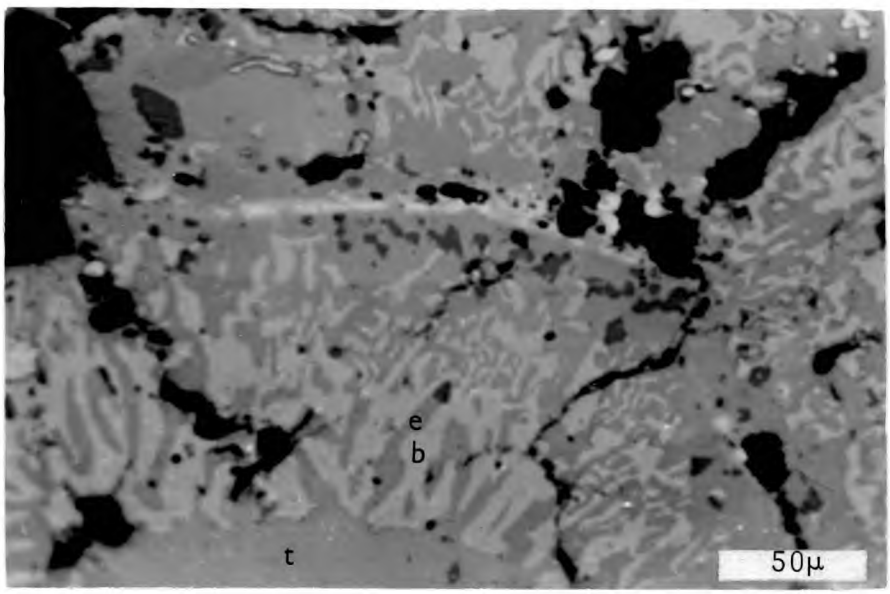


Plate 4.16 - Simplectic intergrowth of enargite (e) and bournonite (b) probably formed by hydrothermal alteration of tennantite (t). Polished section.

Main Orebody the crystallisation temperature of galena may have exceeded 300°C.

Small amounts of calcite, barite and dolomite or ankerite crystallised after the minerals just described, the first two partly as patchy granular replacements of earlier epigenetic minerals and partly as fillings of post-mineralisation fractures, and the last usually as small poikilitic rhombs replacing sulphides. Late calcite veinlets sometimes contain coarse grains of honey-coloured sphalerite. All these late-stage precipitates are considered to be products of local recrystallisation of minerals of earlier generations.

4.5 METAL ZONING

Drill core assays show pronounced heavy metal zoning in both orebodies. Certain broad patterns of zoning are apparent from present information, but the details of what is undoubtedly a very complicated zoning scheme remain to be worked out. The significance of the zoning is obscure, and will be more easily assessed when underground mining and closer drilling have clarified the structural and sedimentological setting of the mineralisation.

Broadly speaking, copper is concentrated in the eastern half of the Main Orebody, where grades of up to 2.2% Cu occur in boreholes 300 ft. to the north of the North Tynagh Fault (Fig. 4.1). Within this area, and elsewhere, copper tends to be still further concentrated in the close vicinity of the North Tynagh Fault and in limestones straddling the lower facies contact of the Waulsortian Bank Formation. In the western part of the Main Orebody, grades of more than 0.5% Cu occur at a few places more than 50 ft. to the north of the North Tynagh Fault,

usually in the upper part of the Lower Muddy Limestone or just above it, but the main copper concentrations are in the immediate hanging wall of the main fault. Copper is concentrated in the same position in the East Extension Orebody.

An interesting feature of copper distribution is that chalcopyrite tends to be more abundant than tennantite in argillaceous host rocks, and this seems to be particularly so when the rocks are sheared. The North Tynagh Fault gouge, for instance, in some places contains numerous streaks, patches and veinlets of chalcopyrite and little or no tennantite. This could be accounted for by selective precipitation of chalcopyrite in and near the conduits through which copper-bearing solutions moved from lower levels. Lacking information about the relative solubilities of the two minerals in complex solutions of their constituents, the writer cannot suggest the possible cause of selective precipitation of chalcopyrite at Tynagh. Migration of chalcopyrite down pressure gradients following relaxation of tectonic stresses may have played some part in concentrating the mineral.

Lead and zinc are concentrated in the central and western parts of the Main Orebody. Inasmuch as high grade zinc mineralisation is only patchily distributed at the Orebody's eastern end, where copper grades widely exceed 0.5%, it can be said that the distribution of zinc is broadly antipathetic with respect to that of copper. The imperfectness of the relationship is illustrated by the fact that sections of mineralisation containing up to 33% Zn occur in the copper-rich area, and do so both close to the main fault and at a distance from it.

In some boreholes, lead:zinc ratios seem to vary in a systematic manner, e.g. vertical transitions from lead-rich

to zinc-rich mineralisation or the reverse, but such features can rarely be correlated between adjacent boreholes, and it is equally common for ratios to vary widely from one assay section to the next.

Local variations in lead:zinc ratios generally do not seem to be related to variations in lithology or structure, though it is sometimes the case that argillaceous or hematitic phases within the bank structure separate mineralisation with widely different metal abundance characteristics, just as they sometimes mark the upper limit of sections of high-grade mineralisation.

Both in the Main Orebody and in the East Extension Orebody zinc is more widely distributed than lead. It is the dominant metal of the two on the northern fringes of both orebodies, and at the western extremity of the Main Orebody as presently defined. This feature may indicate that mineralisation was spasmodic, for Garrels (1941) has shown that galena tends to be more soluble than sphalerite in chlorine-rich hydrothermal solutions due to selective suppression of zinc ion activity by the formation of chloride complexes. Alternatively it may reflect sequential precipitation of epigenetic minerals from a single solution with a chloride ion concentration lower than required to make galena more soluble than sphalerite. Present evidence of a substantial difference in depositional temperature between the two sulphides is too scant and unreliable to invalidate the second alternative.

Apart from a few anomolies that may be due to the presence of silver as a lattice constituent of sphalerite or, as Schultz (1968) maintains, to augmentation of sphalerite by silver-bearing sulphosalts during the late stages of mineralisation, the distribution of silver is compatible with its occurrence, at somewhat variable concentrations, as a lattice constituent of tennantite and as an intimate associate of galena. The mineralogy and distribution of primary silver are discussed in more detail in later chapters.

Such patterns of heavy metal zonation as can be distinguished at this stage are not relatable to variations in sedimentary facies. Nor do they have focal points at the intersections of known or suspected major fractures in the Upper Palaeozoic rocks of the area. Rather, the mineralising fluids are envisaged as having risen, perhaps at more than one time, along a broad front that was defined on its southern side by pre-Carboniferous rocks, and can be described as the zone of the North Tynagh Fault's greatest tectonic influence on its hangingwall block.

4.6 DEFORMATION

Apart from fractures described in a previous section, mineralisation in Waulsortian bank limestones and in Devonian rocks generally contains little or no evidence of deformation even in the immediate vicinity of the North Tynagh Fault. Mineralisation in Lower Muddy Limestone, on the other hand, has suffered profound deformation in a zone that extends at least 100ft. to the north of the main fault. The intensity

deformation apparent in epigenetic minerals varies considerably from place to place.

Pyrite in strongly deformed Lower Muddy Limestone tends to be finely granulated, banded aggregates torn apart, and disrupted elements rotated. Associated sphalerite tends to develop flow banding around pyrite fragments, but it also occurs as replacements of their calcite pressure fringes. Barite crystals are sometimes highly distorted and pulled apart on cleavages. Chalcopyrite and tennantite in strongly deformed material occur as streaks and whisps elongated in the minor stress direction, but occasionally chalcopyrite fills fractures that transect stress-induced banding. Galena similarly occurs in streaky arrangements and is sometimes finely granulated, but it also occurs as microscopic replacements of stress-banded sediments and earlier sulphides, and sometimes tongues into stress-induced cleavages in the sediments. Replacement of deformed materials by chalcopyrite and galena seems to indicate that deformation did not everywhere outlast mineralisation, but it is equally possible that it resulted from local recrystallisation of pre-existing sulphides during or after movement.

Other deformation fabrics in primary mineralisation are gash veinlets with a filling of fibrous calcite. These have been found in protore from close to the main fault and from more than 300 ft. to the north of it. The calcite is sometimes accompanied by subordinate amounts of quartz, feldspar, chlorite or more than one of these minerals. The veinlets are usually less than 3 cm. wide and 5 cm. long and tend to be sinuous or irregular in shape.

According to Schultz (1968), gash veinlets in solid rock are rarely inclined at more than 30° from the horizontal, and

the fibrous crystals they contain have a marked tendency to allignment in vertical or steeply inclined directions. He concludes that the gashes and their fibrous fillings formed penecontemporaneously under the influence of a major compressive stress applied nearly horizontally, and that the stress was due to movement on the North Tynagh Fault.

The fibrous fillings of many gashes are deformed, and some have been partially replaced by sphalerite and/or later epigenetic minerals. Occasionally it seems from its fibrous habit that sphalerite crystallised with calcite in the gashes during their formation, which evidently occurred mainly during the early stages of mineralisation. Movement at that time also caused local fracturing of pyrite, sphalerite and solid hydrocarbon. Intense cataclasis is generally only seen in pyrite, which is sometimes cemented by later pyrite but more usually by undeformed sphalerite or calcite.

Taken as a whole, these fabrics suggest that movement on the North Tynagh Fault took place both during and after mineralisation. It is not possible to say when the most recent movement on the fault occurred, though it will be shown later that the fault has not been active since mid-Tertiary times.

Variations in the intensity of the stresses applied to mineralised rocks as a result of fault movement are presumably due to some extent to the undulating nature of the fault plane and to variations in the width and consistency of the fault gouge.

The attitude of the tension gashes referred to above (which are a potentially fruitful source of further information about the tectonic history of the area) indicates that either the main fault did not develop in response to a vertical major

stress as proposed by Schultz, or else that the major stress direction varied considerably with time.

4.7 ORIGIN

The primary mineralisation at Tynagh is similar in many respects to that of many base metal deposits variously classified as epithermal, telethermal, telemagmatic, leptothermal, low mesothermal and Mississippi Valley type (Lindgren, 1933; Bateman, 1950; Edwards, 1954; Ohle, 1959; Park and MacDiarmid, 1964). The sulphide-sulphosalt paragenesis corresponds closely with that given by Oelsner (1966) for hydrothermal lead-zinc assemblages with associated copper and silver of magnetic (sialic-palingenetic) derivation.

Derry, Clark and Gillat (1965) suggested in a preliminary geological account of the deposit that the sulphide-barite mineralisation and the iron-silica sediments of the Tynagh Iron Formation were derived from solfataric solutions issuing from submarine fissures in a zone following the line of the North Tynagh Fault. Both were thought by them to be related genetically to volcanic activity during the formation of the Waulsortian bank. To account for epigenetic characteristics in the sulphide-barite mineralisation, they proposed that original precipitates suffered chemical re-working by solutions of an unspecified age and nature that ascended the North Tynagh Fault.

Schultz (1968) disputes this interpretation on most counts, and argues from detailed petrofabric analyses that mineralisation post-dated lithification of the youngest Carboniferous rocks now present in the area. He considers that the sulphide-barite mineralisation was deposited from heated solutions rising through the North Tynagh Fault zone during or after late Carboniferous

times, and that the mineralising events were directly or indirectly related to cryptomagmatism that also caused updoming of the Slieve Aughty area. He leaves open the question of the ultimate source of the introduced metals and the part played by non-juvenile waters in their transport, but draws attention to the fact that the lead isotope model ages of galenas from a number of small deposits in west-central Ireland are compatible with an episode of magmatic-hydrothermal mineralisation about 290 million years ago. According to Russell (1968), the most probable source of the metals was the Lower Palaeozoic basement.

The writer is more attracted to Schultz's hypothesis than to one involving exhalative-sedimentary processes of ore formation. It must be allowed that the spatial coincidence of tuffs and sulphide mineralisation suggests a genetic connection between them, but it certainly does not guarantee that vulcanicity and mineralisation occurred simultaneously. Both may have the same root cause - deep-seated magmatic activity accompanied, over a long period of time, by widespread crustal disturbances - and future studies may well show that Lower Carboniferous synsedimentary mineralisation occurred in some parts of Ireland. At Tynagh, however, the evidence that mineralisation wholly post-dated lithification of the host rocks seems overwhelming.

As to the source of the metals, it is envisaged that they were leached from both Lower and Upper Palaeozoic rocks and transported, partly perhaps as chloride complexes, in heated saline solutions or brines whose temperature during sulphide formation may well have somewhat exceeded 300°C. The solutions may have been a mixture of connate brines and magmatic waters. It is possible that a proportion of the sulphur combined in sulphides originated by bacterial sulphate reduction within the Waulsortian bank and its immediate environs. These speculations

are supported by recent studies of present-day thermal waters and associated mineralisation (White, 1968; Browne, 1969; Ellis, 1969) and of fluid inclusions in mineralisation of the Mississippi Valley type (Sawkins, 1968). They are in agreement with general principles proposed by Rickard (1968) and White (1968) for the formation of base metal deposits in sedimentary rocks.

The Tynagh mineralisation has much in common with that at Keel and Silvermines. Mineralogically, all three comprise, in varying proportions, sphalerite, galena, tetrahedrite-tennantite, chalcopyrite, minor sulphosalts, pyrite, marcasite and barite. The striking similarity in the structural setting of the three deposits is shared by the Cu-Hg-Ag mineralisation at Gortdrum.

However, in addition to differences in host-rock lithology in relative metal abundances, there are some interesting differences in mineralogy between the four deposits. For instance, the tetrahedrite-tennantite series is represented at Keel by silver-rich tetrahedrite, at Tynagh by zinc-rich tennantite and at Gortdrum by mercury-rich tennantite. Analyses of Silvermines material are not available. A second notable difference is that the average cadmium content of Keel sphalerite (about 10,000 ppm; Patterson, pers. comm.) is more than twice that of primary sphalerite at Tynagh, while sphalerite concentrates now being produced at Silvermines are reported to be comparatively poor in cadmium. Sphalerite is a very minor constituent of the Gortdrum mineralisation.

These differences do not invalidate other evidence that the four deposits are genetically related. They may be due to local variations in, for instance, the lithology and trace element chemistry of subjacent rocks, and/or the contribution made by magmatic sources to the mineralising process.

PART II

INTRODUCTION

Entrenched in Lower Carboniferous limestones in the immediate hanging wall of the North Tynagh Fault, and immediately overlain by Pleistocene glacial till, is a five million ton body of rubble and mud known as the residual deposit. The unconsolidated materials are worked for lead, zinc, copper and silver, the first three of which are present chiefly as sulphides and carbonates.

Sub-till outcrop dimensions of the deposit are 2,300 ft. from east to west by a maximum of about 550 ft. The base of the deposit shelves irregularly from its eastern and western ends towards a central part in which the unconsolidated materials are about 250 ft. thick.

The deposit is elongated parallel to the strike of the North Tynagh Fault, and the plane of that fault generally forms its southern boundary. Otherwise it is largely bounded by limestones of the Waulsortian Bank Formation, which in places contain strong sulphide-barite mineralisation.

About 85% of the material that the deposit contained when it was discovered in 1961 was of ore grade, and of the original (1962) ore reserve, just under 70% was classified as sulphide ore:

	Short tons	Pb%	Zn%	Cu%	Ag oz/ton
Sulphide Ore	2,890,000	8.8	7.8	0.3	2.9
Oxide Ore	1,350,000	9.6	6.4	1.3	3.8
Total	4,240,000	9.1	7.4	0.6	3.2

A very much more elaborate system of ore classification by treatment types is now used at the mine for grade control purposes (Fitzgerald and Oram, 1969), and about a fifth of the original reserve of sulphide ore has been reclassified to optimise metal recoveries.

The residual deposit was brought into production by open pit methods towards the end of 1965. Since then the operating results of the mine have been as follows:

	1966	1967	1968
Ore treated, short tons	545,693	703,511	709,813
Concentrates produced, s.tons	121,564	190,985	181,950
Lead in concentrates, short tons	42,077	65,750	64,750
Zinc in concentrates, short tons	24,008	39,750	34,500
Copper in concentrates, short tons	1,743	3,300	2,550
Silver in concentrates, troy oz.	1,218,000	2,067,000	1,516,000

NOMENCLATURE

The deposit has been referred to as "residual" and "secondary" by Derry et al (1965) and by Schultz (1966a, 1968). In this thesis the term "secondary" is applied only to supergene minerals and geochemical processes. The terms "residuum" and "residual" will be used without qualification, except where the context requires distinction between materials formed by decalcification of rocks with litte alteration of their non-carbonate constituents ("physical residuum") and decalcification products that have been substantially altered to or augmented by minerals of supergene origin ("chemical residuum").

Distinction will be drawn between residuum that occupies more or less the same position in space as the parent rock did ("in situ") and residuum that has undergone physical transport from its place of origin ("transported"). For convenience, all residuum that contains a "ghost" stratigraphy will be included in the former category.

Because of its extreme physical inhomogeneity, most of the residuum can only be described in such general terms as "a gritty mud". Such descriptions are usually based on visual estimates of size grade abundances in typical material. The size grades referred to, which are partly based on British Standard definitions for inorganic sediments, are:

boulders	more than 8 in.
cobbles/blocks	8 in.- $2\frac{1}{2}$ in.
pebbles	$2\frac{1}{2}$ in.- 1 in.
grit	1 in. - 60 μ
mud	less than 60 μ (approx. 325 mesh B.S.S.)

Mixtures of blocks, pebbles and grit with an estimated average mud content of less than 25 per cent will generally be described as "rubble".

There is only a limited amount of agreement between the terminology used in this thesis and that used on the mine for grade control purposes. For instance, much material that will be referred to in the following pages as sulphide-barite rubble is classified by the mine as oxide ore because it contains more than 15% of total lead or 20% of total zinc in oxidate mineral species.

Finally it should be noted that the term "protore" will be applied to primary mineralisation and mineralised bedrock irrespective of their grade. It will not have the usual connotation that the mineralisation concerned is not economically mineable at the present time, though material in this category is covered by the term.

CHAPTER FIVE

COMPOSITION OF THE RESIDUUM

The possibility has to be considered that the constituents of the residual body are not wholly, or even largely, of local origin. In this chapter the residues that would result from decalcification of the main calcareous rock types of the Tynagh area are compared with the materials that constitute the bulk of the residual body.

5.1 THEORETICAL DECALCIFICATION PRODUCTS OF ROCKS OF THE TYNAGH AREA

It will be apparent from Figs. 4.1 and 5.1 that unmineralised rocks formerly present in the space occupied by the residual deposit were predominantly micrites, biomicrites and crinoidal limestone of the Waulsortian Bank Formation, and included sediments of all the Lower Carboniferous stratigraphic-lithologic units that at present bound the deposit.

Space vertically above the deposit's present outcrop was formerly occupied, to an estimated height of 150-200 ft. at its western end but less elsewhere, by the upper part of the Waulsortian Bank Formation, which probably consisted largely of crinoidal limestones. This was overlain by Calp that was almost certainly more than 500 ft., and perhaps well over 1,000 ft., thick (see page 34.)

Over most of the deposit's length the fault slice along its southern edge probably thickened upwards from the present erosion surface. There is no sound evidence that its northern contact

assumed a southward dip at higher levels. Just below the present erosion level the central part of the slice appears to contain the lower facies contact of the Waulsortian Bank Formation. The slice may, therefore, have been partly or largely represented by Waulsortian limestones of bank facies not far above the present erosion surface.

The main changes in the outcrop extent of the rocks that at present form bedrock in the Tynagh area in quasi-planar denudation surfaces at levels above that of the present would have been westward and southward encroachment of the Calp outcrop on that of the Waulsortian Bank Formation in the hanging wall of the North Tynagh Fault, and shrinkage of the outcrop area of the Tynagh Devonian inlier. The possibility that post-Carboniferous rocks may have overlain the area at levels at which they could have been involved in the formation of the residual deposit is discussed and discarded in Chapter 9.

Partial chemical analyses of the main types of Lower Carboniferous limestone represented in the immediate vicinity of the residual deposit are given in Table 5.1. The materials analysed were taken from boreholes in the mine area or from mining faces in fresh rock and were not visibly weathered or mineralised.

Carbon contents were not determined, but as Schultz (1968) reports that the exceptionally carbonaceous B-bed yields an acid-insoluble residue of 16% by weight that includes a variety of minerals other than carbonaceous ones, it is unlikely that more than 2% of carbon would have been found in even the darkest of the rocks analysed. To judge from the colour and reactivity with acid of representative material, the carbon and non-carbonate content of Calp varies considerably from bed to bed.

Table 5.2 lists the principal constituents of residua that would result from decalcification of the main types of Lower Carboniferous sediment bounding the residual deposit. The table is based mainly on thin and polished section studies of the rock types concerned, and on x-ray diffraction analyses of the pulverised residue of representative material digested in cold dilute hydrochloric acid. In addition to the materials listed, accessory amounts of dolomite and occasional grains of ilmenite, rutile, zircon, and possibly monazite have been observed in unmineralised limestones or their artificial residues. Other minerals commonly present in sediments containing terrigenous materials from granitic and metamorphic terrains (which formed land when the sediments under consideration were being deposited) include apatite, tourmaline, epidote, magnetite and garnet. Since the structure of the deposit leaves little doubt about the provenance of most of the residuum, a comparative study of the resistate minerals of terrigenous origin in the residuum and in the rocks of the Tynagh area was not considered worthwhile.

Most of the fauna that these rocks contain are composed of calcite. Minor exceptions to this that have been observed include the horny brachiopod Orbiculoidea, and conodonts with an exoskeleton composed of apatite. Very much more common are siliceous sponges, the spicules of which are particularly abundant in Calp. In impure limestones, calcareous organisms are sometimes replaced pseudomorphically by silica or (more rarely) pyrite, and it is relevant to this chapter that Zaphrentid corals and Spiriferid brachiopods are most commonly seen in Lower Muddy Limestone. A residuum of Lower Carboniferous rocks might therefore be expected to contain a palaeontogical record of its parentage.

As Figs. 4.1 and 5.1 show, the eastern and central parts of the residual deposit are immediately underlain by protore, and in

Table 5.1 Chemical analyses of wall rocks

Rock type	Weight per cent									ppm		
	$CaCO_3$	$MgCO_3$	SiO_2	Al_2O_3	Fe_2O_3	MnO	Na_2O	K_2O	TiO_2	Ni	Cr	B
Grey Calp	86.1	0.95	10.0	1.05	0.80	0.90	0.03	<2.0	0.10	50	<50	30
	92.0	0.80	5.7	0.40	0.45	0.45	0.02	<2.0	0.07	<10	<50	30
Waulsortian off-bank limestones	83.1	1.55	11.6	1.00	1.50	1.00	0.03	<2.0	0.10	200	<50	20
	86.0	1.30	9.0	2.00	1.00	0.35	0.05	<2.0	0.20	20	<50	30
Waulsortian bank limestone	95.6	1.25	1.9	0.40	0.55	0.12	0.05	<2.0	0.05	<10	<50	20
Lower Muddy Limestone	62.7	1.20	25.0	6.20	3.30	0.30	0.70	<2.0 (1600 ppm)	0.50	50	50	100

$CaCO_3$ by difference

Analyses by Robertson Research Ltd.

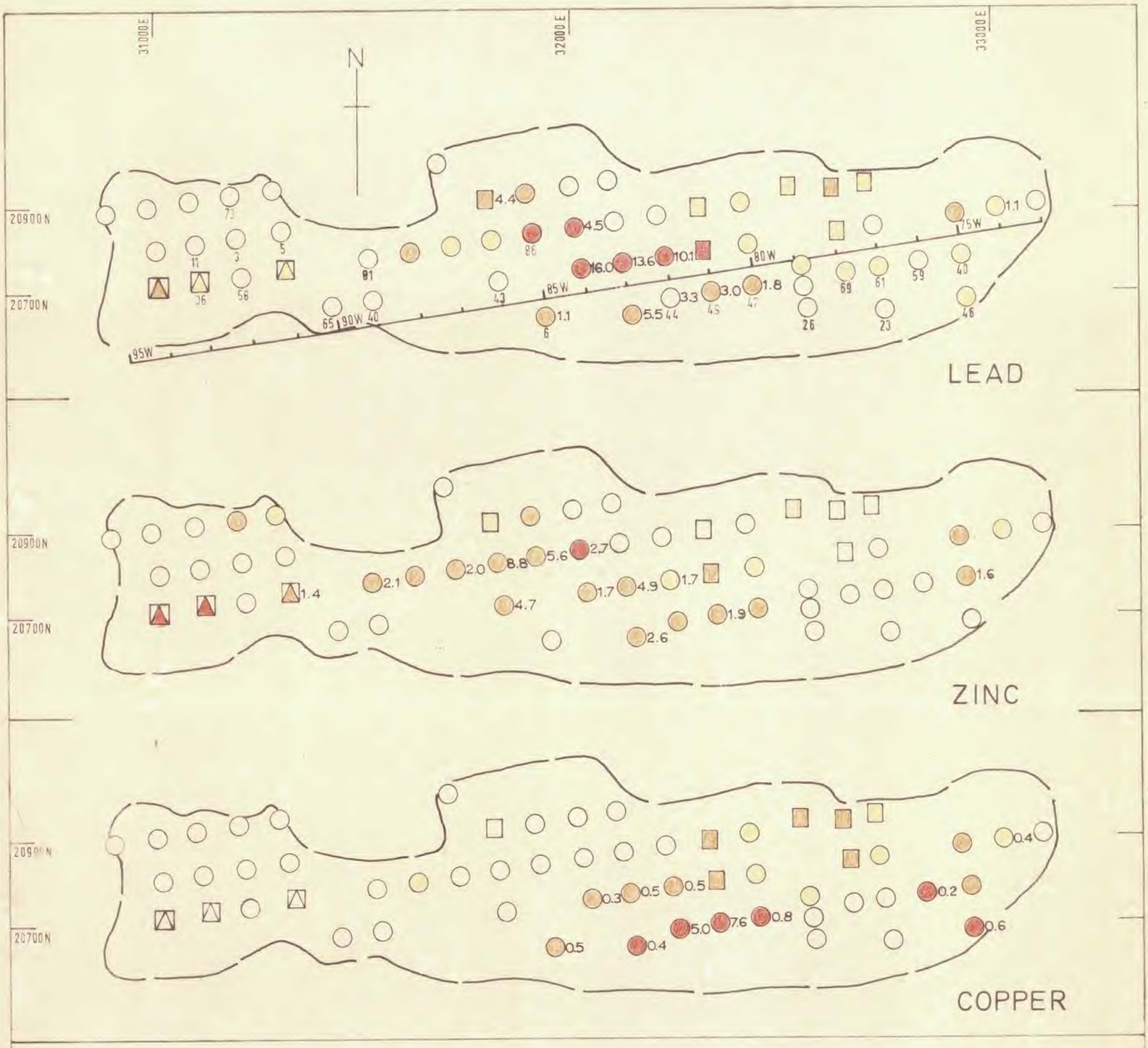
Table 5.2 Non-carbonate constituents of some Lower Carboniferous limestones

Facies	Stratigraphic unit	Approx. wt. %	Main non-carbonate constituents
Basin (Calp)	L1a L1b	10-35 5-15	Quartz (detrital silt and authigenic crystals), illite, siliceous sponge spicules, pyrite/marcasite (including thin beds), carbonaceous matter, chert (nodules, thin beds), muscovite, feldspar, silicified and pyritised organisms.
Waulsortian bank-cover and off-bank	L2a L2b	5-15 5-10	Quartz, illite, pyrite/marcasite, feldspar, chert, carbonaceous matter, muscovite, hematite/chlorite at certain horizons. Authigenic nickelian pyrite only observed in sediments of this facies.
Waulsortian bank	L2m	2-7	Illite, quartz, feldspar, pyrite.
"Lagoonal" (Lower Muddy Limestone).	L3	up to 50	Illite, quartz, muscovite, pyrite, feldspar, silicified and pyritised organisms.

transverse section appear to truncate the Main Orebody. Absolute and relative metal abundances in the truncated protore zone vary semi-systematically from place to place, and assay grade frequencies in rock cored from within 100 ft. of the rock-residuum contact have been plotted in Fig. 5.2 to show variations of this kind. The distribution of barite is not known in comparable detail, but analyses of 41 composite drill core specimens show that the mineral is strongly concentrated in certain parts of the protore zone (Fig. 5.2).

The lithochemical and structural controls of epigenetic mineralisation are well enough established to justify some upward projection of the Main Orebody into the space occupied by the residual deposit, especially in its south-central and south-eastern parts. Mineralisation is likely to have been strongly concentrated in micrites of bank facies within 300 ft. of the North Tynagh Fault, but could also have been present in significant amounts in Waulsortian limestones of other facies, and in Lower Muddy Limestone of the fault slice. Structural considerations suggest that it may have extended into Calp that originally overlay the central part of the area, probably as minor fracture-fillings in the axial region of the main hanging wall fold. Devonian sediments are unlikely to have been heavily mineralised.

Extrapolation of metal distribution patterns shown in Fig. 5.2 suggests that the putative upward extension of the Main Orebody would yield a residuum rich in copper minerals in the eastern part of the area, especially along its southern margin; rich in galena in the central part of the area; and richer in sphalerite then in galena or copper minerals at its western end. It would not, however, be contrary to what is known about metal distribution in protore if the eastern part of the Main Orebody's upward projection yielded



Metal content (Pb/Zn<1.0%, Cu<0.1%) of assay section immediately below residual deposit

Rock footage considered; where no value given, footage=100

Mineralisation concentrated in lower part of rock section considered

Mineralisation concentrated in L3 fault slice

0 FEET 500

FOOTAGE, %	METAL CONTENT, % Pb/Zn	Cu
○ 100	<1.0	<0.1
○ 80-99	<1.0	<0.1
● >20	>1.0	>0.1
● >20	>10.0	>1.0

Note: Rock not sent for assay taken to contain <1.0% Pb or Zn and <0.1% Cu

METAL DISTRIBUTION IN ROCK BELOW THE RESIDUAL DEPOSIT

Fig. 5.2

some sphalerite-rich material.

The mineralisation of the Old Tynagh Mine area is probably represented in sub-till outcrop by fracture-fillings and replacements of little extent, and the same is true of the East Extension Orebody (q.v.). There is no reason to believe that in either area mineralisation in any quantity was present in rocks that have been removed by erosion. Both areas are on the down-ice side of the residual deposit. If the fractures in the first locality did guide mineralising solutions into the superincumbent Waulsortian, mineralisation in the latter would have been 600 ft. or more above the present erosion surface.

It should be pointed out here that the volume change that would result from decalcification of a particular rock type is not simply a function of its carbonate content but also depends on the load applied to the residuum and on the ease of its compaction. The latter is dependent on the shape and elasticity of the constituent grains, the physical homogeneity of the material, and to some extent on whether or not residual minerals are subject to chemical alteration.

5.2 COMPOSITION OF THE RESIDUUM

Most of the residuum consists essentially of one or more of the following types of material: (a) black siliceous mud, (b) fragments of sulphide-barite mineralisation, (c) clay, and (d) limonitic rubble and mud collectively termed "oxides". Specific minerals apart, other constituents of the residuum that can be recognised with ease in the field include blocks of limestone, sandstone and chert, and chunks of timber.

A. Black mud

This material, after which the deposit has been misleadingly

dubbed "the black mud orebody," is estimated to comprise about a third of the total volume of residuum. More than half of it is classified as transported residuum.

The main characteristics of typical black mud are its extreme fineness, its colour and, compared with other types of residuum, its high silica content.

Screen analyses of typical material show that over 95% by weight passes 325 mesh B.S.S. (approximately 50 μ apertures). A substantial proportion of the undersize consists of particles less than 2 μ across. In the moist condition in which it occurs, the mud is jet black and has the consistency and covering power of damp, somewhat gritty soot. (It has also been likened to boot polish, but it is not unctuous to the touch.) Dry material varies in colour from black to medium-grey and has a powdery consistency. When disturbed by mining operations, the black mud forms treacherous sloughs in poorly drained parts of the open pit; in dry spells it produces an all-pervasive dust that has to be laid by water sprinkler relays on haulage roads.

Because of the extreme fineness of most particles, the mineralogical composition of the mud cannot be determined precisely by normal microscopy. The following description is based on a combination of chemical analyses, x-ray diffraction analyses, and optical microscope studies of various size fractions larger than 325 mesh B.S.S. Table 5.3 gives the chemical composition of the black mud component of a sample of lead-zinc ore.

The silica content of typical black mud ranges between 50% and at least 75%. Silica is represented mainly by roundish and subangular grains of quartz in silt and sand sizes. Microscopic pitted crystals of presumably authigenic quartz are fairly common. Clear and milky quartz in crystals and crystalline fragments up to

Table 5.3 Chemical Composition of Black Mud Ore

	I	II
	%	%
Pb	4.79	-
Zn	5.60	-
Cu	0.08	-
As	0.11	-
Fe	5.32	2.33
S	8.50	2.67
BaO	8.45	-
SO_3	5.70	-
CaO	1.35	2.03
MgO	1.91	2.88
CO_2	2.30	3.46
K_2O	1.70	2.56
Na_2O	0.20	0.30
Al_2O_3	7.72	11.63
SiO_2	35.6	53.7
TiO_2	0.32	0.48
C	2.56	3.86
H_2O^-	0.55	0.83
	92.46	86.73
H_2O^+	several per cent.	

I - Black mud ore

II - Calculated after deduction of Pb, Zn, Cu, As, BaO, SO_3 and Fe and S in excess of that contained in 5% pyrite. Approximate composition of black mud component of I.

Analysis by Irish Base Metals Ltd.

2 in. along the prisms are a characteristic constituent of black mud. Fragments of thin chert bands, and chert nodules up to 2 in. across, are also typically found in black mud.

Clay minerals constitute 10-40% of typical black mud, though in some parts of the deposit the latter grades compositionally into material with a clay mineral content of more than 50%. X-ray diffraction analyses show that by far the most abundant clay mineral present is illite. In most samples it is not accompanied by detectable amounts of other clay minerals; in some, kaolinite or montmorillonite is a major or minor associate of illite.

The black mud normally contains 3-8% iron, represented mainly by pyrite and limonite. In parts of the deposit it is highly pyritic and assays up to 25% Fe over 3-5 ft. sample lengths. Pyrite is present as euhedra and anhedral grains with a usual size range of 1-100 μ, framboidal aggregates and other microspheriodal forms, and aggregates of these. Fragments of thin beds or laminae of pyrite, sometimes accompanied by marcasite, are a typical constituent of black mud.

Virtually restricted to black mud are tiny tubes consisting of pyrite, cryptogranular quartz or both. Their length is generally less than 3 mm. and their internal diameter less than 300 μ. They are almost certainly fragments of siliceous sponge spicules that have, in some cases, been partly or wholly replaced by pyrite. They are accompanied by branching and more complicated microscopic tubular forms that are probably the remains, or replacements, of marine organisms of various kinds. It is of interest that Bretz (1950) found what he termed "wire pipes" of pyrite and hematite in the fill of sink structures in Missouri. He reached no conclusion about their origin, but rejected the possibility that they were "straw" stalactites "... until it is proved that cave drip-

water may have its surface tension so decreased that drops with knitting needle and smaller diameter are the general rule ...".

Another characteristic constituent of black mud is a lustrous, jet-black, brittle hydrocarbon, which occurs in angular fragments up to $\frac{1}{2}$ in. across. Partially graphitised hydrocarbon in cellular and irregular or shard-like shapes is often visible under the microscope. Microscopic and submicroscopic particles of graphite and other carbonaceous substances impart the dark colour to black mud, not "melnikovite" (taken to mean amorphous or cryptocrystalline iron disulphide) as suggested by Donovan (1965). The carbon content of typical material probably ranges between 1% and 5% (Table 5.3), but analytical confirmation of this is not available.

Other constituents of black mud, in addition to minerals of the protore assemblage and their supergene alteration products, include minor or trace amounts of sodic feldspar, rutile, chlorite, muscovite and a mineral tentatively identified as epidote.

It is concluded that material with these compositional characteristics is a residuum of Lower Carboniferous sediments of Calp type. In its occurrences as a transported residuum it generally contains rock fragments with the textural and compositional characteristics of decalcified siliceous Calp, and in certain parts of the deposit it has a gradational contact with Calp. It will hereafter be referred to as Calp mud.

B. Sulphide-barite fragments

A large proportion of the deposit's content of base metals and silver is contained in aggregates of sulphides, sulphosalts and barite. These occur in every gradation of size from boulders more than 10 ft. across to submicroscopic particles (Plate 5.1).

Plate 5.1 - Residual aggregate of crustified primary barite and sulphides (mainly pyrite, galena and tennantite). Specimen size about 4in.

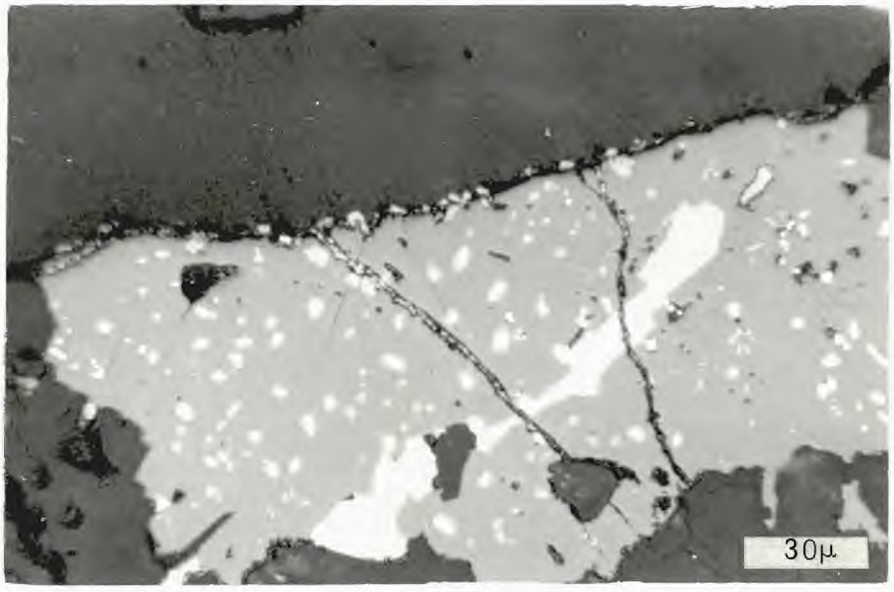


Plate 5.2 - Replacement of primary sphalerite (light grey) by chalcopyrite (white). The grain is encrusted and veined by supergene galena (white). Polished section.

In the smaller size grades, monomineralic grains are common, but grains more than 2 mm. across are usually polymineralic aggregates. Depositional fabrics in constituent minerals, such as colloform banding in sphalerite, are often truncated by the edges of aggregates, the majority of which are obviously fragments of larger masses of mineralisation. Most fragments in all size grades are angular, but fine sphalerite and pyrite grains are quite commonly round or roundish. This is a reflection of the tendency of sphalerite to crystallise in roundish microgranules, and of the tendency of pyrite and marcasite to crystallise in botryoidal and spheroidal habits.

The main sulphides are sphalerite, galena, pyrite and marcasite, and the main non-opaque mineral barite. They occur aggregated with each other in all proportions, and all occur in monomineralic grains. Of these minerals, only pyrite is common as unaggregated crystals, though the other three sometimes occur in this way. Marcasite generally occurs as a subordinate associate of pyrite, and there is morphological evidence that a substantial proportion of the pyrite in colloform habits is an inversion product of marcasite. Tennantite is a major constituent of fragments in certain parts of the deposit, and bournonite, jordanite and enargite are commonly detectable under the microscope. Arsenopyrite is occasionally visible in hand specimen, but its rare associate siegenite has only been seen in polished section. Minor non-opaque constituents include dolomite, calcite, quartz, chlorite and feldspars identified as albite and adularia according to criteria previously described.

These minerals are usually accompanied in residual fragments by others that are manifestly of supergene origin, e.g. cerussite. Obviously supergene minerals apart, it can be said that the sulphide-barite fragments have exactly the same mineral composition as the

main types of protore.

This duplication of mineral species is prima facie evidence that the sulphide-barite fragments are a residual product of mineralisation of the kind that occurs in rocks surrounding the deposit. Previous investigations of protore mineralisation are not an adequate basis for detailed comparison of, for instance, the trace element composition of minerals common to protore and residuum. A limited study of this kind carried out by the writer showed that in both types of material:

i) silver is associated in some undetermined way with typical galena and is also present as a lattice constituent of tennantite;

ii) sphalerite is generally represented by a low-iron cadmiferous variety;

iii) tennantite is represented by a zincian variety containing up to at least 8% Zn, and also contains major traces of silver, cadmium and cobalt.

More detailed information is given in Chapter 7.

With minor exceptions, the crystallisation habits and mutual relationships of mineral components of fragmental material are so similar to those of their protore equivalents that to describe them in detail would be repetitious to a degree. Salient points of similarity that reinforce compositional evidence that the sulphide-barite fragments are a residual product of mineralisation of the type that occurs in rocks underlying the deposit include the following:

a) in both types of material pyrite-marcasite, sphalerite and barite crystallised in greatest quantity, but not in a uniform order, before sulphides and sulphosalts of copper and lead, and galena typically replaces all

other minerals. The sulphides and barite contain small euhedra and corroded grains of feldspar, quartz and dolomite in both;

b) pyrite is represented in residual aggregates by the entire gamut of morphologies present in the rocks of the area, including zoned euhedra and microspherulites composed partly of nickeliferous pyrite, and "whiskery" spheroids that have only been found in situ in Waulsortian off-bank sediments;

c) sphalerite in residual aggregates is as variable in colour and grain size as it is in protore, and in both there is a tendency for the darkest material to be concentrated in the "older" parts of colloform-banded aggregates;

d) much of the galena in residual aggregates contains blebs and oriented inclusions of bournonite and jordanite, duplicating the usual intergrowth habit of these minerals in protore;

e) a solid hydrocarbon is an intimate associate of early-formed sulphides in both types of material, occurring most commonly as an overgrowth on pyrite.

No fragmental material has been found that duplicates the textures of strongly deformed protore in the immediate hanging wall of the North Tynagh Fault, but as Schultz (1968) observes, by no means all the protore that occurs in this position is visibly deformed. Local cataclastic effects in early-formed pyrite are fairly common in residual aggregates as in protore, and textures are occasionally found in other minerals that indicate minor deformation, not necessarily of tectonic origin, at

various stages of mineralisation. Slightly distorted cleavage traces in some residual galena exemplify this.

The only primary texture in residual sulphides for which a close parallel has not been found in protore is one formed by oriented inclusions of chalcopyrite in sphalerite (Plate 5.2). The sphalerite containing such inclusions in the two samples of granular residuum in which they were observed was pale in colour. Chalcopyrite occurred mainly as 5-20 μ roundish or irregular blebs scattered randomly throughout the sphalerite grains or, occasionally, slightly concentrated in particular portions of them. In some grains the chalcopyrite inclusions were distinctly elongated, and apparently oriented in sphalerite cleavage directions. The intergrowths are similar in appearance to "emulsoid" textures illustrated by Edwards (1954) and many other authors as typical products of unmixing of solid solutions of the two phases formed at high temperatures. Unmixing takes place at 350-400°C, and the presence of emulsoid-like intergrowths of the two minerals in natural materials (in which chalcopyrite is generally the subordinate phase) has often been cited as evidence that depositional temperatures exceeded 350°C. The validity of the criterion has been challenged by Brett (1964) and Stanton (1964). The texture has recently been reported in sulphides in equilibrium with present-day geothermal solutions at a temperature of about 275°C (Browne, 1969).

Close inspection of the Tynagh textures leaves little doubt that they are a product of structurally controlled replacement of sphalerite by a later generation of chalcopyrite. The blebs themselves are uninstructive on this point, but exceptionally chalcopyrite occurs also as areas with a careous interface with sphalerite and containing small relics of sphalerite.

Stanton (1964) has suggested that emulsion-like textures result from replacement of sphalerite by chalcopyrite because of "trapping of copper and iron diffusing through sphalerite on the latter's ubiquitously developed twinning". Some quasi-exsolution textures involving galena and minor sulphosalts in Tynagh ores may be analogous in origin.

On a hand-specimen scale and larger, some of the sulphide-barite fragments are recogniseable from their textures as replacements of particular types of limestone. Characteristic textures sometimes produced by epigenetic mineralisation of micrites, biomicrites and crinoidal limestones of the Waulsortian Bank Formation have already been described, and it need only be said here that decalcified material containing such textures is common in the residual deposit. The complicated crustifications of pyrite and sphalerite and the patchy cavity fillings of coarse barite that result from mineralisation of cavernous micrites are particularly common, and sulphide-barite blocks not infrequently contain external and internal casts of crinoid stem fragments.

It is not always possible to be sure that certain minerals are not of supergene origin when they occur in the residuum as monomineralic grains or granular aggregates. This is particularly true of pyrite, which is exceptionally diverse in its morphology and mode of occurrence in unweathered rock, and true to a lesser extent of sphalerite. Small particles of galena and barite are usually recogniseable as cleavage fragments. With the exception of arsenopyrite, supergene formation of which has apparently never been reported, the other sulphides and sulphosalts occur largely in polymineralic aggregates that are texturally identical to, and obviously fragments of, protore. Supergene galena, sphalerite, pyrite, chalcopyrite and barite have been recognised

in the residuum (Chapter 7), but the primary origin of the bulk of the sulphide-barite mineralisation in the deposit is demonstrable in the ways outlined above.

C. Oxides

In this context "oxides" means materials that, considered in bulk, are coloured shades of brown, orange or yellow by their content of hydrated iron oxide. On a hand specimen scale or larger, other colours are imparted by concentrations of such supergene minerals as malachite (green), azurite (blue), cerussite (white) and manganomelane (black).

The materials in this category vary widely in their physical and chemical characteristics, and are best described in relation to their environment (Chapters 6 and 8). Compositionally and texturally, transported oxides differ in no important respect from those that are demonstrably in situ.

D. Limestone and sandstone blocks

The commonest types of limestone in residuum are encrinite, biomicrites and dark, compact well-bedded or laminated limestone. They are petrologically identical to Waulsortian limestones and Calp exposed in the walls of the open pit, and they contain the same fauna. Some limestone fragments contain mineralisation of a type that is common on the fringes of the protore zone, namely stringers and patches of sulphides accompanied by barite and sparry calcite. All are considered to be of local origin.

The sandstone fragments have the same petrological characteristics as sandstones of the Tynagh Devonian inlier. They are silica-indurated, contain fairly abundant microcline and accessory orthoclase, sodic plagioclase and muscovite, and

Plate 5.3 - Fragment of fossil wood Sequoia .

are generally coloured marginally or pervasively by limonite. Sandstone blocks in residuum usually contain no sulphides other than scattered grains and euhedra of pyrite.

E. Clay

By far the most abundant clay mineral in the deposit is illite, which is a ubiquitous constituent of all types of residuum and occurs in places in bedded concentrations several feet thick. Illite is also the dominant clay mineral in the Lower Carboniferous sediments that surround the deposit, in which it is sometimes accompanied by kaolinite. Kaolinite occurs in the residuum, as do clay minerals with the x-ray diffraction characteristics of halloysite and montmorillonite.

F. Wood

Chunks of timber up to 3 ft. in length are common in some of the transported residuum (Plate 5.3). How they occur, and their significance vis-a-vis the age and origin of the deposit are discussed in subsequent chapters.

5.3 SUMMARY AND CONCLUSIONS

Most of the space now occupied by the residual deposit formerly contained crinoidal limestones, biomicrites and micrites of the Waulsortian Bank Formation, which, within the deposit's outcrop area, extended above the present erosion level for up to 150-200 ft. The Waulsortian limestones were heavily, but not uniformly, mineralised in a zone 200-300 ft. wide in the immediate hanging wall of the North Tynagh Fault. Below the present erosion level, Calp was formerly present only in the north-central part of the area, but at one time the entire Waulsortian Bank Formation

had a Calp cover that probably exceeded 1,000 ft. in thickness.

The main constituent materials of the deposit - sulphide-barite fragments and black mud - are, respectively, the physical residua of primary mineralisation of the kind that occurs in the underlying limestones, and of Calp. The main clay mineral in the residuum is also the main clay mineral in the types of limestones that bound the deposit and form bedrock for many miles around it. The residuum contains sandstone fragments that are probably of very local origin, and chunks of fossil wood that are not demonstrably so.

CHAPTER SIX

STRUCTURE OF THE RESIDUAL DEPOSIT

It is in the nature of an open pit operation that structural details only become apparent as mining proceeds. The writer's mapping was carried out largely during the excavation of the upper 40ft. of the deposit, but it did provide enough information for the structure of the unexposed bulk of the deposit to be worked out in outline. This was done mainly by relating mapped contacts between different types of residuum with those apparent in the cores of boreholes drilled to prove the deposit or reflected in the assay data referring to them. The siting of exploration boreholes within the deposit's outcrop area is shown in Fig. 6.1. Additional information about the structure of newly-exposed residuum has been provided from time to time by the mine geologist.

For descriptive convenience, the deposit has been divided across its length into three unequal blocks that roughly correspond to natural divisions, and the blocks sub-divided into their main structural elements. Some of the latter consist of many sedimentary units, but the ultimate sub-divisions of the deposit are far too numerous for all to be described in detail.

6.1 STRUCTURE OF THE WESTERN BLOCK

The main structural feature of this block, in which is included residuum lying to the west of about 31900E (Figs. 6.2, 6.3, 6.4), is an elongated body of dark sulphide-rich material termed the Collapse Breccia (see footnote). This lies in a trench-like depression with an average depth of about 100ft. Large bodies of transported Calp mud occupy depressions in the

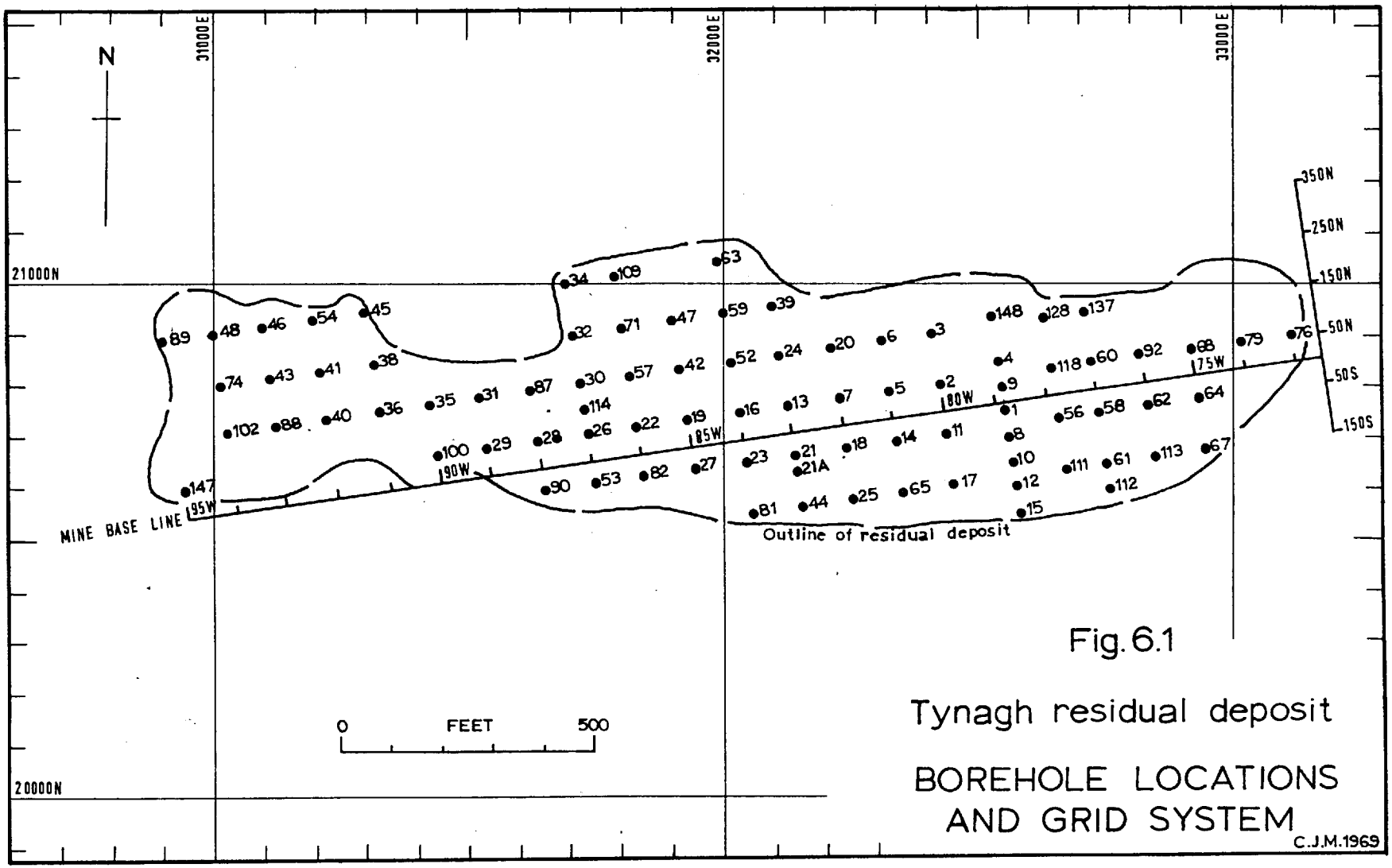


Fig. 6.1

Tynagh residual deposit

BOREHOLE LOCATIONS AND GRID SYSTEM

C.J.M.1969

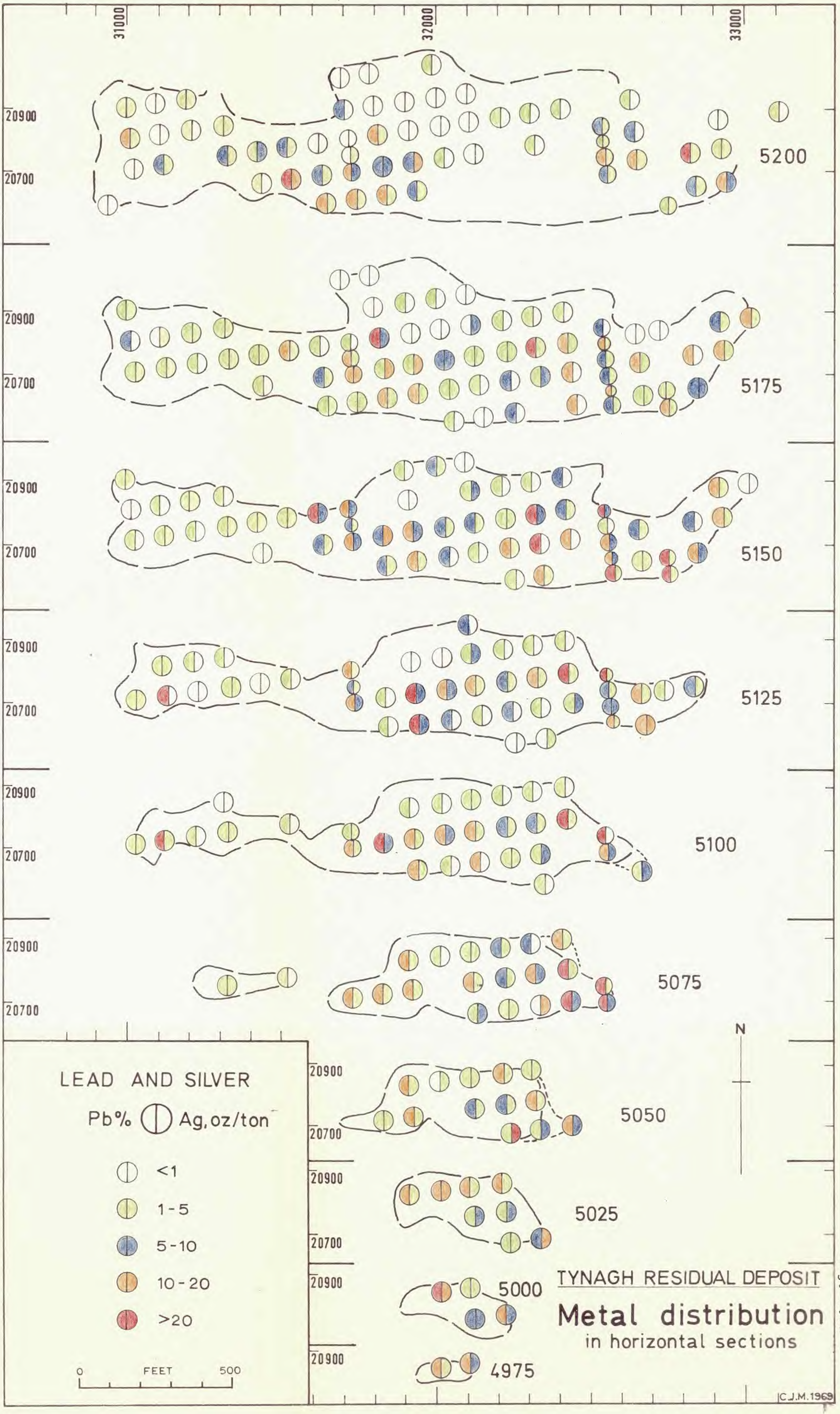

31000
32000
33000
20900
20700
5200
5175
5150
5125
5100
5075
5050
5025
5000
4975
N
LEAD AND SILVER
Pb%
Ag, oz/ton
<1
1-5
5-10
10-20
>20
0
FEET
500
TYNAGH RESIDUAL DEPOSIT
Metal distribution
in horizontal sections
C.J.M. 1969

Fig. 6.5a

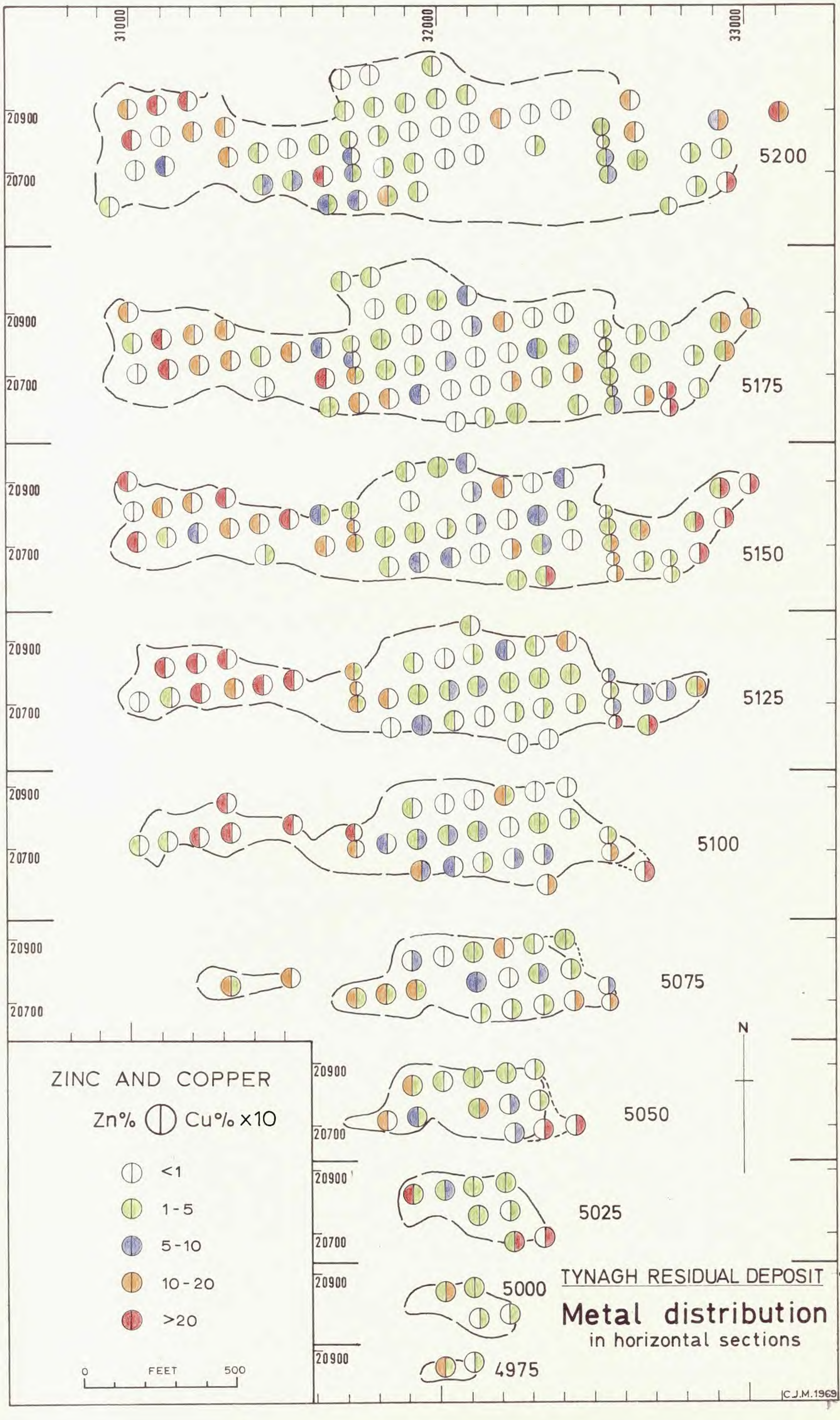

31000
32000
33000
20900
20700
5200
5175
5150
5125
5100
5075
5050
5025
5000
4975
N
ZINC AND COPPER
Zn% Cu% x10
<1
1-5
5-10
10-20
>20
0
FEET
500
TYNAGH RESIDUAL DEPOSIT
Metal distribution
in horizontal sections
C J.M.1969

Fig. 6.5b

Table 6.1 Residual ore types

	Ore types	Main source blocks	Ore proportion (wt.%)	Pb % by wt.	Zn % by wt.	Cu % by wt.	Ag oz/ton	Ag oz/%Pb
1.	Copper-poor sulphide	E	34.5	9.5	11.3	0.2	3.5	0.34
2.	Copper/lead oxide	E	18.5	15.5	1.9	2.3	4.6	0.30
3.	Copper-rich sulphide	E	13.1	15.5	4.3	0.7	5.4	0.27
4.	Zinc oxide	W,E(N)	9.3	2.1	20.1	0.1	0.3	0.14
5.	Lead oxide	E	9.6	13.6	1.5	0.3	5.5	0.40
6.	Lead/zinc oxide	W	6.8	7.8	6.9	0.2	0.2	0.03
7.	Zinc oxide Calp mud	C(N)E(N)	2.8	2.5	10.2	0.1	0.6	0.24
8.	Gossan talus	C,E	2.0	1.5	0.4	0.2	6.3	4.10
9.	Gossan	C,E	1.6	2.8	0.2	0.3	10.1	3.61
10.	Lead oxide Calp mud	C(N)E(N)	1.2	13.6	2.1	0.2	1.8	0.13
11.	Silver Calp mud	C(N)	0.6	1.5	0.7	0.5	7.3	4.87
			100.0					

Notes

a) The proportions and grades refer to ore in reserve at 1st January 1967. By this date about 30% of the original ore reserve had been mined, the bulk of the production being of ore types 1-4.

b) The basis of ore classification is such that some categories of oxide ore, especially 2 and 5, include much sulphide-rich material.

c) Ore type 9 is largely derived from the Fossil Gossan, but includes some silver-enriched Waulsortian bank oxides from the eastern block.

d) Most of the sub-grade residuum is Calp mud.

upper part of the Collapse Breccia, and its south-western part is underlain by transported gossan and multi-coloured muds containing gossan fragments. The transported materials are flanked to the south by decomposed Lower Muddy Limestone of the fault slice, and widely underlain by an in situ residuum of Waulsortian limestone.

A. Transported gossan and speckled deposits.

On present evidence, the oldest of the transported materials in this block, and probably in the deposit as a whole, comprise a body of gossan rubble and gritty mud that plunges eastwards below the Collapse Breccia from the SW corner of the deposit (Plate 6.1). The shape and extent of the unit are as yet uncertain, but borehole intersections suggest that it is up to 60 ft. in vertical thickness and lies in a gulley bounded to the south by the plane of the L2/L3 fault. Exposures of gossan rubble in the upper benches of the deposit showed that it was crudely sorted, with graded elements having dips of up to 10° towards the long axis of the containing cavity. At the time of its infilling, the latter may have been partially roofed by massive protore (see below).

The main constituents of the gossan rubble are barite (in angular and sub-angular fragments usually less than 6 in. in size), limonite and clays. Beudantite is locally conspicuous, indicating that some of the parent protore was rich in galena. Small subangular pebbles of weathered Devonian sandstone occur intermixed with the gossan rubble.

Footnote: For reasons that will become apparent, the structure of the deposit presents problems of nomenclature. In what follows, mine nomenclature has been used for some of its structural components, others are named according to some feature of their composition, position in the deposit, or origin.

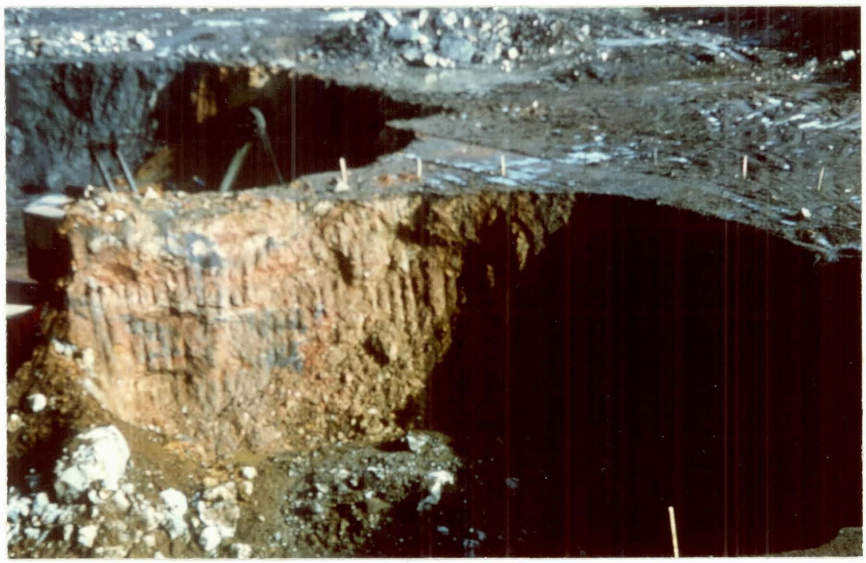


Plate 6.1 - Transported gossan rubble adjacent to the L2/L3 fault plane (in shadow). 5200 bench, west end.

Plate 6.2 - Transported gossan fragments in a Calp mud matrix. 5200 bench, west end.

In the deeper parts of the unit the gossan rubble apparently grades into fine-grained materials containing varying amounts of Calp mud and residual sulphide, especially pyrite. Supergene concentration of lead and zinc as carbonates has taken place in the gritty muds, which assay up to 50% Pb and 25% Zn. Chalcopyrite is the main host of the small amounts of copper (usually less than 0.2%) in some of this material, from which were recovered the grains illustrated in Plates 5.2 and 7.3. This mineralogical feature is anomalous, since chalcopyrite is otherwise extremely rare in the western part of the residual deposit. The same is true of the cerussite-rich materials that the unit contains.

Residuum of essentially the same kind was exposed in the upper benches of the deposit, where it occurred as irregular masses and sheets up to 10 ft. thick immediately between the weathered limestone floor of the deposit and dark bouldery residuum described in the next section. The black and orange muds in this position were poorly stratified but clearly sedimentary in origin. They contained small unsorted fragments of gossan, protore, Calp, Lower Muddy Limestone, and occasionally weathered sandstone. Rock fragments were angular to sub-rounded in shape and occurred "floating" in a muddy matrix. Mixtures of Calp mud and gossan fragments had a characteristic speckled appearance (Plate 6.2).

A noteworthy feature of sheeted bodies is that they contain polished, undulating partings similar in appearance to slickensides. It seems to be a characteristic of the partings that they are sub-parallel to the rock-residuum contact irrespective of its attitude. They are thought to have resulted from compaction, perhaps accompanied by small-scale movement of one part of the sheet over another.

Compositionally the sediments of this unit are unexceptional inasmuch as they are mixtures of materials that are common in other parts of the deposit. Their source is uncertain and as such had better be discussed in the general context of the deposit's formation.

B. The Collapse Breccia

The Collapse Breccia is the largest single body of sulphide ore in the deposit. It contains approximately one million tons of residuum, of which about a half contains 10-20% Zn in sulphide form, and a smaller proportion is rich in galena. (Fig.6.5). Copper values rarely exceed 0.5%.

The residuum that constitutes the unit is for the most part a chaotic mixture of boulders, cobbles and smaller fragments of protore with varying proportions of Calp mud and clay. The slimes (-350 mesh B.S.S.) content of the material normally ranges between 15% and 40%.

Features of the Collapse Breccia to which it owes its name are the considerable size range and rudimentary sorting of its constituents, and its almost total lack of stratification. Protore boulders 6ft. and more in size are common in parts of the unit. Some are sub-angular to sub-rounded, partly due to chemical decomposition of their peripheries, but much of the blocky material is angular and unabraded (Plates 6.3, 6.4). Elongated rock fragments and chunks of fossil wood lie at all angles in matrices of dark mud and grit, and platey fragments of thin-bedded Calp have no preferred orientation. Exceptionally, fine-grained residuum displays colour variation between thin bands differing in clay mineral content. This has been seen in muds interstitial to boulder accumulations, suggesting that in some places coarse and fine materials were not deposited simultaneously. The banding is generally contorted, sometimes horizontal.

Plate 6.3 - General view of the upper levels of the residual deposit from its western margin. Exposed in the near mining face are dark, bouldery ores of the Collapse Breccia, and weathered Waulsortian limestones. At P is a relict mass of almost in situ protore.

Plate 6.4 - Detail of the Collapse Breccia, showing angular protore fragments "floating" in gritty mud.

Plate 6.5 - Edge of the Collapse Breccia, separated from weathered Waulsortian limestones (right) by a narrow oxide selvage. 5180 bench, 20750N 30950E

Most of the protore fragments are recognisable from the textures of their primary constituents as a debris of mineralised Waulsortian limestone. Some contain sulphide-barite pseudomorphs of crinoid ossicles, indicating that the host rock was a bioclastic limestone of the type that abounds in the northern wall of the block. The northern part of the unit contains occasional boulders of bioclastic limestone. Primary sedimentary structures in these boulders have no preferred orientation: "spirit level" fossils show that some have been overturned.

The distribution of large boulders and spatial variations in the primary metal tenor of the Collapse Breccia indicate that the unit amounts to a series of eluvial deposits arranged around relics of an ancient relief formed by differential weathering of mineralised and unmineralised limestones.

This arrangement is exemplified by the bouldery residuum at the western end of the Collapse Breccia (Plate 6.3, Figs. 6.2, 6.3). The boulders in this area are typically richer in zinc than lead, the assay grade of 5 ft. sections of virtually unaltered protore cored from the interior of two boulders being:

Zn%	Pb%	Cu%	Fe%
26.0	5.0	0.2	14.0
26.0	2.3	0.2	3.0

They are intimately mixed with smaller fragments of protore of the same type, and with varying amounts of Calp mud. The mean size of protore fragments tends to decrease northwards, and the relative abundance of Calp mud to increase in the same direction. Chunks of fossil wood occur in the northern part of the unit in this area.

The bouldery residuum overlies an irregular ridge of Waulsortian limestone that is about 100 ft. wide on traverse 94W and apparently provides concealed relief of up to 75 ft. on its southern side. The ridge strikes approximately E-W, and decreases eastwards in height and width.

In the upper levels of the deposit the ridge was represented by ribs of weathered limestone and by a partially disaggregated mass of protore with the same primary mineralogy and textural characteristics as the boulder material. The protore mass was bounded to the south by the plane of the L2/L3 fault, forming a partial roof over the materials described in the previous section. It was cut by strong joints striking N-S (the dominant joint direction of the Tynagh area) and dipping eastwards at 70-80°.

This situation is duplicated in kind in other parts of the Collapse Breccia. Boulder accumulations and apparently in situ relics of mineralised and unmineralised Waulsortian limestone were present in upper benches at several places on the southern margin of the unit, while in its NE quarter, where the unit is represented chiefly by black gritty muds that typically contain more lead than zinc, the uppermost bench contained an accumulation of galena-rich boulders and a partially disaggregated mass of galena-rich protore. The latter is thought to have been a relic of a high-level westward extension of the protore body designated 6p in Fig. 6.3. Southward extrapolation of the Calp/Waulsortian contact in the area concerned suggests that strong mineralisation did not extend more than a few tens of feet above the present surface of the deposit.

In summary, ther is much evidence that the fragmental protore of the Collapse Breccia is a disaggregation product of parts of the Main Orebody that lay within the deposit's outcrop area and largely below the present erosion level. The pattern of primary metal zonation in the Collapse Breccia reflects that in the unweathered part of the Main Orebody.

The source of the Calp mud that comprises a major proportion of the Collapse Breccia cannot be specified precisely.

Some of the mud may be a residuum of Calp that originally overlay the Main Orebody, though much of it probably washed into the zone of protore decay after the Main Orebody had been stripped of its Calp cover.

C. "Sink fill"

Overlying the virtually structureless mass of the Collapse Breccia is a large composite body of polymict sediment displaying varying degrees of stratification. Because it appears to be entrenched in the Collapse Breccia, and contains an unusual abundance of fossil wood, the material is known on the mine as "sink fill", a term that has been retained here mainly because it is briefer than more accurate alternatives.

The most heterogeneous part of the body is centred on 31400E and extends almost the full width of the deposit's central cavity. It appears to occupy an irregular depression of uncertain depth between two of the main eluvium accumulations that comprise the Collapse Breccia.

Exposures to date show that the southern part of the body comprises thick ungraded sheets of sulphide-barite rubble and Calp mud dipping at up to 40° towards a southward-plunging axis that roughly corresponds to grid line 31350E. The larger protore fragments, which are up to 2 ft. across, have the same physical and mineralogical characteristics as those of equivalent size in the western, zinc-rich part of the Collapse Breccia. In places the only basis of distinction between the Collapse Breccia and the "sink fill" is that the latter generally contains fossil wood. It is pertinent to the origin of the "sink fill" and of the deposit as a whole that thin sections of the fossil wood show that it has been fairly strongly compressed and probably waterlogged for a long period of time (Chaloner, pers. comm.; Levy, pers. comm.).

The northern part of the "sink fill" consists, in the upper levels of the deposit, of structureless and faintly-bedded Calp mud. In places the Calp mud contains clay beds up to 2 ft. thick and mechanical segregations of sulphide-barite rubble. Angular blocks of partially decomposed and almost fresh Waulsortian limestone up to 2 ft. in size, and smaller subangular fragments of weathered Devonian sandstone, are occasionally found"floating" in a Calp mud matrix. Materials of this kind persist to depths of about 50 ft. below the till, and appear to lie in a gulley-shaped depression following the northern margin of the deposit. (Figs. 6.2, 6.3).

A limited amount of mapping in the upper part of the unit failed to produce a coherent picture of its internal organisation. One well-defined basin structure with an axis roughly corresponding to that referred to above was observed in the uppermost mining bench, and sedimentary layering dipping at up to 30° in various directions was noted in the shallower parts of the unit. The mine geologist has since reported pronounced contortions of finely laminated grey and black muds in its deeper parts.

The disturbed appearance of the deeper parts of the "sink-fill", the presence of a well-defined basin of sedimentation at higher levels, and the fact that parts of the body appear to occupy a cavity with walls steeper than the angle of rest of the surrounding residuum, all suggest that the sediments of this unit accumulated in a series of (at times) interconnected depressions that continued to deepen as these were filled. This mechanism has been invoked by Bretz (1950) to account for similar relationships between various types of residuum filling limestone cavities in Missouri.

It is conjectured that the depressions in which the"sink fill" accumulated in some cases originated as hollows in a hummocky surface of pre-existing residuum, but in all cases

were deepened by subsidence. There were three possible causes of subsidence - compaction of pre-existing residuum, metasomatic alteration of the underlying limestones and compaction of their solid alteration products, and straightforward dissolution of the limestones. Compaction of the Collapse Breccia has certainly taken place, but it is difficult to prove that it was even a contributory cause of differential subsidence of the "sink fill". Metasomatic alteration of the underlying limestones to materials occupying less volume has also occurred, but the alteration zone is not uniformly wider, or its contents conspicuously more compact, below the steep-sided parts of the "sink fill" than elsewhere. The main cause of subsidence was probably straightforward dissolution of the underlying limestones, since the most steep-sided part of the "sink fill" overlies a pronounced westward-plunging depression in the deposit's floor that is likely to have been one of the main arteries of the subterranean drainage. Here and elsewhere in the deeper parts of the deposit there are borehole indications that the transported residuum is separated from their weathered limestone floor by a clay selvage that may well be partly or wholly a residue of the dissolved limestones.

The effects of solutional entrenchment are apparent in the shape and structure of many, perhaps most, ancient residual deposits in limestone, irrespective of their composition and of the lithology and structure of the containing rocks. According to Bretz (1940, 1952), who has studied the phenomenon in great detail, the process does not appear to be dependent on chemical alteration of the fill (in particular, oxidation of pyrite), or to be promoted by the differential pressure of the fill on its floor. In the writer's view it probably resulted at Tynagh chiefly from channelling of groundwaters along the rock-residuum contact by features of its buried relief, which were

gradually emphasised as a result. Provided that they are continuously recharged, even strongly alkaline phreatic solutions can, over a long period of time, dissolve large quantities of calcite (see Chapter 9.1). At Tynagh the entronchment process may have been relatively rapid, since free acid was being generated in parts of the zone of weathering, but weathering of sulphides is not thought to have been a pre-requisite for entrenchment.

D. L3 Oxides and grey grits

An in situ residuum of the fault slice constitutes the southernmost part of the block over most of its length and depth. Materials recognisable as such include streaky brown and orange oxides with a high clay mineral content and usually a clear "ghost" stratigraphy. In the upper levels of the deposit materials of this kind, containing a large and apparently unsubsided relic of Lower Muddy Limestone, were concentrated at the western end of the block. Further east the situation is confused, but the fault slice seems to be represented by dark grey clayey grits overlain by pale, patchily mineralised bioclastic limestone. This suggests tectonic complications within the fault slice, and subsequent mapping has shown that it is dislocated around 31400E by a strong fault dipping NE at up to 80° (Whitehead, pers. comm.). The faulting undoubtedly pre-dated weathering, but it is relevant to the present subject in that it may have had the effect of bringing into what is now the upper part of the fault slice, sediments transitional between the Waulsortian Bank Formation and the Lower Muddy Limestone (represented by the second type of residuum referred to above).

The northern limit of the L3 oxides is generally sharply defined, and clearly represents the L2/L3 fault. In places, structures arising from tectonic drag at the margins of the fault slice have been faithfully preserved by its residuum. In the upper levels of the deposit, the line of fault was marked locally by a mass of friable pyrite up to 10 ft. thick and 100 ft. long: microscopic studies showed that the pyrite was originally aggregated with coarsely crystalline dolomite, and hence almost certainly hypogene in origin.

E. In situ Waulsortian oxides

Underlying the transported materials described in previous pages, and flanking them on their northern and western sides, are brown,yellow and orange oxides characterised by their high zinc content and their low tenor of lead, copper and silver (Table 6.1). Physically and chemically they are very inhomogeneous, including at the one extreme competent rock composed largely of smithsonite, and at the other clayey material composed largely of limonite and illite. The dominant physical type is a clinkery rubble with an estimated porosity of about 40%. Evidence of the parentage of the oxides is that they contain numerous relict blocks and occasional smithsonite pseudomorphs of crinoidal and biomicritic Waulsortian limestones.

The true width of the oxide zone varies from less than a foot to about 70 ft. , and its attitude from vertical to horizontal. In places it has a gradational contact with unaltered Waulsortian limestone through a zone of partial weathering up to about 250 ft. wide (Fig. 6.2). There is a rough relationship between the width and the attitude of the zone of intense oxidation, which tends to be narrowest where it is steep (Plate 6.5). Where it is not steep and is bounded by fairly pure, well-bedded limestones with shaley interbeds, the zone of partial

weathering tends to be broad. In places, the zone of partial weathering contains masses of limestone that have simply suffered disaggregation, yielding a pale grey calcite powder containing liberated bioclasts (Plate 6.6).

As might be inferred from their distribution and composition, the materials of this unit are a residuum of the deposit's original wallrocks. Chemical aspects of their formation are discussed in Chapter 8, but it should be noted here that it largely or wholly post-dated that of the Collapse Breccia and the "sink fill". Field evidence of this is that relict stratification in the zone of partial weathering is sometimes transected by indistinct pipe-like bodies of Calp mud that evidently resulted from very slow intrusive subsidence of the latter during wallrock weathering. The Calp mud often has what could almost be described as a replacement relationship with the altered wallrocks.

The altered wallrocks might be expected to yield some information about the origin of the cavity occupied by the transported residuum described earlier. Although the original geometry of the cavity has been substantially modified by pure solution of its wallrocks, their metasomatic alteration by chemical processes involving losses in volume, compaction of their solid alteration products, and limited deformation of the cavity's altered wallrocks by subsidence of its fill, there remains some evidence that:

a) except where it was formed by the plane of the L2/L3 fault, the wall of the cavity was uneven, and contained slightly overhanging bed-ends;
b) it was not decorated with dripstone or flowstone deposits;
c) the bedding attitude of the wallrocks was normal for the area.

Plate 6.6 - Friable disaggregation products of crinoidal limestone (grey) containing relict bedding cut by a downward intrusion of Calp mud. 5180 bench, 20900N 31000E.

As Fig. 6.3 shows, the upper part of the oxide zone has two pronounced off-shoots. The most persistent, which strikes north-westwards into the wall of the deposit for an unknown distance at 31300E, is shown in Plate 6.8. This remarkable feature, which will be referred to again later, evidently resulted from selective alteration of the Waulsortian limestones along a steep linear structure of some kind, subsidence of their residuum, and, at the same rate, decalcification and subsidence of the overlying Calp. The controlling structure may have been a fault with the same strike as one referred to in the previous section, but this hypothesis cannot at present be tested. It may be significant that the deepest part of the "sink fill" lies on the same line.

The second offshoot (Plate 6.7) originated in the same way, but at a time when Waulsortian limestones at the margin of the deposit had been denuded of their Calp cover. Striking evidence of its youthfulness is that small ice-abraded pebbles and glacial erratics - Galway Granite and schist - were found in the fill at depths of up to 20 ft. below the glacial erosion level, showing that at least that amount of subsidence has taken place since the Saale or Weichsel glaciation (see section 6.4). Not all the fill materials had subsided by the same amount, for some limestone blocks could be reliably correlated with beds in the wall of the cavity less than 10 ft. above.

6.2 STRUCTURE OF THE EASTERN BLOCK

This block stretches from the eastern end of the deposit to about 32200E. It resembles its western counterpart in having a core of dark residuum and a partial envelope of in situ oxides formed by weathering of Waulsortian limestone and upfaulted Lower Muddy Limestone. In other respects it is radically different.

Plate 6.7 - Solution-subsidence structure extending from a glacial erosion surface (A) in crinoidal limestones. The fill materials include a large upended block of weathered crinoidal limestone that has subsided from just below the glacial erosion surface,(B), and a diffuse body of Calp mud (C) containing glacial erratics. 5200 bench,20900N 31600E.

Plate 6.8 - Solution-subsidence structure with steep walls of weathered crinoidal limestone (right). The upper part of the fill is a sagged residuum of interstratified Calp and bioclastic limestone. It shows pronounced deformation of the "ghost" stratigraphy. 5200 bench, 20900N 31300E.

In particular, along its northern edge the core materials overlap a subsided residuum of Calp in which relics of primary stratification dip steeply southwards. Thin sedimentary deposits of re-worked residuum (described in a later section) cover parts of the block.

A. Core deposits

Forming the core of the block are dark transported materials consisting largely of protore fragments, Calp mud and clay. Fossil wood and fragments of Devonian sandstone are conspicuously rare.

The core materials lie in a cavity that deepens westwards and becomes progressively less symmetrical about its long axis in that direction due to steepening of its northern boundary.

As Fig. 6.2 shows, the core is subdivisible into a main mass of blocky and gritty residuum with a relatively high content of fragmental protore, and a steep southward-tonguing body consisting predominantly of Calp mud that does not persist to the bottom of the unit. The base of the Calp mud body evidently increases in depth westwards, and the length of its main tongue into the rubble and grit deposits tends to diminish in the same direction.

Protore fragments in the rubble and grit deposits exposed to date are generally angular, unsorted, and intimately mixed with Calp mud and (especially along the southern margin of the unit) grey clay. The size of individual blocks rarely exceeds 1 ft., and the unit as a whole does not appear to contain boulder accumulations comparable to those in the Collapse Breccia.

Most of the disaggregated protore is much richer in galena than sphalerite, and some is rich in tennantite and other primary copper minerals. In the upper benches of the unit fragments of tennantite-rich mineralisation are particularly common in its eastern and southern parts: lower down they are relatively more widespread.

There is a marked similarity between the primary mineralogy of the protore fragments and that of the mineralisation in bedrock below the eastern block.

Some of the protore fragments are recognisable from their content of argillaceous rock relics as disaggregation products of mineralised Lower Muddy Limestone. Fragments of this kind are concentrated on the SW margin of the unit in dark clayey material resulting from decay and subsidence of well-mineralised shaley limestones of the fault slice.

The sulphide rubble and grit deposits contain widespread evidence of their sedimentary origin. Their secondary stratification is rudimentary but distinct, being chiefly manifest in variations in the relative abundances of Calp mud and protore fragments between sheets and lenses of material that vary in observed thickness from a few inches to over 20 ft. Rubble and mud concentrations grade into each other laterally and vertically, and the coarse-grained constituents of both generally show no signs of abrasion or sorting. Calp mud layers exposed in upper levels of the deposit contained mechanical segregations of granular pyrite or hydrocarbon fragments as thin whisps, lenticles and impersistent bands (Plate 6.9). The segregated particles showed no sign of preferred orientation or of lateral or vertical gradations in size. They appeared to have resulted from differences in the settling rate of Calp decomposition products in still water rather than from the winnowing action of running water.

Plate 6.9 - Detail of re-sedimented Calp mud, showing streaky accumulations of pyrite.

Observations and measurements in the upper 40 ft. of the deposit showed that graded elements were generally sub-horizontal. In the shallow eastern parts of the core, strings of protore fragments in Calp mud had low-angle dips towards the axis of the deposit; while further east, dips of up to 30° in various directions were recorded locally. The latter could not be rationalised and may not have been a true reflection of the depositional attitude of the materials concerned. Close inspection of Calp mud interstratified with sulphide rubble usually revealed unsystematic dislocation of secondary depositional features on slips with a throw of an inch or so.

The internal organisation of the large body of transported Calp mud that forms the northern part of the core is unclear. Mapping in the 5180 and 5160 mining benches showed that the upper part of the body included thick sheets of gritty sediment that appeared to have been deposited in local basins elongated roughly E-W. Coarse-grained constituents of the sediments included fragments of Calp, ironstone and protore. Towards the western end of the block the contact between the Calp mud body and sulphide rubble and grit deposits was generally a well-defined feature dipping southwards at 25-30°. Further east it was less distinct, the two types of material tending to occur largely in interdigitating lenses with vague outlines.

The sedimentation history of the eastern core deposits will be discussed later, when the origin of the containing cavity has been considered.

B. L3 oxides and grey grits

In situ weathering products of the argillaceous limestones and shales of the fault slice occur in a narrow strip along the southern side of the block over most of its length and depth.

Their width and character vary laterally and in depth, reflecting variations in the original shape and lithology of the fault slice. The two main types of residuum closely resemble those that represent the fault slice in the western block, but in this area there is no evidence that they have a faulted contact. In places they contain numerous protore fragments, indicating that the fault slice was heavily mineralised.

Locally the fault slice is represented by little more than a clayey gouge. (Plate 6.10). Elsewhere its original shape in the zone of weathering is uncertain, partly because primary mineralisation and supergene processes described in Chapter 8 have masked the usual differences between residua of Lower Muddy Limestone and Waulsortian limestone, and partly because northward subsidence of its shaly residuum has taken place along the line of the L2-L3 fault (Fig.6.2). Tectonic complications of its shape were influential in determining the eastern limit of intense rock weathering, and hence the present outline of the residual deposit (Fig.6.3).

C. In situ Waulsortian oxides

Underlying the southern part of the core, and extending around its eastern margin, is a rubbly limonitic residuum of Waulsortian limestones. It contains numerous angular fragments of partially oxidised protore, most of them much richer in galena and/or primary copper minerals than sphalerite, and constitutes the mine's chief source of high-grade lead/copper oxide ore. (Table 6.1). As discussed elsewhere, some of the material has been substantially enriched in silver by supergene processes. Rubbly oxides of this type occur in what can best be described as an irregular wedge-shaped zone that thins and dips away from the North Tynagh Fault and plunges westwards in the hanging wall of the decomposed fault slice. Mining has shown that the

Plate 6.10 - Large exposure of the North Tynagh Fault plane in the south-east corner of the open pit. The dark material at A is tectonised Lower Muddy Limestone. The horizontal ridges are artificial.

base of the zone is highly irregular, comprising ribs and pinnacles of limestone separated by muddy and blocky oxides without secondary stratification. This is a partial decomposition effect, not one arising from burial of surface relief.

The upper limit of the zone is in places indistinct, post-depositional oxidation of adjacent sulphide rubble of the core deposits having yielded a similar type of residuum, but in general it is well-defined and fairly regular. Local irregularities have arisen from subsidence of pipe-like bodies of sulphide rubble into the oxide mass. This probably took place during its formation.

Only faint vestiges of "ghost" stratigraphy have been seen in oxide rubble exposed to date, probably due to the massive nature of their parent rocks. Such relics of primary sedimentary structure as were discernible in the upper levels of the deposit suggested that the weathered limestones were arranged in thick beds dipping at up to 25° to the north-west. Rock relics were disorganised, probably due to settling of the residuum, which has an estimated porosity of 30-40%. No evidence was found that mineralisation was concentrated in sheets conformable with the sedimentary layering, and some protore fragments were clearly relics of vein-type mineralisation.

Northwards, the oxide rubble passes gradationally into an argillaceous residuum of limestones of Waulsortian off-bank facies. Expressively but misleadingly termed "peaty mud" in mine geological reports, this material is dark brown in overall appearance, and somewhat earthy. In detail it is various shades of brown, yellow and grey, and varies in texture from clayey to rubbly. It has a clear "ghost" stratigraphy.

Except in areas of local subsidence, relict stratification generally dips at angles of less than 25° to the west and north-west, and tends to flatten in those directions. In places it is

transected by pipe-like and irregular bodies of polymict rubble and mud that are described in a later section.

D. "Draped" Calp

This unit contains the most striking evidence of all that gradual subsidence was a major factor in the structural evolution of the deposit, for it retains, in varying degrees of perfection, a "ghost" stratigraphy of rocks that may have lain as much as 150 ft. above the present level of their residuum. The rocks concerned chiefly belonged to the Calp succession, and included a thin but distinctive cherty ironstone horizon that is fairly widely developed near the base of the Black Calp in the north-eastern part of the mine area.

As Fig. 5.1 shows, the original dip of the decomposed rocks was probably 10-20° towards the north and north-west. The relict stratification of their residuum, however, dips generally southwards at an average of about 35° in the eastern part of the block (Figs. 6.2, 6.3; Plate 6.11). In the zone of partial weathering at the margin of the deposit the dip direction of primary stratification tends to swing anticlockwise from north-west (in slightly weathered rocks) to south (in their residuum). The picture is complicated by local variations, some of them very abrupt, in the strike direction and the dip of primary stratification in the zones of partial and complete decalcification, and by the presence in the residuum of small impersistent faults and folds. Plate 6.12 shows a good example of contortions reminiscent of drag folds in decomposed ironstone. Structures of this intensity are not known in the unweathered rocks of the area.

The structural peculiarities of the residuum in this area are best explained by analogy with the well-exposed weathering phenomenon, also involving the lower part of the Calp succession,

Plate 6.11 - General view of "draped" L1 ironstone. 5180 bench, NE margin.

Plate 6.12 - Contorted relict bedding in "draped" ironstone residuum. The latter is overlain (above A-A) by polymict sediments containing ironstone fragments, and (above B-B) by bouldery till. 5180 bench, 20800N 32700E.

Plate 6.13 - Contact between partially decalcified thin-bedded Calp with anomolous southward dips, and subsided Calp mud (left). 5160 bench, 20900N 32150E.

Plate 6.14 - Vertical contact between almost unweathered Calp and steeply subsided Calp mud. 5160 bench, 20800N 32400E.

Plate 6.15 - Tight fold caused by differential subsidence of partially weathered Calp or by lateral compression of the residuum. 5160 bench, 20800N 32400E.

that is shown in Plate 6.8. In the words of Bretz (1950), whose descriptions of solution-subsidence phenomena in weathered limestones are unsurpassed: "Gravity has pulled... layers down into V-shapes suggesting an isoclinal syncline. It has worked slowly enough to avoid breakage and brecciation, has literally stretched the (shale) layers. This structure is impossible as a detrital fill in an open vertically-walled sink or as a collapse filling of a subjacent cave. It could only form if concommitant solutional widening of the opening.... were going on during subsidence".

Using the Calp ironstone as an index horizon, it can be shown that formation of the eastern part of the cavity containing the core deposits of this block involved subsidence of the Calp by as much as 100 ft. Subsidence is thought to have taken place after Waulsortian limestones adjacent to the North Tynagh Fault in the SE quarter of the mine area had been stripped of their Black Calp cover, and to have resulted from impounding of percolating waters by compact micritic limestones, and selective dissolution of the overlying crinoidal limestones.

Westwards, subsidence has affected rocks progressively higher in the Calp succession and to a progressively greater degree. The rock-residuum contact tends to verticality, and the zone in which relict stratification can be traced from the rock into the residuum is generally very narrow or absent (Plates 6.13, 6.14). Intense deformation of the bedding is often apparent in this zone (Plate 6.15), and for varying distances from the contact the residuum typically contains near-vertical trains and disrupted relics of laminated Calp. These and other features too numerous to mention indicate that subsidence has taken place over a considerable vertical distance, and was accompanied by strong deformation both of the decomposing walls of the containing structure and of its fill. How great a

distance is impossible to say at this stage, but the fact that the subsided materials so far exposed include fragments of drusy quartz fracture fillings does suggest that they originated well above the present erosion level.

Joint fillings in Black Calp exposed in the wall of the deposit consist almost entirely of calcite. The stratigraphical level at which calcite gives way to quartz as a joint filling in this rock type is unknown, since exposures of Black Calp are poor in the Tynagh area, and drillholes were generally sited so as to pass as quickly as possible into Waulsortian rocks.

6.3 STRUCTURE OF THE CENTRAL BLOCK

The main structural pecularity of this block is that it has at its centre a large disaggregated mass of protore weathered superficially to a fossil gossan. The latter's talus, included in this block for descriptive convenience, has spread eastwards and westwards over the core deposits of the other two blocks.

It is neither necessary nor, at this stage, possible to describe the structure of the block in detail, firstly because it is similar in many respects to that of parts of the deposit, and secondly because at the time of the writer's last visit to Tynagh less than a fifth of the total vertical thickness of the residuum in this area (which contains the deepest part of the deposit) had been exposed by mining. Its main structural features are shown in Figs. 6.2 and 6.3.

A. L3 grey grits and slump deposits

The fault slice is represented in this block partly by dark grey muddy grits containing flat-lying relict stratification and remnants of a Tournaisean fauna (Zaphrentid corals and Spiriferid brachiopods in particular), and partly by a highly dis-

turbed body of clayey rubble that extends eastwards and westwards out of the block approximately along the projected hanging-wall contact of the fault slice. Fragmental constituents of the latter include rotten Tournaisean shale, protore and gossan. Steeply inclined and strongly contorted secondary stratification is discernible locally, but most of the material is structureless. Enough has already been said about mechanisms of residuum transport at Tynagh for this particular accumulation of slumped and re-sedimented residuum to need no further explanation. There is no reason to suppose that any of its constituents (which apparently do not include fossil wood) were not of very local origin.

Slumping has largely obliterated the hanging-wall contact of the fault slice in the upper 40 ft. or so of the deposit. At depth, drillholes indicate that the contact swings sharply northwards around 32200E, and there is a marked increase in the protore content of the clayey residuum that lies to the south of its presumed course. Both may reflect tectonic structural complications of the fault slice in this area.

B. Sulphide rubble

The largest compositional unit of the block is a mass of disaggregated protore, mostly unsorted angular fragments of galena-rich mineralisation less than 1 ft. in size, in an apparently structureless matrix of Calp mud. Overall, Calp mud is the more abundant of the two types of material, but at depths below the sub-till unconformity of 250 - 300 ft. the rubble mass apparently grades into a virtually unaugmented disaggregation product of what has been referred to previously as the steep central portion of the Main Orebody (q.v.).

A situation paralleled in the Collapse Breccia is that the upper part of the rubble body contains a large "raft" of massive protore formed by replacement of Waulsortian biomicrite (unweathered remnants of which are still present). The "raft" and its transported derivatives will be described in the next section.

Several lines of evidence suggest that the fragmental protore of this unit represents a disaggregated upward extension of the Main Orebody that has retained some semblance of its original shape because volume losses during its weathering were made good by interstitial sedimentation of Calp mud. This seems the most plausible explanation for the field relationships described above, and for the following points of observation:

(i) the disaggregated protore is mineralogically and texturally very similar to that in the underlying (truncated) portion of the Main Orebody, except that it includes, in the upper parts of the deposit at least, mineralisation formed by pseudomorphic replacement of crinoidal limestone;

(ii) discounting modifications of their ore metal tenor by supergene processes described in Chapter 8, e.g. slight enrichment in silver and perhaps copper, the unconsolidated materials resemble the underlying bedrock mineralisation in grade, and contains the same general pattern of heavy metal zonation (Fig.5.2).

(iii) the mine geologist reports that the upper parts of the unit contains "occasional thick (up to 3 ft.) clay bands.. giving the appearance of a ghost stratigraphy".

This last feature, allied with the presence of the pseudomorphic replacements referred to above, suggests that the upper part of the rubble mass is an augmented residuum of well-mineralised bioclastic limestones with shale interbeds. Down-folded sediments of this kind are not likely to have extended far above the present erosion level in the area concerned, since it lies on the axis of the main hanging-wall syncline. Even allowing for some drag on the fault slice, the base of the Black Calp may have overlain the south central part of the residual deposit by less than 100 ft.

The muddy matrix of the unit may be partly or largely a residue of the once-overlying Calp, flushed down into the protore zone by the solutions responsible for the latter's disaggregation.

C. The Fossil Gossan and Gossan Talus

The "raft" of massive protore referred to in the previous section originally consisted largely of fairly coarse-grained galena-rich mineralisation. Some time before the last glaciation of the area it suffered intense oxidation, yielding a rather friable rock mass known as the Fossil Gossan. This consists chiefly of residual primary barite, coloured hues of red, brown and yellow by (mainly) limonite (Plate 6.15 and 6.16). It is not known to contain supergene hematite. Weathering processes described in Chapter 8 have impoverished it in lead, zinc and copper, but enriched it in silver to such an extent that it is worth working for that metal alone (Table 6.1).

The cross-sectional shape of the Fossil Gossan cannot be determined precisely from borehole information, and its horizontal extent is uncertain because the semi-coherent rock mass grades physically into a large accumulation of its

Plate 6.16 - Fossil Gossan (two exposures) overlain by transported Calp mud. The Calp mud that appears to underlie the smaller exposure has been displaced by mining; the long, low ridge of oxide rubble is also artificial. 5180 bench, 20900N 32000E.

Plate 6.17 - Gossan talus underlain by stratified sulphide rubble and Calp mud. 5180 bench, 20800N 32300E.

transported derivatives, termed gossan talus. Figs. 6.2 and 6.3 give some idea of its outline, which in plan is elongated roughly E-W and slightly crescentic. There is some evidence that the base of the gossan body has a low-angle dip to the north - in conformity with the presumed dip of the mineralised limestones of which it is a relic.

The Fossil Gossan had a small sub-till outcrop, and there can be little doubt that its upper part stood proud of the surrounding residuum for some considerable time before the last glaciation of the area. On all but its northern side it is partially mantled by a talus of angular, unsorted gossan fragments containing, in its upper levels at least, thin lenses of Calp mud. The talus mantle extends eastwards, southwards and south-eastwards over several of the bodies of dark residuum described in previous pages (Plate 6.17).

The thickness of the talus body varies up to about 50 ft. Contouring of its base (Fig. 6.6) suggests that talus mantling the sulphide rubble deposits to the east and south-west of the Fossil Gossan lies in cavities that originated by subsidence of the sulphide rubble, and were probably modified by subsidence during and/or after accumulation of the talus.

The talus is well-compacted, and has a bulk density only slightly less than that of average Fossil Gossan material. The calculated volume of talus now remaining is about a million cubic feet. If it is assumed that:

a) the area of the parent gossan averaged about 15,000 sq. ft.;
b) the parent gossan had approximately the same bulk density as the Fossil Gossan and
c) about 10% of the original volume of talus has been removed from the area by glacial action

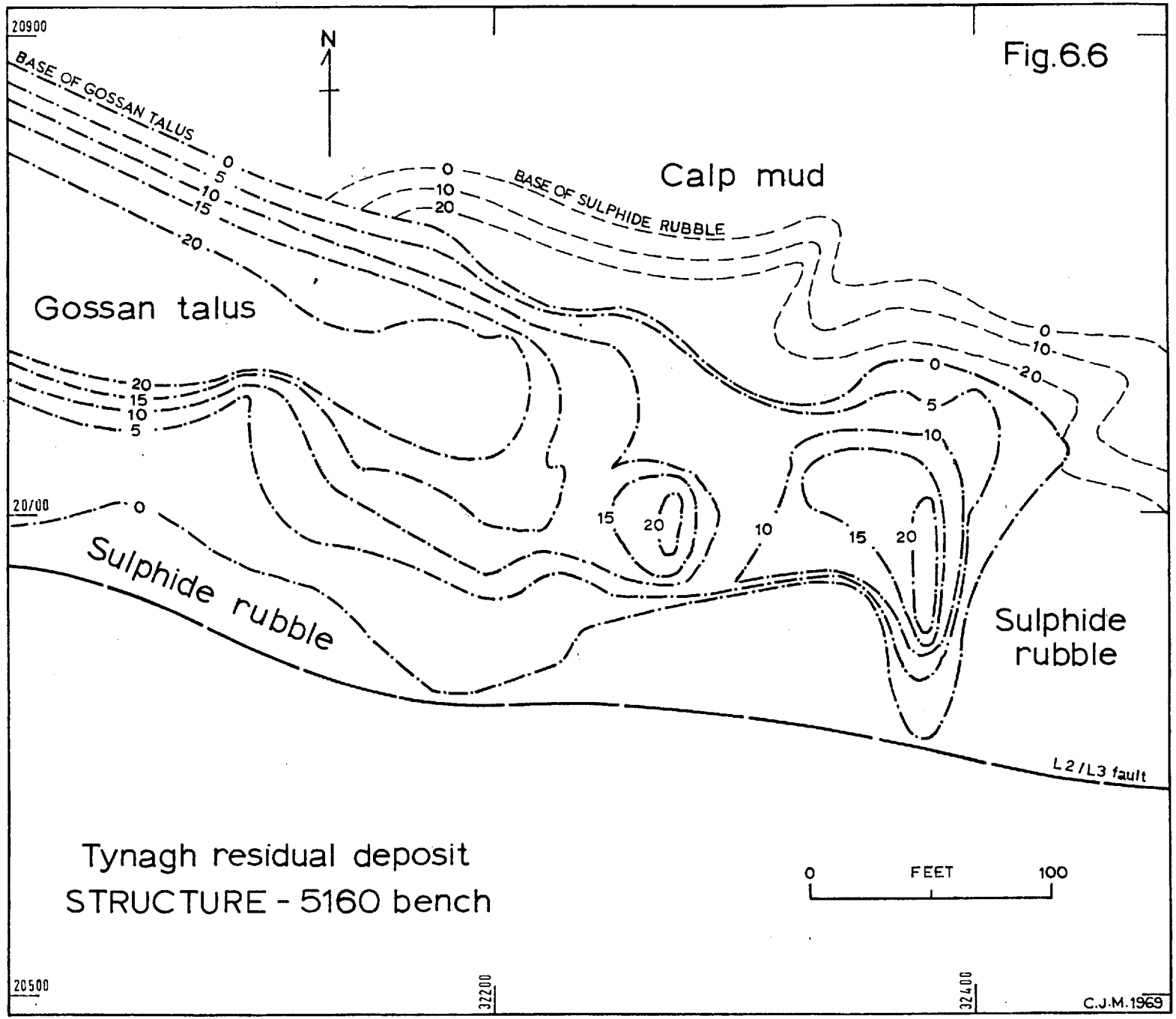


Fig.6.6
20900
N
BASE OF GOSSAN TALUS
0
5
10
15
20
Calp mud
BASE OF SULPHIDE RUBBLE
0
10
20
Gossan talus
0
10
20
0
5
10
20
15
10
5
20/00
0
15
20
10
15
20
Sulphide rubble
Sulphide rubble
L2/L3 fault
Tynagh residual deposit
STRUCTURE - 5160 bench
0
FEET
100
20500
32200
32400
C.J.M.1969

then the talus could have resulted from denudation of the Fossil Gossan by 60-75 ft. The gossan rubble underlying the Collapse Breccia would represent another 20-30 vertical feet, but it is by no means certain that this material is also a derivative of the Fossil Gossan.

D. Transported Calp mud

The northern side of the Fossil Gossan is overlapped and underlain by Calp mud lacking a ghost stratigraphy and hence classified as a transported residuum. Little is known about its internal organisation, except that the upper part contains roughly stratiform accumulations of granular pyrite (including fragments of the thin bands of pyrite that are characteristic of Black Calp), and appears to have accumulated in a shallow depression elongated roughly E-W.

The younger materials were evidently deposited during or after gossan formation, for they form plug-like downward intrusions into the Fossil Gossan (Plate 6.16), and have been substantially enriched in silver by chemical processes discussed in Chapter 8.

E. In situ Calp mud

The north-central wall of the deposit is formed by gently flexed Black Calp, folded into this position by tectonic deformation (Plate 6.18). To the south of it is an extensive area of partially and wholly decomposed Calp with clear "ghost" stratification, including persistent bands of pyrite, chert and decomposed shale(Plate 6.19).

Decalcification evidently took place at a fairly uniform rate over much of area, the residue settling onto its solid rock "floor" without major disruption of inherited primary

Plate 6.18 - Gently flexed Black Calp exposed in the north-central wall of the open pit. The lower part of the wall is coloured by hydrated ferric oxide precipitated from waters discharging along a spring line formed by a clay band in the Calp.

Plate 6.19 - Subsidence structure in Calp mud with a "ghost" stratigraphy. The sagged materials include a grey clay band (decomposed shale) underlain by a 6in. chert band. 5180 bench, 20950N 31750E.

structures. What thickness of rock the Calp mud represents is uncertain, for it does not appear to contain any reliable marker horizons. A tentative correlation of clay bands in its lower part with shale beds exposed in the wall of the open pit indicates subsidence of about 50 ft.

While the relict stratification is generally flat-lying to undulatory, it contains in places synclinal folds of widely varying width and intensity, and apparently with no preferred axial orientation. Some of the more abrupt sags are circular in horizontal section. Structures of this kind seem to be particularly common in parts of the Calp mud succession containing a clay band underlain by a chert band, and are thought to have resulted from solutional undermining of the latter during weathering.

Towards the southern margin of the unit, deformation of inherited bedding tends to become more intense and widespread. In places, it is totally disrupted to form breccias of upended or chaotic rock relics in a matrix of Calp mud.

6.4 SUPERFICIAL DEPOSITS

A. Sub-till sediments

Lying unconformably on eastern parts of the residual deposit proper, and immediately overlain by glacial till, are sediments, generally less than 20 ft. thick, consisting largely of redistributed residuum of very local origin. They are concentrated in two main areas, one on the SE margin of the deposit and the other in its NE corner (Fig. 6.3).

Those along the SE margin of the deposit comprise gritty grey, black and brown muds containing small unsorted angular to subrounded fragments of protore, gossan, Calp and

Waulsortian limestone and, rarely, sandstone. Their content of reworked gossan increases westwards, i.e. towards their overlap onto the gossan talus. The main compositional difference between the sediments in this area and materials of similar type forming underlying units of the residual deposit proper is that the former contain occasional blocks and pebbles of unaltered limestone, which in some cases show signs of abrasion by ice. This suggests that some of their constituents may have been derived from a till older than the one now mantling the deposit.

The sediments in the NE corner of the deposit have a similar composition, but include additionally numerous angular chert and ironstone fragments (the majority less than 3 in. in size), and abundant fossil wood.

In the first of the two areas mentioned the sediments are arranged in irregular beds, small lenticular bodies and chaotic masses with an aggregate width not exceeding 10 ft. and apparently increasing towards the North Tynagh Fault. Dips of up to 15° were measured on their basin-shaped lower contact.

As Plate 6.20 shows, the structure of the sediments in the NE corner of the deposit is highly complicated. The only feature of their composition that appears to be time-related is that in the thicker parts of the sedimentary mass the deeper materials tend to be dark timber-bearing muds and sulphide rubble containing many ironstone fragments, while those overlying them tend to consist chiefly of oxide rubble and muds and appear to be devoid of timber. The first type of material occurs partly as a filling of pipe-like cavities in an in situ residuum of argillaceous limestones (Plate 6.21). The attitude of the cavities varies from vertical to sub-horizontal

Plate 6.20 - Poorly organised sediments, perhaps solifluction deposits, in a local subsidence structure at the NE margin of the open pit.

Plate 6.21 - In situ residuum of argillaceous bioclastic limestones in the NE wall of the open pit. The dark materials at A-A are the fill of what was formerly a bedding-plane passage in the limestones.

and their apparent width from a few inches to a few feet. Their vertical persistence is uncertain, but one cavity is known to extend more than 100 ft. below the base of the till. Undisturbed varve-like sedimentary banding was observed in the fill of the cavity shown in Plate 6.21, indicating that the sediments accumulated in void formed in solid limestones when the residual deposit was smaller than it is today. Most of the pipe-like sedimentary bodies are structureless above present mining levels, but some may be stratified in their deeper parts.

As a whole, the sediments in the NE corner of the open pit area evidently accumulated in a complex solution-subsidence structure resulting from lateral expansion of the residual deposit's envelope of decomposed limestone. Those that occur along the SE margin of the deposit may lie in depressions caused by subterranean decay of mineralised limestones in the immediate hanging-wall of the North Tynagh Fault and compaction of their residuum. The same mechanism may account for the "gulley deposits" of polymict residuum exposed in upper benches of the residual body close to its SW margin (Fig. 6.2). The materials concerned comprised chaotic and crudely stratified mixtures of sulphide-barite rubble, transported gossan, and dark gritty muds of L3 derivation, and apparently lay in a shallow depression meandering along and across the hanging-wall contact of the L3 fault slice. No timber was found in them.

B. Glacial till

Pre-glacial relief in the upper surface of the residual deposit has been wholly suppressed by the deposit's complete mantle of glacial till, which ranges in thickness from about 10 ft. to about 50 ft. (Fig. 6.7). The deposit's outcrop area is more or less coincident with a topographic high formed by the 1,300 ft. long "tail" of a drumlinoid hill alligned roughly E-W.

The summit of the hill (260 I.O.D.) is underlain by 40 ft. of till and overlies Waulsortian bank limestones forming the western rim of the residual deposit.

Within the deposit's outcrop area, anomolously large thicknesses of till at several places clearly reflect infilling by glacial debris of pre-glacial depressions, notably those in which the sediments described in the previous section accumulated. A possible exception occurs over the western part of the L3 fault slice, where till up to 40 ft. thick fills a sub-surface depression of uncertain origin.

The till of the Tynagh area was studied in some detail by Donovon (1965) in the course of his geochemical investigations. In summary, it is calcareous throughout, virtually unstratified, and consists largely of materials that are of local origin. These include representatives of all the rock and residuum types underlying the till in the neighbourhood.

The colour of the till varies with depth. According to Donovon (whose opportunities for studying the matter were better than the writer's) the upper 8-10 ft. is generally light grey to light brown, the lower part medium to dark grey, and the contact between the two main colour zones, which is believed to be related to the position of the water table, usually sharp.

Donovon attributed the till to the retreat stage of the Midland General (Weichsel) glaciation, during which continental ice sheet streamed generally south-eastwards through the area from an ice-shed a few miles to the west. In doing so it digested and augmented deposits of the Munster General (Saale) glaciation, including blocks of granite and metamorphic rock carried south-eastwards into the area from ice gathering grounds in the Connamara Mountains (Plate 6.22) Glacial materials in the sediments described in the previous section may have been derived from the Saale till.

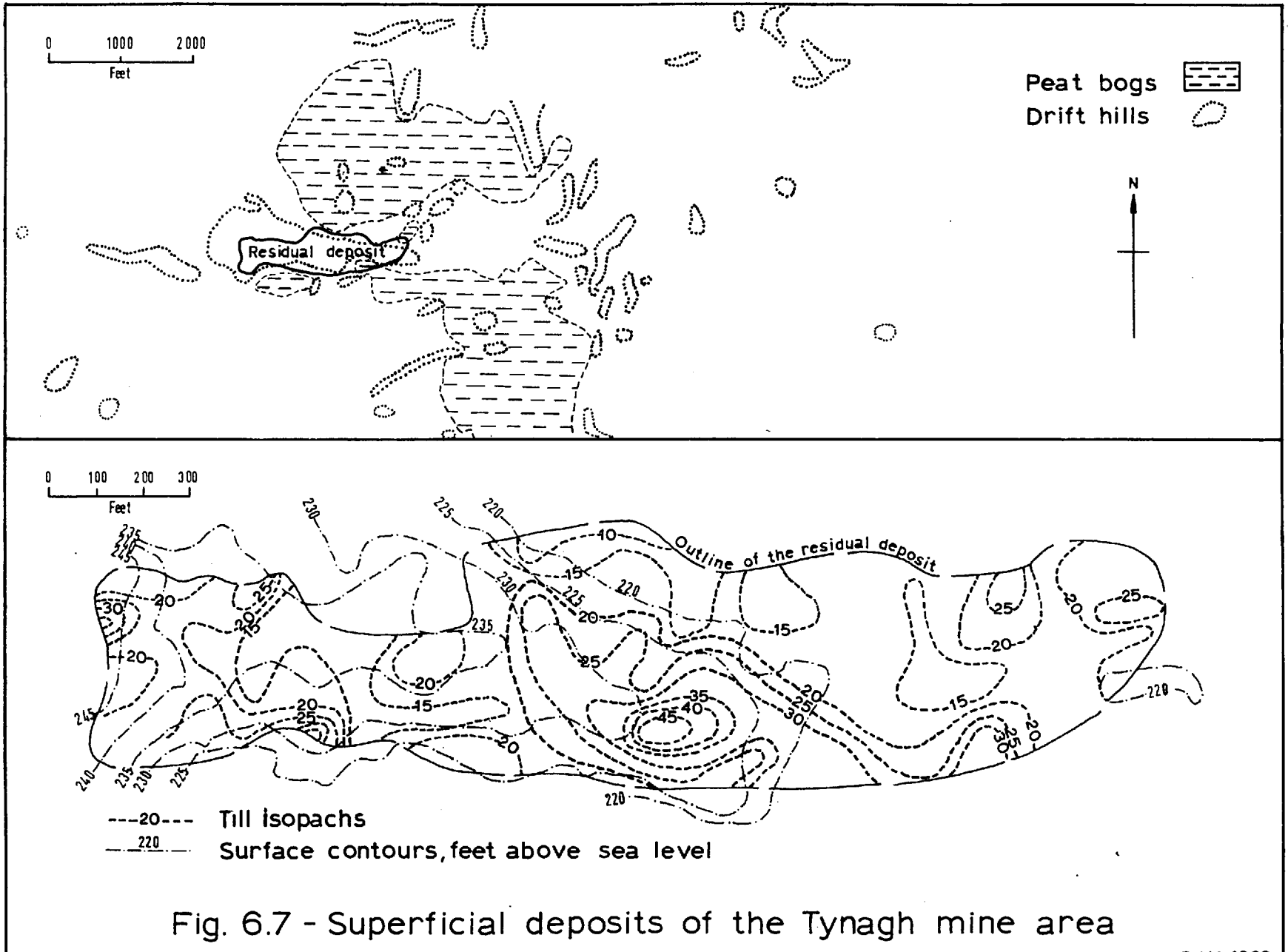


Fig. 6.7 - Superficial deposits of the Tynagh mine area

C.J.M. 1969

Plate 6.22 - Glacial erratics of Galway Granite, with Weichsel till in the background.

Plate 6.23 - Subsidence-controlled peat bog development at the north-east margin of the residual deposit.

There is no material record of earlier glaciations in the Tynagh area, but relics of a boulder clay thought to be Elsterian in age have been reported from a locality 20 miles SW of Tynagh (Jessen et al., 1959). Other references to the glacial history of the area will be found in Chapter 9.

For reasons discussed elsewhere, movement of ice over the residual deposit on at least two occasions had little effect on its structure. The till overlying the deposit does, however, contain substantial amounts of re-worked residuum, including blocks of sulphide-barite rock several inches across and smaller fragments of oxidised protore. It was not standard practice to assay till during the proving of the deposit, but the few assays that are available show that in places it contains up to 1.7% Pb., 0.1% Zn and 1.8 oz/ton Ag. (These values do not all refer to the same assay section).

Copper-stained sandstone boulders presumably derived from the Tynagh Devonian inlier have been discovered in till as much as five miles away in a glacial dispersion fan broadening south-eastwards, and pieces of galena in till 1½ miles to the south of the residual deposit. However, Donovon found that, except in the neighbourhood of the Old Tynagh Mine, strongly anomolous copper and lead values (in excess of 300 ppm and 2,000 ppm respectively, compared with background values of 70 ppm and 380 ppm) were virtually restricted to soils in an area more or less coincident with the residual deposit and extending eastwards from it for about 1,000 ft. As might be expected, he found anomolous zinc concentrations to be more widespread, values in excess of 2,000 ppm occurring in soils over the North Tynagh Fault zone as far east as 48W. It is of interest that the zinc anomaly originating from the residual deposit extends for more than 1,000 ft. to the north of it, reflecting substantial post-glacial chemical dispersion of the metal in that direction.

While it is true that the ice-dispersed residuum probably included much gossanised material containing little lead, zinc or copper, the recent discovery of the East Extension orebody has shown that the residual deposit was not the only potential source of dispersed mineralisation in its vicinity. In conclusion, therefore, it seems that only a small volume of material was scoured from its surface by the Weichsel ice sheets. How much the deposit may have been denuded by earlier glaciations is discussed in Chapter 9.

C. Post-glacial subsidence

While there is no convincing evidence of post-glacial subsidence of any part of the residual deposit's core, it has already been mentioned that decay of limestones at its periphery since the Saale or Weichsel glaciations has caused local subsidence of glacial debris by 20 ft. or more. Subsidence of this kind may have had an important influence on the topography and vegetation of the residual deposit's immediate surrounds, especially in an area at the NE margin of the deposit. Here the till is overlain by peat bog, at the base of which occur lacustrine sediments up to at least 3 ft. thick (Plate 6.23). The sediments comprise grey marls and plants debris with an abundant fauna (1) indicative of shallow, very slow-moving or still water conditions (Kerney, pers. comm.). Similar deposits were found at the base of a peat bog in the other in area of accumulation of what have been referred to as sub-till sediments.

(1) Identifications by Dr. M. Kerney include Valvata cristata Müller, Lymnea peregra (Müller), Pisidium nitidum Jeyns, Planorbis laeris Alder, Planorbis crista (Linne), Segmentine complanata (Linné), and Sphaerium corneum (Linné).

There does not seem to be a general relationship between the distribution of peat bog and of decomposed bedrock outside the immediate neighbourhood of the residual deposit. The two bodies of decomposed Calp known to occur to the north of the main residual deposit (Fig. 3.3) lie in poorly drained terrain with an extensive peat cover but underlain for the most part by solid rock. They do not themselves have any specific surface expression, either in the topography or in the vegetation.

6.5 SUMMARY AND CONCLUSIONS

In previous pages it has been shown that the residual deposit can be broadly subdivided into a core of disaggregated protore mixed in varying proportions with Calp mud and clay, and a peripheral envelope of heavily weathered rocks that have undergone varying degrees of subsidence without total disruption of their primary stratification. It has also been shown that the core deposits have inherited a pattern of primary metal zoning from a disaggregated upward extension of the Main Orebody, and that in places this pattern appears to have suffered little modification by physical processes of weathering. Nevertheless, virtually all the materials of the deposit's core are mixtures of residuum from different sources, and sedimentary processes, allied with and to some extent dependent on subsidence, have played a major part in complicating its structure.

It is not at present possible to rationalise all the observed and drill-indicated features of the deposit's structure. It may never be possible to do so unless working faces are scrupulously mapped as mining proceeds.

On available evidence, however, the physical development of the deposit is thought to have been roughly as follows:

1. Subterranean weathering of the Main Orebody (meaning here the well-mineralised zone in its pristine state) began on a large scale when high-level mineralisation became subject to strong oxidation in or not far below an erosion level 100 - 150 ft. or so above that of the present. This may have required the virtual stripping of the Calp from the area concerned, for experience at Tynagh and elsewhere has shown that only a thin Calp cover can be an effective barrier to underground weathering.

2. The western part of the mine area was probably the first to be stripped of its Calp cover, and the process is thought to have exposed galena-rich mineralisation in the upper part of the Waulsortian Bank Formation. There is a suggestion of a westward increase in the lead content of high-level protore towards the western end of the mine area, and the Waulsortian bank cover limestones in the NW wall of the open pit do contain what appear to be low-grade remnants of a high-level ore zone. It also seems that the gossan rubble underlying the Collapse Breccia was transported westwards into its containing cavity, and that the Fossil Gossan is a relatively young feature.

3. Previously or contemporaneously, structurally-controlled cavern formation took place in the micritic limestones in the western part of the mine area, and some of the weathering products of the high-level mineralisation, apparently preceeded by those of its Calp cover, accumulated in the cavern system.

4. Oxidation of high-level protore resulted in large-scale subterranean disintegration of the Main Orebody. The processes involved are discussed in Chapter 9.

5. In the western part of the area, where the host rocks were pure and massive and the mineralisation probably fairly localised, disintegration involved an element of catastrophic collapse. Throughout the process, the Collapse Breccia, which may have been extensively roofed by Waulsortian limestones at this stage, received influxes of Calp mud from uncertain sources. At times, substantial amounts of timber and occasional sandstone pebbles were washed in with the Calp mud.

6. Disaggregation of the ore zone is thought to have taken place by stages in a continuously waterlogged environment (see Chapter 9), and to have had as a side-effect solutional undermining and compensatory subsidence of Calp still overlying its central and eastern parts. In the eastern part of the area the solution-subsidence structure was gradually filled by protore-rich slump deposits originating mainly along its southern margin, and by inwashes of Calp mud from sources along its northern margin.

7. Protore in the south-central part of the area probably began to disintegrate under a substantial cover of decomposed Black Calp and somewhat after the events outlined above. Its decalcification products are thought to have retained a "ghost" stratigraphy due to the massive nature of the mineralisation and interstitial sedimentation of Calp mud.

8. Formation of the gossan talus occurred fairly late in the deposit's history, and contemporaneously with sedimentation of Calp mud. A large source body of Calp mud resulted from gradual expansion of the residual deposit along the axis of the hanging wall syncline.

9. Sedimentation of residuum continued into the glacial Pleistocene, and may have been particularly active when the deposit entered the periglacial zone. Sedimentation, but not residuum formation, was brought to an end by the Weichsel glaciation.

10. The field relationships of the transported materials and the shape of their containing cavity have been continuously modified by dissolution and metasomatic alteration in the underlying limestones, and by compaction of the overlying materials. It is usually not clear which was the most important cause of subsidence at a particular place, but it seems likely that solutional self-entrenchment of the residuum was the predominant cause of subsidence during the early history of the deposit, and remained so for a longer time in its deeper parts.

CHAPTER SEVEN

DESCRIPTIVE MINERALOGY

Nearly seventy mineral species were identified in the residual deposit during the present study (Table 7.1). This total includes 39 species formed by weathering, nine of which also occur in unweathered materials. Many of the minerals vary considerably in minor and trace element composition.

This chapter is devoted to a systematic description of the deposit's mineral constituents. Because they are so numerous, it has not been possible to describe all the species in detail, and the main emphasis of the chapter is on the mineralogy of elements whose behaviour during chemical weathering of the residual deposit (Chapter 8) is particularly clear. The distribution and intergrowth relationships of most species are dealt with in other chapters, and so will only be mentioned briefly here. Supergene alterations of primary minerals are described and illustrated in Chapter 8.

7.1 MINERALOGY OF LEAD

The main primary host of lead in the residual deposit is galena, with which are commonly associated small amounts of jordanite-geocronite and bournonite.

Cerussite is by far the most abundant secondary mineral of lead. A supergene variety of galena is widespread in small amounts. Other supergene minerals of lead are, in general order of decreasing abundance, beudantite, anglesite, mimetite, dundasite, bayldonite, and possible hidalgoite. Lead has been detected in trace amounts in smithsonite, malachite and allophane.

Table 7.1 Mineralogy of the Tynagh Residuum

Sulphides

Galena*
Sphalerite*
Wurtzite(?)
Chalcopyrite*
Chalcocite
Covellite*
Digenite
Bornite
Acanthite(?)
Greenockite
Hawleyite
Pyrite*
Marcasite
Arsenopyrite
Siegenite
Realgar
Orpiment

Sulphosalts

Jordanite
Geocronite
Bournonite
Tennantite
Tetrahedrite
Enargite

Sulphates

Barite*
Anglesite
Chalcanthite
Rozenite

Carbonates

Cerussite
Dundasite
Smithsonite
Aurichalcite
Malachite
Azurite
Calcite
Dolomite
Ankerite

Oxides

Cuprite
Tenorite
Goethite
Hematite
Magnetite
Manganomelane
Arsenolite
Quartz*
Rutile
Ilmenite

Arsenates

Mimetite
Beudantite
Hidalgoite(?)
Bayldonite

Native metals

Copper
Silver
Arsenic

Silicates

Hemimorphite
Illite*
Kaolinite*
Montmorillonite*(?)
Halloysite(?)
Allophane
Orthoclase
Albite
Microcline
Plagioclase
Muscovite
Sericite
Chlorite

Others

Hydrocarbon
Graphite
Fluorite

*Represented by supergene and non-supergene generations

A. Galena, PbS

(i) Primary occurrence

Galena is the main ore mineral of lead at Tynagh, and is the host of at least 75% of the total silver in primary mineralisation. The average galena content of residual sulphide ores is about 13%. Continuous vertical thicknesses of 100 ft. and more of galena-rich residuum assaying 20-40% Pb are present in parts of the deposit. Similarly, impressive concentrations occur in protore, which has an average galena content of about 5%.

Most of the galena in the deposit occurs in aggregates of anhedral grains formed by replacement of pyrite, sphalerite, primary copper sulphides and limestone, e.g. Plate 4.8. As was mentioned in Chapter 4, porphyroblastic euhedra up to 5 mm. on edge were formed by replacement of sphalerite, pyrite and limestone (Plates 4.11-13), and some galena was deposited as small crystals on the walls of cavities in mineralised Waulsortian limestones (Plate 7.1).

In the unaltered parts of residual primary aggregates, galena generally occurs in intimate intergrowths with other primary sulphides and barite. It commonly contains numerous microinclusions of bournonite and/or jordanite (q.v.) (Plate 4.14). Visually homogeneous galena rarely occurs in areas of polished section more than a few millimetres across. The commonest supergene replacement products of galena are cerussite, binary copper sulphides and, more locally, anglesite.

The size of galena grains in anhedral mosaics varies within the width limits 10μ to at least 5 mm. Lamellar twinning is quite often seen in specimens lightly etched with hydrobromic acid. Grains in anhedral aggregates generally have no strongly preferred orientation, but fragments of veinlet-type mineralisation in which

galena grains are elongated normal to the walls of the filled fissure are sometimes found in residual sulphide ores. Movement on the North Tynagh Fault during and after mineralisation caused stress orientation of galena grains in some protore in the immediate hanging wall of the fault (see section 4.6).

Irrespective of the distance of their source from the North Tynagh Fault, aggregates of galena sometimes display partial granular polygonisation ("annealing") on etching. Stanton (1964) has shown that granular polygonisation is a textural characteristic of galena and other minerals that have suffered dynamothermal metamorphism or strong tectonic deformation. As Gregor'yev (quoted in Stanton, 1964) has pointed out, however, the texture is also very common in galena that has probably not been affected by either process. At Tynagh it is thought to have resulted from grain boundary equilibration during the original crystallisation of the sulphide. The slight distortion of galena cleavages that is occasionally seen in polished section is more likely to have been caused by crystallisation stresses than by tectonic deformation. There is no evidence that plastic deformation of sulphides was a concommitant of residuum formation.

Spectrographic analyses of five specimens of primary galena (Table 7.2) indicate that the mineral varies compositionally only in its trace element content. Reflected light microscopy, x-ray powder photography and electron probe microscanning of specimens from all parts of the residual deposit and the Main Orebody give no indication of major chemical variation in galena, e.g. by substitution of selenium or tellurium for sulphur towards the isostructral species clausthalite , PbSe, and altaite, PbTe. Comparative data for the clausthalite and altaite are as follows:

Table 7.2 Partial spectrographic analyses of Tynagh primary galenas

	Quantitative ppm ± 15%					
Element Sensitivity	Ag 1	Cu 1	Sb 100	As 1000	Bi 10	Mn 16
Sample						
1	200	740	560	ND	ND	16
2	1300	820	3370	ND	ND	ND
3	2000	2500	3000	ND	ND	68
4	580	22	600	ND	10	ND
5	355	4400	1200	ND	10	ND

Analyst: J.McM.Moore

ND = Not detected

Very minor to trace amounts of barium, iron, zinc and cadmium were detected in all specimens, presumably due to the presence of admixed minerals including barite, pyrite and sphalerite.

Sample locations

1. Residual primary galena, 84W 50N, elevation 5091
2. Protore galena, 85W 150N, elevation 4910
3. Protore galena, 84W 150N, elevation 4890
4. Residual primary galena, 86W 50N, elevation 5100
5. Residual primary galena, open pit, 5120E bench at about 32850E 20650N

	Galena, PbS	Clausthalite, PbSe	Altaite PbTe
Unit cell size, Å (Dana, 1944)	5.93	6.16	6.44
Reflectivity%, yellow light (Millman and Gray, 1962)	48.2	47.5-53.7	65.8-66.0
Vickers Microhardness, load 100g. (Young and Millman, 1964)	57-86	46-72	34-38

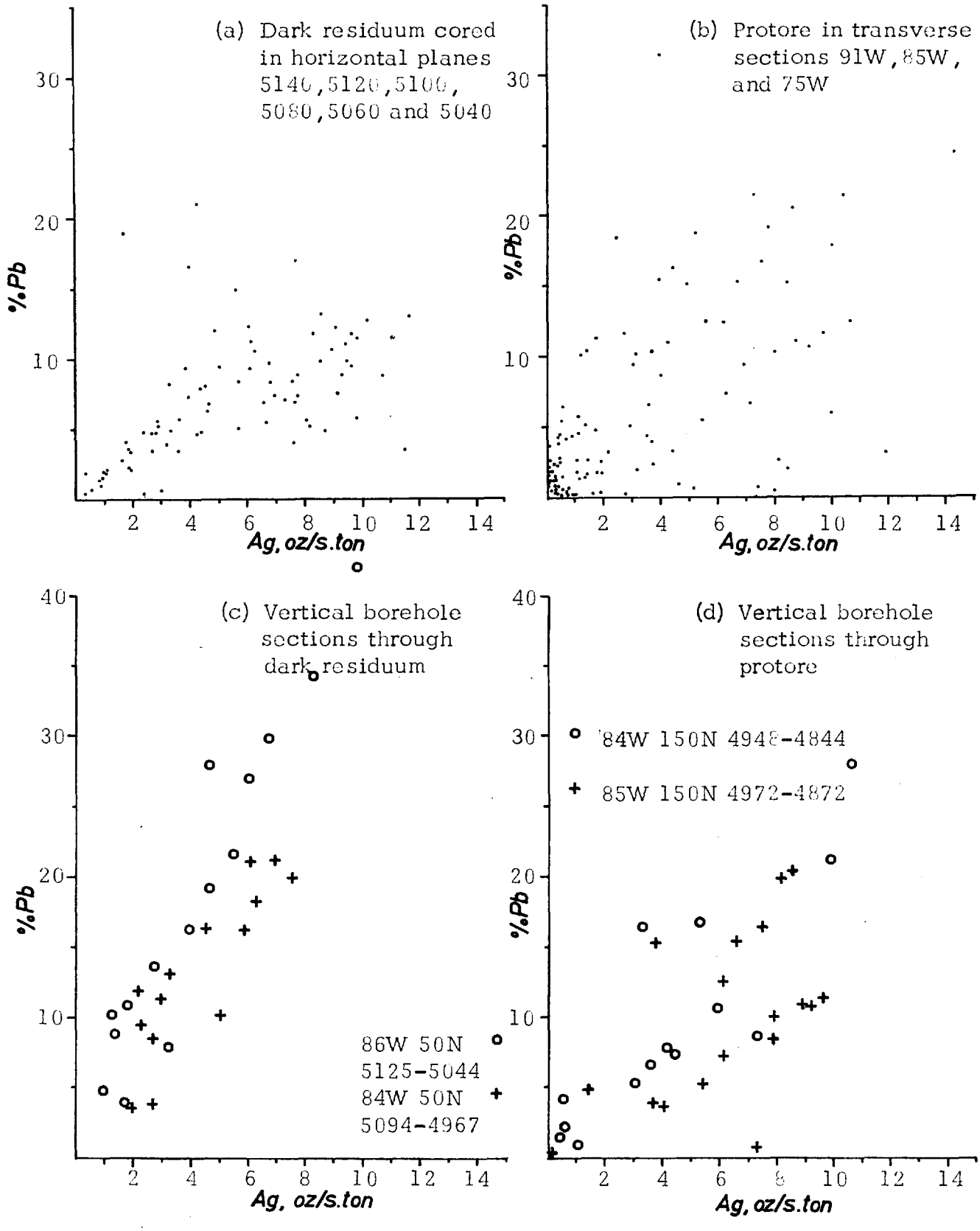
Alabandite, MnS, is also structurally related to galena, which may account for the presence of minor traces of manganese in two of the analysed galenas.

Elements detected spectrographically in all specimens included copper, silver, antimony, cadmium and barium. Zinc was found in all but one of the specimens. Arsenic was not detected in any of them, but it should be pointed out that the detection limit of the method for this element was 1,000 ppm.

Because of its economic importance in the deposit, the case of silver deserves special consideration. Assay data commonly show a strong positive correlation between lead and silver in copper-poor (Cu<0.5%) primary mineralisation, whether residual or in bedrock. The silver content of such mineralisation normally ranges between 0.2 and 0.6oz/%Pb, equivalent to about 600 ppm and 1,800 ppm in galena respectively (Fig. 7.1a). These figures relate to assay samples of whole rock that normally weigh between 30 and 60 pounds, of which galena may comprise up to about 50%.

Silver:lead ratios exceeding 1oz/%Pb are common in copper-rich primary mineralisation (Fig. 7.1b), and occur locally in mineralisation containing little copper and much more sphalerite than galena. It will be shown later in this chapter that the tennantite that occurs at Tynagh is an argentiferous variety, and that a small proportion of the total primary silver in the deposit

Fig. 7.1a



LEAD/SILVER RELATIONSHIPS IN DARK RESIDUUM AND PROTORE

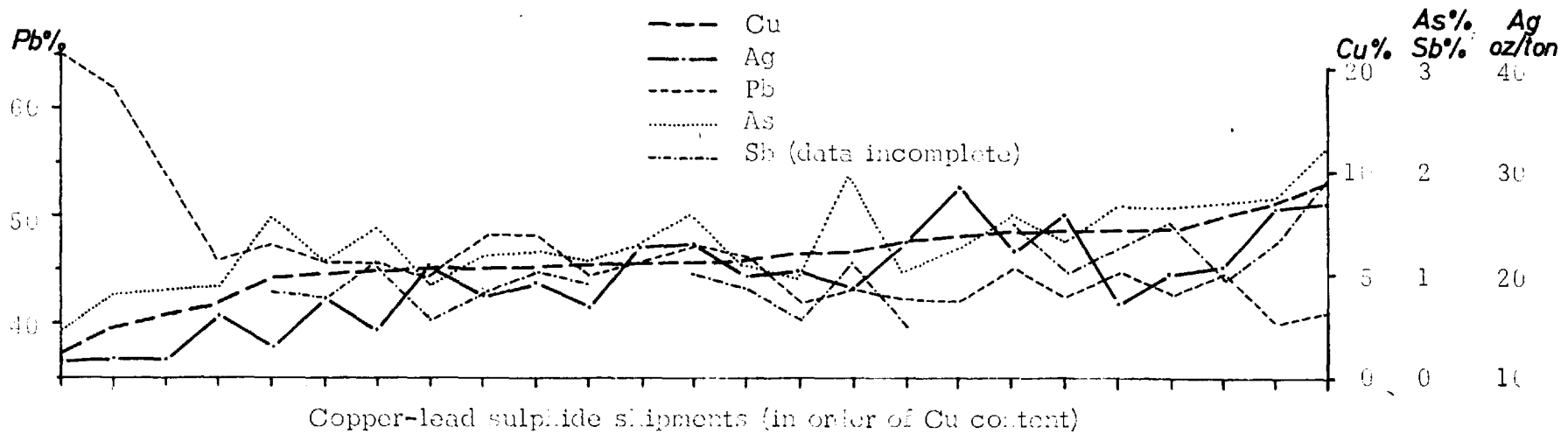

Pb%
60
50
40
Cu
Ag
Pb
As
Sb (data incomplete)
Cu%
As% Sb%
Ag oz/ton
20
3
40
10
2
30
5
1
20
0
0
10
Copper-lead sulphide shipments (in order of Cu content)

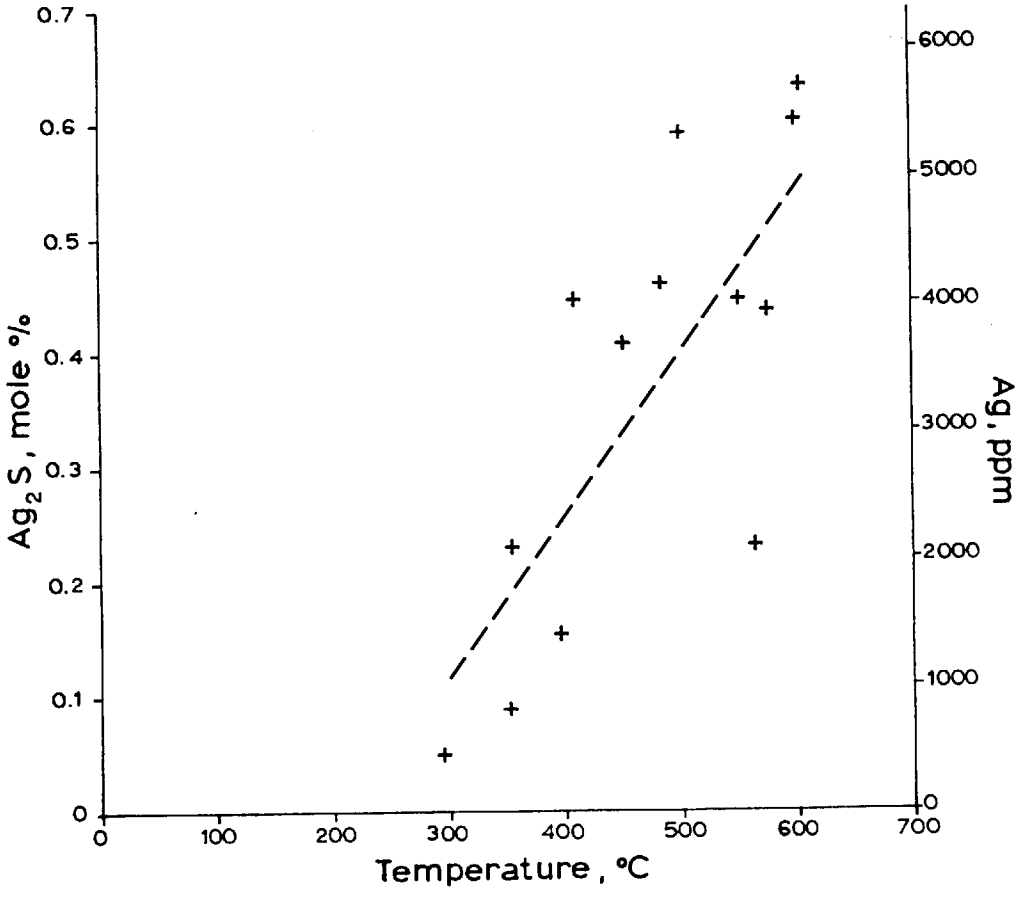
Fig. 11

is intimately associated with sphalerite.

The silver contents of the analysed galenas ranged between 200 ppm and 2,000 ppm. Several of the values agreed fairly well with those obtained by assigning to galena all the lead and silver reported by assay in the drill-core section from which the analysed galena came. For instance, sample 4, containing 580 ppm of silver, came from a drill-core section of residual sulphide ore in which the calculated silver content of galena ranged within the narrow limits 500-750 ppm over 41 vertical feet. This correspondence can also be demonstrated for specimens 2 and 3: the other two samples came from unassayed hand specimens. It may be fortuitous, but it does tend to confirm that galena is the main host of silver in the material concerned, and it suggests that the silver content of galena is locally fairly uniform.

Exactly how silver occurs in Tynagh galena has not been established. It is far from certain that galena can accommodate even 200 ppm of silver as a lattice constituent at low temperatures and pressures. Nissen and Hoyt (1915) concluded from experiments with artificial melts that the upper limit of silver solubility in galena at atmospheric temperatures was well below 2,000 ppm. Ramdohr (1955) has suggested that the silver content of galena in equilibrium with high temperature hydrothermal solutions may normally not exceed 1,000 ppm or so, that of low temperature galena about 100 ppm. More recently, Hutta and Wright (1964) have shown that the equilibrium concentration of dissolved silver in galena synthesised hydrothermally at almost constant pressure (approximately 680 atm) is about 300 ppm at 300°C, increasing to 5,000 ppm at 600°C (Fig. 7.2). They noted no change in the unit cell size of the species with increasing silver content. Their solubility values had a fairly broad scatter, but they did indicate

Fig. 7.2



SILVER INCORPORATED BY HYDROTHERMALLY SYNTHESISED LEAD SULPHIDE, PbS. After Hutta and Wright, 1964

a sympathetic relationship between the depositional temperature of galena precipitated from silver-bearing solutions and the mineral's silver content in the temperature range investigated (300-600°C).

Hutta and Wright did not investigate the effect of variations in pressure on the solubility of argentite in galena, and they were not able to explain variations in its solubility at a given temperature. The latter were substantial, and did not seem to be due to failure of silver to reach an equilibrium concentration in galena synthesised during short runs. As these investigators point out, if such variability can result under the simplified and carefully controlled conditions of the laboratory, one might expect still greater variation under the more complex and changing conditions of nature.

The chief possibilities are, nevertheless, that Tynagh galena contains silver as a metastable solid solution of Ag_2S (which is isostructural with galena above 179°C), as a constituent of one or more argentiferous minerals included in galena, or both. In the writer's view it may contain minor traces of dissolved silver, but contains the element mainly in the form of inclusions of one or more argentiferous minerals. Microscopic inclusions of sulphosalts, among which tennantite (q.v.) is known to be argentiferous and bournonite and jordanite (q.v.) may also be so, are widely distributed in galena. Furthermore, the few spectrographic analyses made to date (Table 7.2) show a general sympathy between silver, copper and antimony in the trace element composition of galena. Nesterova (1958) has shown by calculation that silver, in common with other trace elements reported spectrographically in Tynagh galena (Cu, Sb, Bi), probably occurs in galena mainly as a constituent of inclusions of independent minerals that are generally too small to be detected by standard methods of optical microscopy.

The main argentiferous contaminant in the galenas he investigated seemed to be a form of Ag_2S (argentite or acanthite).

An important implication of the striking uniformity in the primary Ag:Pb ratios in some parts of the deposit (which is illustrated by Fig. 7.2) and the fact that sulphosalts included in galena commonly appear to have formed by exsolution **is that some,** perhaps most, of the primary galena at Tynagh crystallised at temperatures above 300°C. It may be significant in this context that there seems to be some system in the way that the calculated silver content of galena in copper-poor primary mineralisation varies in space. Where the Main Orebody and its residual derivatives are concerned, the area in which primary galena seems to be relatively richest in silver is close to the North Tynagh Fault on 32200E. This phenomenon is reminiscent of that recently described by Hall and Heyl (1968) in the Illinois-Kentucky lead/zinc district, where there is a marked increase in the silver content of galena towards the postulated source area of the ore solutions. Detailed investigation of trace element distribution in protore minerals at Tynagh was not within the scope of the present research, but it would certainly seem to be warranted in the case of galena.

(ii) Supergene occurrence

Supergene galena is widely distributed in small amounts at all levels in the residual deposit. Its distribution is described more fully in Chapter 8. It largely occurs as replacement rims 5-30 in width around particles of microgranular sphalerite in the finer fractions of the residuum, and as ramifying replacement veinlets and irregular areas in sphalerite (Plate 7.2). In its common occurrence as a rim replacement of sphalerite grains, the Tynagh

Plate 7.1 - Octahedral galena crystals encrusted by pyrite lining void in residual sulphide-barite aggregate. x 2.

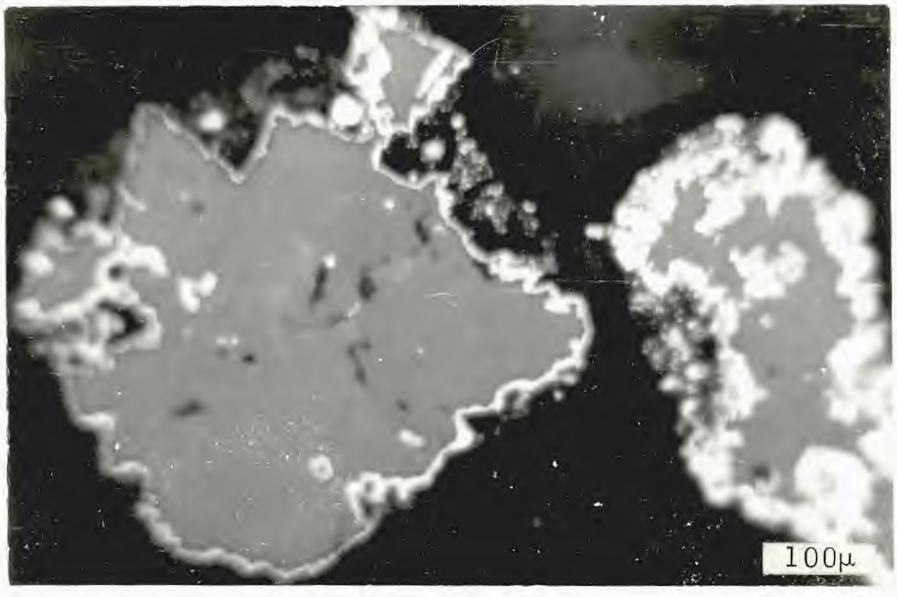


Plate 7.2 - Replacement rims of supergene galena on residual primary sphalerite. Polished section.

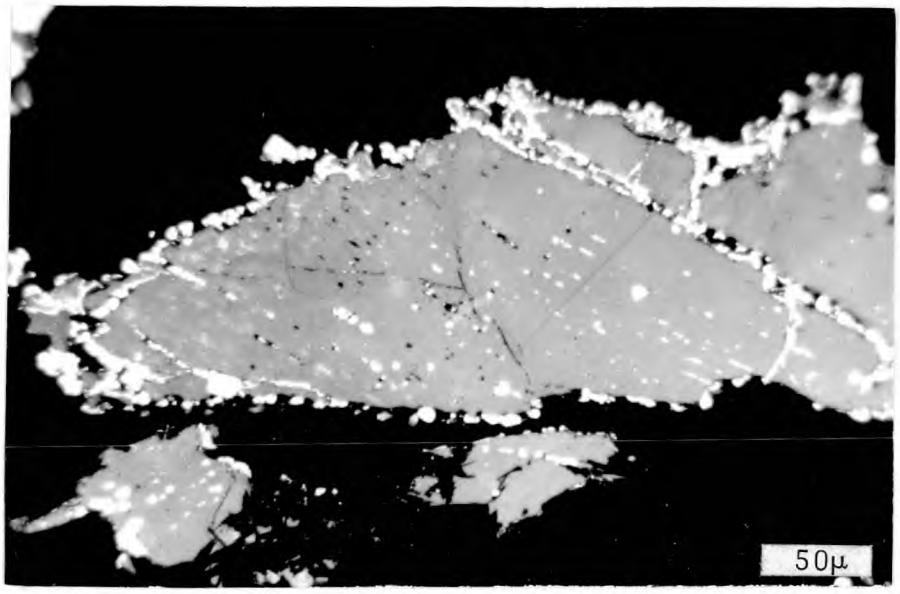


Plate 7.3a - Supergene galena encrusting and veining primary sphalerite grain with inclusions of chalcopyrite and pyrite. Polished section. Oil immersion.

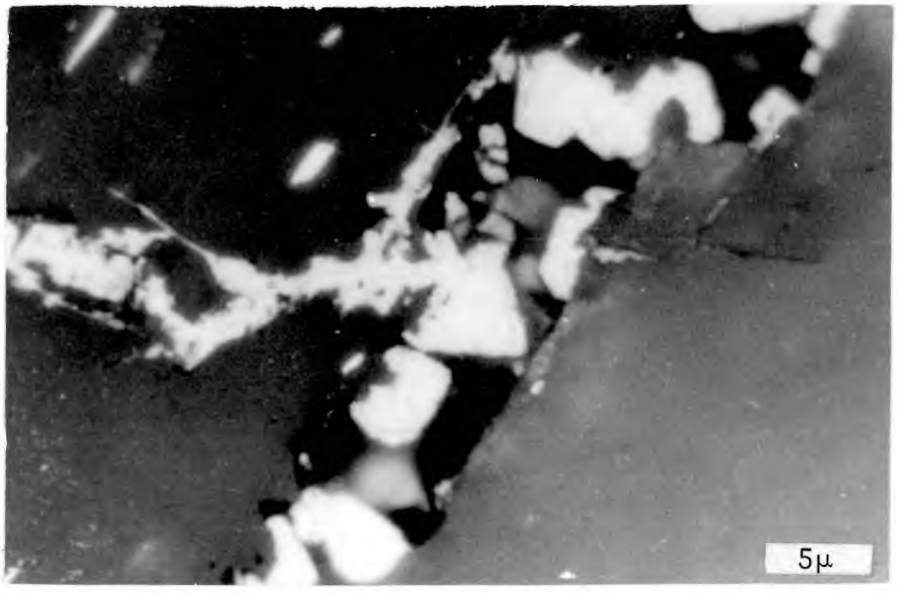


Plate 7.3b - Detail of Plate 7.3a, showing galena crystals lining solution-enlarged sphalerite cleavage.

material closely resembles the supergene galena that occurs at Broken Hill, Zambia (Taylor, 1938) and at Balmat, New York (Brown, 1936). Rare instances of marginal replacement of residual pyrite and tennantite grains by supergene galena have been observed at Tynagh. A small proportion of the mineral takes the form of tiny crystals up to about 100 μ in size, usually cubes but sometimes octahedral in habit, encrusting sphalerite (Plate 7.3).

As described in Chapter 8, supergene galena sometimes occurs in intimate association with other supergene sulphides, notably greenockite. It has been widely replaced by cerussite.

Because supergene galena occurs at Tynagh in such small concentrations, generally in fine intergrowths with sphalerite and/or cerussite, it proved impossible to isolate pure material for spectrographic analysis. There is no visible difference between the optical properties of supergene and hypogene galena in reflected light, and no impurities were detected in three specimens of the former by qualitative electron probe examination.

It is not uncommon for galena from the oxidised zone of an orebody to have a substantially higher assay content of silver than galena from depth. For example, Smith (1922) notes that galena at Broken Hill, New South Wales, contains 15-30 oz of silver at depth, but up to 1,045 oz in the oxidised zone. Enrichments of this order presumably reflect supergene concentration of silver as acanthite or some other silver mineral. In some districts it has been shown spectrographically that supergene galena tends to be empoverished in silver and other trace elements relative to hypogene material (El Shazly et al, 1957; Boyle, 1965). Spectrographic analysis of an approximately 9:1 (by weight) mixture of sphalerite and supergene galena from Tynagh showed it to contain only 3 ppm of silver, equivalent to

a maximum of about 30 ppm in galena.

B. Bournonite, $PbCuSbS_3$

Bournonite is widespread in primary mineralisation as a minor associate of galena, in which it generally occurs as 5-30μ blebs with smooth outlines that in some cases are elongated in galena cleavage directions (Plate 4.14). Larger (up to 50μ) grains are generally found at the margins of galena areas in polished section: they too tend to have smooth junctions with galena. From textural evidence it usually seems that either bournonite replaced galena, or that the two minerals were deposited simultaneously. Structural considerations make it unlikely that intergrowths exemplified by Plate 4.14 resulted from exsolution of bournonite from galena.

Bournonite was recognised in polished section by its greenish grey tint, distinct anisotropy and weak pleochroism in white light, by its superior hardness relative to galena, and by the presence in it of characteristic parquet-type twinning. The identification was confirmed by x-ray powder photography of selected grains.

Qualitative electron probe microanalysis of specimens of bournonite from several parts of the deposit showed that they contained little or no arsenic. Thus seligmannite, $PbCuAsS_3$, which may form a complete isomorphous series with bournonite by mutual substitution of arsenic and antimony, has not been identified at Tynagh.

Dana (1944) notes that up to 1.69% Ag has been reported in bournonite, and that the mineral frequently contains traces of silver. None was detected in Tynagh bournonite by electron probe examination, indicating that its silver content is generally or locally less than 5,000 ppm (the detection limit for this element at the voltage used).

C. Jordanite, $Pb_9As_4S_{15}$. Geocronite, $Pb_9(Sb,As)_4S_{15}$ [1]

These two sulphosalts closely resemble bournonite (q.v.) in their distribution, overall abundance and modes of occurrence at Tynagh. They largely occur marginal to galena aggregates in granular intergrowths with bournonite (with which they share grain boundaries), and as discreet microscopic blebs included in galena (Plate 4.15). Their abundance relative to that of bournonite varies widely from one specimen to another. Of the two, jordanite seems to be considerably the more common (see below).

Some doubt exists about the structure of jordanite and geocronite and the ideal proportions of their constituent elements. The probability is that they are both monoclinic and members of an extensive compositional series formed by mutual substitution of arsenic and antimony (Douglass et al, 1954; Roland, 1968). According to Roland, analyses of jordanite generally fall within the range $Pb_{26-28}As_{14}S_{46-48}$. Roland has shown experimentally that jordanite is unstable in the Pb-As-S system above $549\pm3^{\circ}C$, and may be the high-temperature dimorph of hexagonal gratonite ($Pb_9As_4S_{15}$), inversion occurring at or below $250^{\circ}C$. The atomic proportion of arsenic to antimony in analyses of geocronite given by Dana (1944) and Douglasset al (1954) range from approximately 1:1 to about 2:1.

Particularly when they occur as discreet grains too small for microhardness measurement, jordanite, geocronite and several other common sulphosalts of lead are hard to distinguish optically from each other in reflected light (Table 7.3). Orientation

---

[1] As mentioned in the text, the formulae of jordanite and geocronite are uncertain. Those given express the atomic proportions proposed for jordanite by Roland (1968) and for geocronite by Douglass et al (1954).

Table 7.3 Physical characteristics of some lead sulphosalts in polished section

MINERAL	Approx. Pb%	Colour	OPTICAL PROPERTIES IN REFLECTED LIGHT Reflectivity % (λ=575nm)	Anisotropy (colours, CN)	Twinning	Vickers Microhardness (load 100g)
JORDANITE $Pb_9As_4S_{15}$	70	White, faint pinkish	41.6-44.5 (U)	Strong (grey/blue/violet/ brownish pink)	Common, lamellar	181-198
GEOCRONITE $Pb_9(Sb,As)_4S_{15}$	70	White, faint bluish green tint	41.5-43.5 (U)	Distinct (as jordanite)	Common, lamellar	133-153
GRATONITE $Pb_9As_4S_{15}$	70	White; yellowish tint against galena	42.3-42.7 (U)	Weak-distinct	Not observed	(d)123-156 (e)133-140
MENEGHINITE $Pb_{13}Sb_7S_{23}$	60	White; slightly bluish against galena	37.3-42.1 (U)	Strong (tan/brown/ blue-grey)	Rare	113-155
BOULANGERITE $Pb_5Sb_4S_{11}$	52	White, bluish green tint; greenish grey against galena	37.0-41.4 (U)	Strong (tan/brown/ blue-grey)	Not observed	116-151
BOURNONITE $PbCuSbS_3$	42	Greyish white, distinct blue or bluish green tint	(a)36.8-37.9 (b)37.2-38.2 (c)35.7-36.1	Distinct (blue/grey/brown/ purplish)	Common, often parquet type	(a)168-183 (b)163-194 (c)159-175
JAMESONITE $Pb_4FeSb_6S_{14}$	40	White; faint greenish tint against galena in some orientations	35.0-40.6	Strong (grey/tan/brown/ blue)	Common, lamellar	67-123

(U) Measurements made on unoriented specimen (a) ||010 (b) ||100 (c) ||001 (d) basal section (e) prism section

Sources : Formulae from Dana (1944); reflectivity values from Millman and Gray (1962); other optical data from Uytenbogaardt (1951) and Douglass et al (1954); microhardness values from Young and Millman (1964).

Table 7.4 X-ray powder data for geocronite

1. Geocronite (approximately $Pb_9(Sb,As)_4S_{19}$, Sb:As 9.5:5.0), Silver King Mine, Utah (Douglass et al, 1954)

2. Geocronite, Tynagh

1		2	
dÅ (measured)	I	dÅ (measured)	I
3.71	6	3.71	m
3.54	10	3.53	vs
3.39	8	3.39	vs
3.18	8B	3.18	vs
3.06	9	3.06	s
2.98	7	2.98	s
2.89	9	2.89	s
2.80	5	2.79	m
2.72	5	2.72	w

vs = very strong, s = strong, m = moderate, w = weak

Footnote: Except where otherwise stated, Tynagh specimens for which x-ray data are given in this thesis were photographed using an 11.46 cm camera and CuK_α (λ =1.542Å) radiation filtered by nickel. Line spacings were measured with a Hilger and Watts micrometer scale reading to $\pm$0.05 mm, and line intensities determined visually. Necessary corrections for film shrinkage were made.

effects may diminish intensity differences in reflection pleochroism and anisotropy between jordanite and geocronite. Recognition of jordanite-geocronite in Tynagh ores is often aided by the presence of distinct lamellar twinning. The strong anisotropy and distinct pleochrosim of many grains show that the mineral is jordanite rather than geocronite.

Electron probe microanalyses of grains with the optical properties of jordanite-geocronite in four specimens of Tynagh primary mineralisation showed that all contained $70\pm3\%$ lead, and that those in three contained about 12% arsenic and little or no antimony. X-ray powder photography confirmed that the mineral was jordanite rather than gratonite.

Grains in the fourth specimen were found to contain substantially more antimony than arsenic by weight. The arsenic content of the mineral was too low (<5%) to be measured, but the x-ray powder agreed well with that of geocronite (Sb:As atomic proportion about 1.9:1) from the Silver King Mine, Utah (Douglass et al, 1954) (Table 7.4). It is interesting to note that an early (1841) synonym of geocronite was kilbreckanite, after a locality in County Clare where the mineral has an atomic ratio Sb:As 1.2:1 (Dana, 1944).

No silver (<5,000 ppm) was detected in jordanite or geocronite during the electron probe investigations.

D. Cerussite, $PbCO_3$

Cerussite is by far the most abundant and widespread secondary lead mineral in the residual deposit and in the weathered rocks surrounding it. It is present in all parts of the deposit, and in some constitutes the main ore mineral of lead.

The crystallisation habits and modes of occurrence of cerussite are extremely diverse. In its largest concentrations, the mineral occurs as crumbly aggregates, some several feet across, of randomly-oriented elongated prismatic crystals up to 3 cm in length, and in clusters and individually as smaller tabular, elongated and equant prismatic crystals deposited in cavities. The latter commonly overgrow malachite (Plate 7.4), less commonly mimetite and azurite. Cerussite is also widespread as a granular replacement of galena, and occurs locally as a replacement of other sulphides and barite. Small-scale replacement of fossil wood by granular cerussite has been observed. Other forms of the mineral are an incoherent microcrystalline powder, and spherical aggegates up to 3 cm in diameter of radiating fibrous crystals. The latter typically occur in clayey matrices.

Replacement of cerussite by anglesite has taken place locally, and crude pseudomorphs of dundasite and mimetite after cerussite crystals occur in oxide ores in the SE quarter of the deposit.

Most of the cerussite in the deposit is colourless, white or slightly pinkish in hand specimen. Some is superficially coloured dark grey to almost black by coatings of manganomelane, limonite and tenorite. A pale blue variety of the mineral has been found in very small amounts.

Minor constituents of pale blue and colourless cerussite reported by qualitative x-ray fluorescence analysis (Table 7.5) were strontium, calcium, copper and zinc. Some or all of these elements may substitute for lead in the cerussite lattice. Limited isomorphous substitution is known between cerussite, strontianite ($SrCO_3$) and aragonite ($CaCO_3$). Dana (1951) notes the possibility

Table 7.5 Qualitative x-ray fluorescence analyses of Tynagh supergene minerals.

Mineral	Non-essential elements	
	Major (>1%)	Minor (<1%)
Allophane (colourless)	Zn	Pb,Ca,Mn,Fe,Cu
Allophane (blue)	Zn,Ca	Pb,V,Mn,Fe,As
Allophane (brown)	Pb,Ca,Zn	Cu,K
Cerussite (colourless)		Sr,Ca,Cu,Zn
Cerussite (blue)		Cu,Zn,Sr,Ca
Cerussite ("black")	Mn	Ca,Co,Zn,Cu
Dundasite		Zn,Ca,Cr,Fe
Malachite		Zn,Pb,K,Ca,Sr, Mn,Fe
Mimetite (yellow)		Zn,Cu,Fe,Ca
Mimetite (green)		Zn,Cu,Ni,Fe,Ca, K
Smithsonite (pale brown)	Fe	Co,Mn,Ca,Cu,Pb, Ba,S
Smithsonite (green)	Cu	Cd,Ca,K,Mn,Fe, Ni,Pb

Analyses by Imperial College Analytical Services Laboratory

that up to about 3% of zinc may occur in cerussite by substitution, and that the blue colour of some cerussite may be due to substitution of copper for lead. Cerussite is isomorphous with witherite, $BaCO_3$, but it rarely contains more than trace amounts of barium. No barium was detected in Tynagh material.

A qualitative spectrographic analysis of colourless crystalline cerussite indicated the presence of trace amounts of silver. As Smith (1922) found at Broken Hill, New South Wales, it is common for cerussite to contain very much less silver than primary galena in the same deposit. The silver content of the mineral may depend to some extent on whether or not it forms as a direct replacement of the metal's primary source. No silver was detected by electron probe microanalysis of a cerussite replacement of galena at Tynagh, but then no silver was detected in the galena either. Boyle (1965) reported less than 50 ppm of silver in cerussite at Keno Hill, Alaska, compared with 100-1,000 ppm in malachite and more than 1,000 ppm but less than 1% in anglesite.

E. Dundasite, $PbAl_2(CO_3)_2(OH)_4 \cdot 2H_2O$

Dundasite is a fairly rare constituent of argillaceous residuum in the eastern half of the deposit. It occurs intimately associated with cerussite, allophane and supergene clay minerals, the first of which it sometimes replaces pseudomorphically. In mixtures with these minerals it has been found at one place concentrated in irregular pockets up to about a foot across.

The usual crystallisation habits of dundasite at Tynagh are as microgranular aggregates and as small spheroidal tufts of tiny acicular crystals. Pale blue, pale lilac and colourless varieties occur. All have x-ray powder patterns that agree closely with that of A.S.T.M. standard aurichalcite.

It is not known whether minor elements detected in a specimen of Tynagh dundasite - Zn, Cu, Cr and Fe - were present as lattice constituents or as admixed impurities. Calcium may perhaps substitute for lead, and iron and chromium for aluminium.

F. Anglesite, $PbSO_4$

Relative to cerussite, anglesite is rare at Tynagh. X-ray diffraction analyses of residual lead ores show that it is fairly widespread in very small amounts. It typically occurs in dark pyritic residuum, and in the oxidised residuum of galena-tennantite mineralisation. In the first it has been observed as a replacement of galena and cerussite, and in the second as granular intergrowths with covellite that are thought to be pseudomorphous after galena, and as microscopic aggregates with limonite and native silver veining and encrusting residual tennantite (Plate 7.12).

The composition of Tynagh anglesite was not investigated in detail. The x-ray powder patterns of two specimens did not indicate major diadochic substitution of strontium or barium for lead, and no silver (<5,000 ppm) was detected in one specimen by qualitative electron probe microanalysis.

G. Beudantite, $PbFe_3(AsO_4)(SO_4)(OH)_6$

Beudantite typically occurs at Tynagh in the oxidised residuum of limestones mineralised by galena, tennantite, barite and pyrite. It is particularly common in partially gossanised materials that have been enriched in silver by supergene processes. In these it forms a characteristic assemblage with native silver, anglesite and limonite. Other common associates are cerussite, malachite, azurite and mimetite.

The usual mode of occurrence of beudantite is as a fluffy cryptogranular powder in small cavities in oxide rubble. Occasionally such cavities are lined by beudantite as crustified aggregates of radiating fibrous crystals up to 1 mm long. It also occurs as a constituent of microscopic replacement veinlets in primary sulphides, especially tennantite.

The mineral is generally canary yellow, but green and dark brown varieties also occur in small amounts. The latter are, in some cases, intimate mixtures of beudantite with malachite and limonite respectively.

The x-ray powder patterns and refractive indices of Tynagh beudantites usually agree fairly well with those of A.S.T.M. standard beudantite from Horhansen Nassau, Germany (Table 7.6). One specimen of a pale green powdery material identical in occurrence to beudantite was found to have a distinctly anomalous powder pattern and a mean refractive index lower than that of beudantite (Table 7.6). Both were similar to those of the structurally related mineral hidalgoite, $PbAl_3(AsO_4)(SO_4)(OH)_6$, but in the absence of confirmation that the mineral concerned contained aluminium in place of iron this identification must be regarded as tentative.

Beudantite is one of a group of isostructural basic salts with the general formula $A^{+2}B_3^{+3}(C^{+5}O_4)(SO_4)(OH)_6$. Possible diadochic substitutions in beudantite include Sr and Ca for Pb, Al for Fe, and P for As. In addition, analyses of beudantite sometimes show that it contains many other elements. Boyle (1965), who has termed beudantite "one of the 'chemical sinks' among the secondary minerals" found trace amounts of 15 elements in beudantite from Keno Hill, Alaska, including 100-1,000 ppm of silver.

Table 7.5 X-ray powder data for beudantite and hidalgoite

1. Beudantite, $(PbFe_3(AsO_4)(SO_4)(OH)_6)$, Horhansen Nassau, Germany (A.S.T.M. 11-147)
2. Beudantite, Tynagh
3. Hidalgoite, $(PbAl_3(AsO_4)(SO_4)(OH)_6)$, San Pascual Mine, Mexico (Smith et al, 1953)
4. ?Hidalgoite, Tynagh

1		2		3		4	
dÅ (measured)	I	dÅ (measured)	I	dÅ (measured)	I	dÅ (measured)	I
5.89	70	5.90	s	5.75	90	5.75	s
3.63	40	3.62	m	3.51	90	3.52	s
3.05	100	3.07	vsb	2.98	100	2.99	vs
2.95	40			2.86	20	2.84	mb
2.79	40	2.82	m	2.83	30		
2.52	30	2.52	m	2.48	40	2.47	w
2.25	70	2.26	m	2.26	40	2.26	m
1.96	40	1.96	m	2.20	40	2.20	m
1.82	40	1.82	m	2.02	50	2.02	w
Mean R.I.	1.97	1.95 ± 0.02		1.705-1.713		1.71 ± 0.02	

vs = very strong, s = strong, m = moderate, w = weak, b = broad

This profusion is probably partly a reflection of the fact that beudantite typically occurs in cryptogranular mixtures with other secondary minerals. It was found during the present study that whereas microchemical testing of untreated "beudantite" often showed copper and zinc to be present, the only cations microchemically detectable after the material had been treated with warm dilute HCl and then washed with distilled water were lead, iron and arsenic. Acid treatment usually caused green beudantite to assume a yellow colour.

The beudantite group is isostructural with the alunite group of basic sulphates, and with the plumbogummite group of hydrated basic phosphates and arsenates. The alunite group includes argentojarosite, $AgFe_3(SO_4)_2(OH)_6$, which is a common associate of beudantite in the oxidised zones of argentiferous sulphide deposits and may be present at Tynagh (see Chapter 8).

H. Mimetite, $Pb_5(AsO_4)_3Cl$

Mimetite is widespread in small amounts in oxidised residuum in eastern and southern parts of the deposit. Small pockets of mimetite "sand" comprising numerous interpenetrating hexagonal prisms up to 1 mm. long with slightly dished basal planes have been found, but the mineral usually occurs as microbotryoidal aggregates and felted crusts of tiny acicular crystals (Plate 7.5). Mimetite commonly encrusts malachite, azurite and cerussite, and sometimes replaces crystals of the last pseudomorphically. Overgrowths of the three carbonates on mimetite are much less common but do occur.

The colour of the mineral ranges from bright yellow to leaf green through various shades of yellow and green. The only compositional difference that has been detected analytically between

Plate 7.4 - Cerussite crystals intergrown with colloform malachite. x1.5.

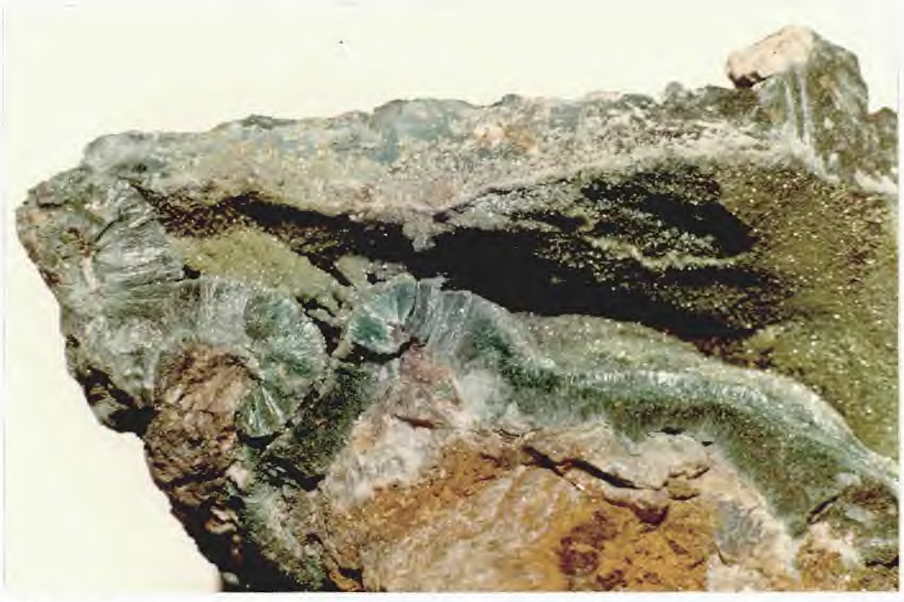


Plate 7.5 - Thin crust of mimetite (yellowish green) on colloform fibrous malachite. x2.

bright yellow and bright green material is the presence of minor amounts of nickel and potassium in the latter (Table 7.5).

Other elements detected in mimetite include calcium, iron and zinc. The first may be present in substitution for lead, there being an extensive isomorphous series between mimetite and chlorapatite, $Ca_5(AsO_4)_3Cl$. Mimetite forms a complete isomorphous series with pyromorphite, $Pb_5(PO_4)_3Cl$, by mutual substitution of phosphorus and arsenic, and a limited series with vanadinite by diadochic substitution of vanadium for arsenic. No phosphorus or vanadium were detected in either of two specimens of Tynagh mimetite analysed qualitatively. Molybdenum, which is commonly reported as a minor constituent of pyromorphite-mimetite, was also not detected.

The source of chlorine combined in oxidation products in mineral deposits is often problematical. Base metal chlorides and oxychlorides are relatively restricted in their distribution, occurring mainly in deposits now or formerly near a coast line, in a semi-arid region or in an area where oxidation of sulphides has taken place at the same time as dissolution of halide evaporites. Members of the pyromorphite-mimetite series (which theoretically contain less than 3% Cl) are widespread by comparison and apparently form under a variety of climatic regimes, and in places remote from the sea and the other potential sources of dissolved chlorine referred to above.

As discussed elsewhere, a likely source of chlorine now combined in mimetite at Tynagh was chloride inclusions in minerals of the protore assemblage, especially barite. Other possible sources were rainwater carrying dissolved chlorine of marine origin - the sea is now only 25 miles from Tynagh, and may have been nearer in Tertiary and Cretaceous times (see Chapter 9) -

and surface or underground waters containing chlorine dissolved from rock-forming minerals, especially apatite. The rocks of the Tynagh area are not known to contain evaporitic halides, and it will be shown later that evaporites were probably not present in beds removed from the Tynagh area by erosion since the residual deposit began to form.

I. Bayldonite, $(Pb,Cu)_7(AsO_4)_4(OH)_2.2H_2O$

A deep green mineral found as 1 mm. microbotryoidal concretions and as thin crusts overgrown by azurite in a specimen of oxide rubble from the eastern end of the deposit was identified as bayldonite from its x-ray powder pattern (Table 7.7). That the latter does not fully agree with that of A.S.T.M. standard bayldonite of unspecified composition from Cornwall may reflect compositional differences between the two specimens. The composition of the Tynagh material was not established. Lead and copper substitute for each other over an extensive but indefinite range in the species, and small amounts of iron may substitute for (Pb,Cu) (Dana, 1951). Lead (27.8-40.5%) predominates by weight over copper (13.2-24.6%) in all analyses cited by Dana. Bayldonite commonly occurs in association with duftite, $(Pb,Cu)_2(AsO_4)(OH)$, as an alteration product of mimetite, e.g. at Tsumeb, S-W Africa. Duftite has not been identified at Tynagh.

7.2 MINERALOGY OF ZINC AND CADMIUM

The main primary host of both zinc and cadmium at Tynagh is sphalerite, which may be in part pseudomorphous after wurtzite. Primary wurtzite has not been observed. Very locally, a substantial proportion of total primary zinc is contained in zincian tennantite, which also contains trace amounts of cadmium.

Table 7.7 X-ray powder data for bayldonite

1. Bayldonite, $(Pb,Cu)_7(AsO_4)_4(OH)_2.2H_2O$, Cornwall, England (A.S.T.M. 6-0335)

2. Bayldonite, Tynagh

1		2	
dÅ (measured)	I	dÅ (measured)	I
4.92	50	5.18	m
4.54	50B	4.50	mb
3.36	10	3.37	vw
3.21	70	3.23	s
3.14	100	3.15	vs
2.93	60	2.92	s
2.71	60	2.70	m
2.65	40	2.64	w
2.24	50	2.23	m

vs = very strong, s = strong, m = moderate, w = weak, vw = very weak, b = broad

The most abundant and widespread secondary zinc mineral is smithsonite, which tends to be slightly cadmiferous but probably contains less cadmium overall than the widespread supergene sulphides greenockite and howleyite. The residual deposit also contains small amounts of cadmiferous supergene sphalerite and (probably) wurtzite, and minor quantities of hemimorphite and aurichalcite. Zinc has been detected analytically as a minor to trace constituent of malachite, allophane, cerussite, mimetite and beudantite. The presence in the residuum of hydrozincite, identified visually in drill cores by company geologists, has not been confirmed.

A. Sphalerite, β-ZnS. Wurtzite, α-ZnS

(i) Primary occurrence

Sphalerite is the main host of zinc and cadmium and a subsidiary host of silver in primary mineralisation. It is virtually ubiquitous in the residuum, and is the most widespread of the ore minerals in protore. It is a major constituent of large tonnages of both types of material. The distribution of sphalerite in the residual deposit is described elsewhere.

Primary sphalerite occurs in the residual deposit in two main forms:

a) as anhedral to subhedral microgranules, the majority less than 20μ in size, in complex aggregates with some or most of the other minerals of the protore assemblage;

b) as free, monomineralic grains and microgranules, the majority again less than 25μ in size.

Included in the first category are boulders up to 6 ft. across of which sphalerite comprises 30-40% by volume.

A small proportion of the residual sphalerite occurs as well-developed crystals or crystalline fragments up to 5 mm. across. In polymineralic aggregates the crystals generally occur as inclusions in pyrite or barite, or as overgrowths on aggregates of microgranular sphalerite.

The intergrowth relationships of sphalerite with other primary minerals are best explained by reference to the depositional history of the mineral in protore, which was described in Chapter 4. It is worth noting that microgranular inclusions of sphalerite are very common in the other main sulphides and in barite. This partly explains the difficulty that has been experienced in excluding zinc from lead sulphide concentrates, and the common occurrence of traces of sphalerite, as microgranules protected from weathering by a barite matrix, in heavily oxidised residuum.

Much of the microgranular sphalerite has a colloform habit, in the sense that its aggregates display colour variation between concentric zones with curved or scalloped outlines. The usual colour range is from very pale yellow to deep reddish brown in thin section. Individual colour zones range in width from less than 5μ to about 100μ, and geometrically related groups from less than 1 mm. to about 2 cm. Junctions between colour zones tend to be diffuse, but where they are sharp they are often not coincident with sphalerite grain boundaries, and there is usually no marked difference in mean grain size across them. These features suggest that the colour-banded aggregates are a crystallisation product of an original gel precipitate, or that the microgranular mosaics resulted from re-crystallisation of zinc sulphide deposited in some other habit.

Regarding the first possibility, there is a distinct tendency in some specimens of colloform sphalerite for pale zones to be considerably wider than dark zones in parts of the aggregate furthest away from the original surface of deposit. According to Edwards (1954), this is evidence that the aggregates aquired colour contrast by Liesegang diffusion of an ionic solution of iron through a sulphide gel. Roedder (1968) has lately disputed the reliability of this and other criteria of colloidal precipitation of sphalerite. The absence in the Tynagh colloform sphalerite of syneresis cracks (cracks that result from dehydration of a gel) suggests that the colour banding is a result of rhythmic deposition of shells of sulphide that varied slightly in composition. The fact that some of the colloform sphalerite appears to have formed as a replacement of solid materials rather than as a cavity lining has the same implication (Park and MacDiarmid, 1964).

Some or most of the colour-banded sphalerite in microgranular mosaics may be a recrystallisation product of the hexagonal ZnS polymorph, wurtzite. Textural evidence of this is that the primary mineralisation contains small amounts of colloform sphalerite in radiating fibrous and bladed habits that are generally considered to be more characteristic of wurtzite than sphalerite (Schultz, 1968). Original primary wurtzite has not been observed at Tynagh.

The colour range of sphalerite in non-banded aggregates is approximately the same as that of the material just described i.e. very pale yellow to reddish brown in thin section. In non-collomorphic aggregates the distribution of colour tends to be patchy. Diffuse concentric colour zoning is sometimes detectable in constituent microgranules at high magnifications. It has also

been observed in fairly coarse-grained sphalerite, though this is usually uniformly honey-yellow or pale brown. Lamellar twinning is commonly visible in relatively coarse-grained sphalerite.

Spectrographic analyses (Table 7.8) support the evidence of concentrator returns, whole-rock analyses and visual inspection that the primary sphalerite at Tynagh is, predominantly, an iron-poor cadmiferous variety.

The colour of the mineral indicates that its iron content is generally low (see footnote), and the concentrations reported spectrographically suggest that the actual figure rarely exceeds 1%. The material investigated spectrographically did not represent the full colour range of sphalerite at Tynagh - the darkest variety in particular is almost impossible to isolate in sufficient quantity, since it generally occurs as narrow bands in colloform aggregates - but against this it must be taken into account that the most iron-rich of the samples may have contained a trace of

---

Footnote: Manning (1967) has recently suggested that the brown colour of iron-bearing sphalerite is due to lattice-interstitial Fe^{+3}, and that the ratio of interstitial Fe^{+3} to substitutional Fe^{+2} may not be constant in all sphalerites. One might expect sphalerite formed at relatively high temperatures to accomodate a higher proportion of interstitial Fe^{+3} (ionic radius 0.64Å) to substitutional Fe^{+2} (0.74Å) than relatively low-temperature material. The fact that the magnetic susceptibility of sphalerite varies systematically with its total iron content suggests that the $Fe^{+2}:Fe^{+3}$ ratio of the species tends to be constant, and in general there seems to be a fairly good correlation between the colour of sphalerite, its refractive index and its total iron content. Gray (1961) has shown that, for any given wavelength of incident light, the reflectivity of sphalerite increases in general sympathy with total iron content. The imperfectness of the relationship may be accounted for by the fact that other elements commonly present in sphalerite affect its physical properties. The reddish hue of iron-poor sphalerites may in some cases by mainly due to the presence of manganese, tin, indium, silver or molybdenum, and their yellow colour to the presence of cadmium, copper, germanium, calcium or mercury (Deer et al, 1962).

Table 7.8 Partial spectrographic analyses of Tynagh sphalerites

	ppm ± 25%	Quantitative ppm ± 15%									
Element	Fe	Mn	Cd	Ge	Ga	In	Co	Sn	Sb	Cu	Ag
Sensitivity	500	30	100	16	16	30	25	10	200	3	3
Sample											
1	4300	640	1800	16	16	ND	25	ND	ND	180	250
2	4000	ND	10000	ND	ND	ND	ND	ND	ND	130	28
3	1900	30	880	ND	16	ND	ND	ND	ND	3	3

Analyst: J.McM. Moore

ND = Not detected

Very minor to trace amounts of barium and lead, probably present in admixed barite and galena, were detected in samples 1 and 2.

Sample locations

1. Protore sphalerite (reddish-brown microgranular), 86W 50N, elevation 5042.
2. Residual primary sphalerite (pale brown coarse crystalline), open pit, bench 5180W.
3. Supergene sphalerite (pale yellow coarse crystalline), open pit, bench 5200W.

pyrite. Spot electron probe microanalyses of sphalerite in colour-banded aggregates showed a positive relationship between total iron content and colour, up to 9,000 ppm Fe being detected in the darkest bands and less than 2,500 ppm in the palest.

Cadmium invariably reports preferentially in sphalerite-rich sulphide concentrates. Analyses of 16 consignments of such concentrates show Zn:Cd ratios ranging between 113:1 and 179:1, with a mean of 142:1. The last figure is equivalent to 4,700 ppm of cadmium in sphalerite. Since the concentrates probably contained a little cadmium sulphide, the indicated average cadmium content of the residual sphalerite that they contained was probably somewhat lower, say 4,000-4,500 ppm. This compares with an average of 5,900 ppm in two primary sphalerites analysed spectrographically.

There is no evidence that the mean cadmium content of sphalerite varies substantially or systematically from one part of the residual deposit to another. The distribution of the element in protore is unknown.

Sphalerite, being isostructural with hawleyite, β-CdS, can accommodate up to at least 4% Cd as a lattice constituent, and wurtzite, which is isostructural with greenockite, α-CdS, probably somewhat more. The cadmium content of both rarely exceeds 1%, however, and is usually less than 0.5%. It appears to depend entirely on the availability of the element in the mineralising solutions (Fleischer, 1955), which in turn may be subject to regional or district-wide controls. El Shazly et al (1957) have suggested that this is the case on the British mainland, and it has already been remarked that the average cadmium content of sphalerite in certain Irish deposits tends to increase northwards across the country. If this is a reflection of district-wide zoning, it reduces the chances that cadmium-rich (Cd>0.75%) sphalerite occurs at Tynagh in any quantity.

The spectrographic analyses support the evidence of whole-rock assays and concentrator returns that Tynagh sphalerite contains minor traces of silver. The specimen containing 250 ppm Ag came from a six-foot core section of protore assaying:

An - 4.74% Ag - 0.93oz/ton Pb - Trace Cu - Nil

A few stringers of galena were visible in hand specimen, but every effort was made to eliminate contaminating minerals from the material analysed, which was selected under a binocular microscope at high magnification.

Silver, generally in amounts of less than 100 ppm, has been reported in sphalerites from numerous mineral deposits in many parts of the world (Fleischer, 1955). The association seems to be as common in Ireland as it is elsewhere. Sphalerite at Keel typically contains 250-550 ppm Ag, and 250 ppm was reported by El Shazly et al (1957) in sphalerite from Ballyhickey.

How silver typically occurs in sphalerite is uncertain. Valency considerations and the comparatively large size of the Ag^{+} ion (1.13Å, against 0.74Å for Zn^{++}) preclude cationic substitution of silver in sphalerite, and militate against its accommodation in lattice interstices or in the metal sites of non-stoichiometric sphalerite. It is generally held, therefore, that sphalerite containing more than about 50 ppm of silver is contaminated by one or more argentiferous minerals. This is the case at Keel, where silver reported analytically in sphalerite is in fact concentrated in microscopic inclusions of argentian tetrahedrite (Patterson, pers. comm.). Tynagh sphalerite commonly contains microscopic inclusions of tennantite (q.v.), but there is no clear relationship between their observed abundance and the silver tenor of galena-poor sphalerite mineralisation. As Taylor and Radtke (1969) have recently shown, silver in argentiferous

sphalerite at Flat River, Missouri, is probably concentrated in sub-micron-sized inclusions of a discrete phase that are not detectable by normal techniques of optical microscopy. The present study has not resolved whether or not this is so at Tynagh. It is worth further investigation.

The present paucity of analytical data does not justify detailed discussion of other aspects of the trace element composition of Tynagh sphalerite, but the following points deserve a brief mention:

a) Gallium, germanium, indium and manganese have a much greater affinity for sphalerite than for galena (Goldschmidt, 1954). Tynagh sphalerite contains all these elements in trace amounts, but only manganese was detected spectrographically in galena (q.v.). Germanium, in common with manganese and cadmium, reports preferentially in zinc sulphide concentrates.

b) El Shazly et al (1957) have suggested that the indium, manganese and tin contents of sphalerite may vary sympathetically, and the gallium, germanium and antimony contents vary antipathetically, with the depositional temperature of the mineral. Fleischer (1955) has also suggested that there may be an antipathetic relationship between the depositional temperature of sphalerite and its germanium content. However, Fryklund and Fletcher (1956) consider that, iron and manganese apart, it is probably very rare for elements that substitute cationically in sphalerite, among which they include germanium, gallium and indium, to be present in equilibrium concentrations in solutions from which sphalerite is deposited. Except for a manganese content of 640 ppm

in one, both the analysed primary sphalerites from Tynagh were deficient in all the elements mentioned above.

(ii) Supergene occurrence

Supergene zinc sulphide is widespread in the residual deposit as a replacement product of fossil wood. Assays show that zinc comprises up to at least 67% of fossil wood ash, the value being equivalent to about 50% by volume of the whole wood sample to which it refers (Table 7.9).

Table 7.9 Partial analyses of fossil wood

Sample	Ash %	Zn	Cd	Fe	Pb	Cu
		Wt. % in ash				
1	86.4	58.08	0.04	0.94	0.70	0.01
2	70.5	43.20	13.75	0.44	5.29	0.01

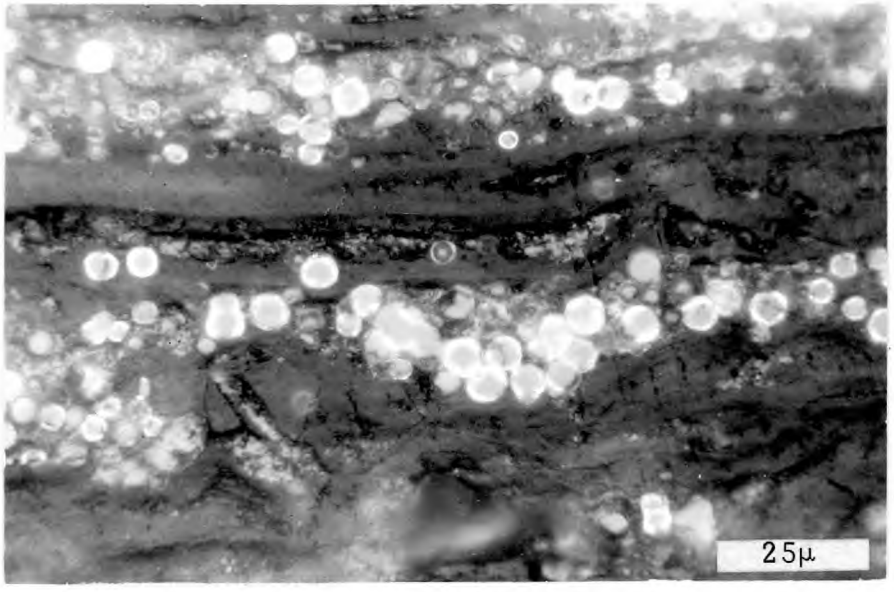
Source of samples

1. Collapse Breccia, 5200W bench.
2. Probable cave fill, 5160E bench.

Analyses by Irish Base Metals Ltd.

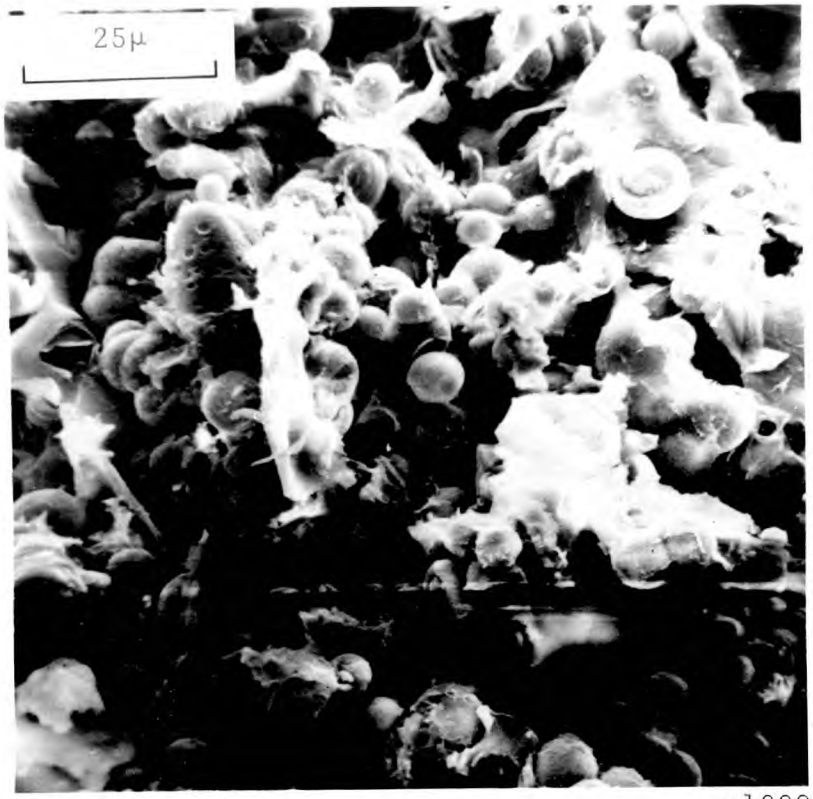
In polished section the sulphide is seen to occur predominantly as microspherulitic replacements of wood and infillings of wood cells, and subordinately as microcrustified linings of cells and as pseudomorphic and non-pseudomorphic replacements of wood tissue (Plates 7.6, 7.7). Its colour is generally pale yellow

(a)

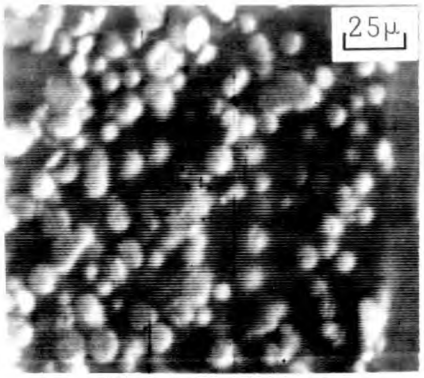


(b)

Plate 7.6 - Supergene zinc sulphide as cell linings (a) and microspherules (a)(b) in fossil wood Sequoia. Polished sections.

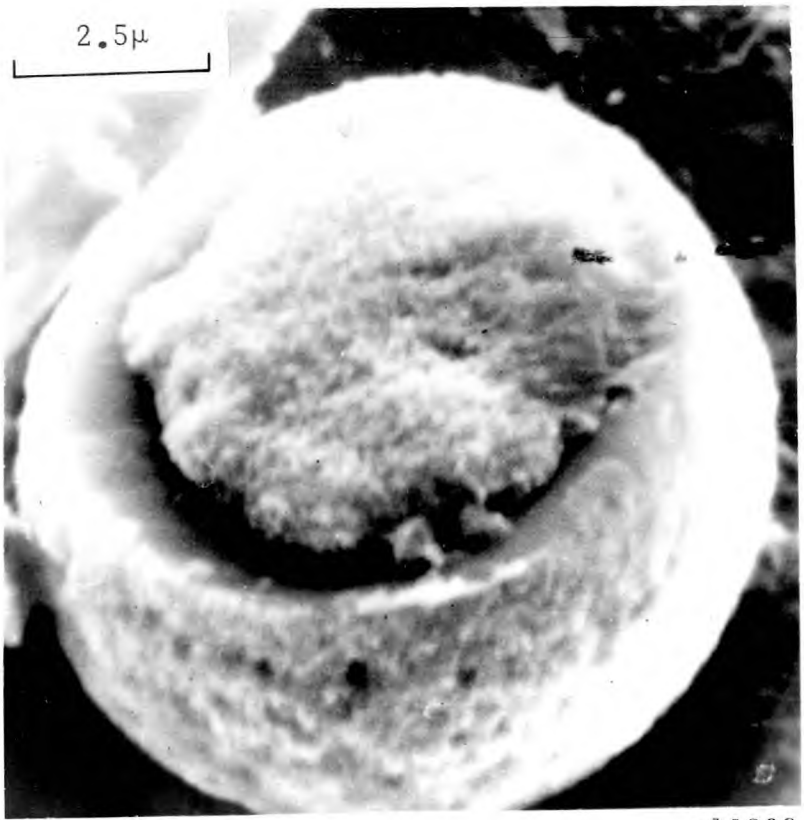


x1000



Electron image

Zinc distribution



x10000

Plate 7.7 - Micrographs of supergene sphalerite in fossil wood.

Left: Scanning electron microscope images

Above: Electron probe micrographs

or pale brown. Most spherulites are 5-10μ in diameter. As Plate 7.7 shows, their external surfaces are minutely rugose, perhaps reflecting the fibrous internal structure that is deduceable from their cross-shaped interference figure in reflected light under crossed nichols. Some have a shape akin to that of a cottage loaf. Muir (pers. comm.) has pointed out that their size range, morphology and mode of occurrence are all consistent with their having formed by replacement of fungi, but the apparent rarity of non-sulphide spherular bodies of the same size in fossil wood throws doubt on this.

In reflected light the sulphide appears to be wholly isotropic, but the structure of the microspherulites, and x-ray diffraction analyses of fossil wood exemplified in Table 7.10, suggest that the original form of the sulphide may have been wurtzite, and that wurtzite is still present in association with sphalerite. Uncertainty on this point arises from the fact that the reflection anisotropy of wurtzite is extremely weak (Millman and Gray, 1962), and that wurtzite is readily converted to sphalerite by mechanical deformation (Deer et al, 1962), which is an almost inevitable result of polished section preparation. Millman and Gray report a slight reflectivity difference between the two species, but reliable reflectivity values could not be obtained for Tynagh material because of strong dispersion effects.

Electron probe microanalyses of microspherulites in one of the wood specimens referred to in Table 7.9 showed that they were essentially pure ZnS, and contained little or no iron (<2,500 ppm), manganese, cadmium, mercury, indium or silver (all <5,000 ppm). Some of the cadmium reported in both specimens of fossil wood is, nevertheless, thought to be present as a lattice constituent of zinc sulphide.

Table 7.10 X-ray powder data for sulphides of zinc and cadmium

1		2		3		4		5		6		7	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
								3.583	100	3.56	w	3.59	w
						3.36	100	3.357	59	3.36	s		
		3.309	100	3.28	50							3.27	vw
								3.160	100	3.16	vw		
3.123	100	3.128	86	3.12	70							3.12	vs
		2.925	84	2.91	30	2.90	40			2.93	vw		
2.705	10												
		2.273	29										
								2.450	25				
						2.058	80	2.068	57	2.061	m		
1.912	51	1.911	74	1.90	100			1.898	42			1.89	s
				1.79	30			1.791	17				
		1.764	52			1.753	60	1.761	45	1.757	m		
								1.731	18				
						1.680	10	1.679	4				
1.633	30	1.630	45	1.62	100							1.625	ms

vs = very strong, s = strong, m = moderately strong, w = weak, vw = very weak. All d-spacings measured.

1. Synthetic β-ZnS; A.S.T.M. standard 5-0566.
2. Synthetic α-ZnS; A.S.T.M. 5-0492
3. Wurtzite (natural α-ZnS), Pribam, Czechoslovakia; A.S.T.M. 3-1093.
4. Hawleyite (natural β-CdS), Keno Hill, Yukon; A.S.T.M. 10-454. 5. Synthetic α-CdS; A.S.T.M. 6-0314
6. Tynagh, cadmium bloom on clay (illite and quartz reflections omitted), 5200W bench.
7. Fossil wood (hydrocarbon reflections omitted), 5200W bench.

Relatively minor amounts of supergene zinc sulphide have been recognised in other milieu. Crystals of pale yellow sphalerite up to 2 mm. on edge were found overgrowing supergene pyrite in a small cavity formed by weathering of limestones walling the western end of the residual deposit. Probable sphalerite is occasionally found as corroded overgrowths, generally less than 2μ in width and corroded by a later generation of supergene galena, on supergene galena formed by rim replacement of primary sphalerite grains in dark residuum. Similar rimming effects have been described elsewhere by Wang (1915) and Brown (1936).

The partial spectrographic analyses of Tynagh sphalerites given in Table 7.8 suggest that the supergene variety of the mineral may, characteristically, have a lower content of certain trace elements than typical hypogene material. El Shazly et al (1957) found that, compared with epigenetic sphalerites from nearby deposits, nine English sphalerites of supergene origin contained less silver, cobalt, germanium and antimony, but had approximately the same average cadmium content (2,400 ppm, against 880 ppm for the one Tynagh sample).

B. Hawleyite, β-CdS. Greenockite α-CdS.

Cadmium sulphide is widely distributed in small amounts in the residual deposit and the weathered rocks immediately surrounding it. It is exclusively of supergene formation, occurring chiefly as a powdery impregnation of various types of residuum and as a bloom on fossil wood. Up to 13.75% Cd, equivalent to 12.5% CdS in whole wood, has been reported in fossil wood ash (Table 7.9), suggesting that one or both of the mineral monosulphides of cadmium occur by replacement of fossil wood. Other aspects of their occurrence, and details

of their distribution, are dealt with in Chapter 8.

The deposit evidently contains both greenockite and hawleyite, but detailed investigations of the mineralogy of cadmium sulphide at Tynagh has been hampered by its typical occurrence in fine-grained mixtures with other minerals. It is virtually impossible to differentiate visually between microgranular sulphides of zinc and cadmium in a matrix of fossil wood. Greenockite has been specifically recognised in Calp mud with a vivid yellow bloom as rare doubly-terminated prismatic crystals up to 5 in size. The identification was confirmed by partial electron probe microanalysis. X-ray diffraction analyses of similar materials and of fossil wood given in Table 7.10 indicate that greenockite is usually accompanied at Tynagh by its cubic dimorph hawleyite.

The paragenesis and relative abundances of the two species in Tynagh residuum are unknown, and apart from establishing the essential purity of the greenockite crystals referred to above, no attempt was made to study their composition. Limited diadochic substitution of zinc, mercury and other elements for cadmium is possible in both species. Their conditions of formation are reviewed elsewhere.

C. Smithsonite, $ZnCO_3$

Smithsonite is the main supergene mineral of zinc at Tynagh, and is a constituent of most residual ore types. Large concentrations occur in oxides peripheral to the western and north-eastern parts of the deposit. Local concentrations occur in limestones up to at least 250 ft. to the north of the residual deposit proper.

The commonest supergene associates of smithsonite are goethite/limonite, cerussite and hydrated manganese oxides. In places smithsonite is accompanied by cadmium sulphides and by very small amounts of putitatively supergene barite.

Most of the smithsonite in the deposit occurs in aggregates of roundish anhedral grains 20-80μ in size. A small proportion takes the form of tiny rhombohedral and scalenohedral crystals up to about 1mm. in size. The euhedral variety is generally found lining voids in cavernous aggregates of smithsonite ("dry bone") formed by replacement of limestone, or as clusters on bedding planes and fractures in partially weathered limestone.

The mineral is usually colourless or a pale to medium shade of brown. It also occurs in small quantities in leaf green, pale green, pale blue and pale yellow varieties (Plate 7.8). The bright yellow "turkey fat" variety of smithsonite, which Schaller and Fairchild (1938) have shown to be coloured by inclusions of cadmium sulphide, has not been found at Tynagh.

Qualitative analyses of pale brown and leaf green smithsonite are given in Table 7.5. The main colouring agent in the former is probably admixed limonite, though some of the contained iron may be in the lattice of the smithsonite. The leaf-green smithsonite is evidently the cuprian variety of the mineral, of which copper in substitution for zinc may constitute up to at least 6% (Dana,1951). The x-ray diffraction pattern of the Tynagh material does not indicate that it is inhomogeneous, or that its unit cell dimensions differ markedly from those of pure smithsonite.

All of the other elements detected in Tynagh smithsonite (Co, Mn,Ca,Cd and Pb) may be partly or wholly present as lattice constituents. Smithsonite is isostructural with the carbonates of Ca and Mg, Cd, and of divalent Fe, Mn and Co, and it probably

Plate 7.8 - Cuprian smithsonite. x1.5.

forms limited solid solution series with all of them. Additionally or alternatively, calcium and lead may be present respectively as included calcite and cerussite, manganese and cobalt as included oxides, and cadmium as included sulphide. Otavaite, $CdCO_3$, which has similar physical properties to smithsonite, has not been recognised at Tynagh.

D. Hemimorphite, $Zn_4Si_2O_7(OH)_2.H_2O$

Small amounts of hemimorphite as colourless tabular crystals up to 1 mm. in length occurs intergrown with aurichalcite in the NE corner of the residual deposit (see below). Here and elsewhere it may also occur as an intimate admixture with allophane (q.v.).

X-ray diffraction traces of zinc oxide concentrates sometimes have small peaks assignable to hemimorphite (d-spacings 3.10Å and 6.70Å), but the mineral has not been firmly identified in the material concerned by optical means. Hemimorphite may be fairly widespread as a minor associate of smithsonite.

E. Aurichalcite, $(Zn,Cu)_5(CO_3)_2(OH)_6$

Aurichalcite has been found only in the NW corner of the residual deposit, where it is a rare constituent of oxides formed by the weathering of limestones containing sphalerite and primary copper minerals. It occurs as radiating and unordered aggregates of elongated pale blue platy crystals up to 1 mm. in length. In intimate intergrowths with hemimorphite, it forms crude pseudomorphs of crinoid stem fragments and other calcite bioclasts, and occurs as streaks and lenses in the surrounding residuum.

The mineral was identified by chemical means and from its x-ray powder pattern, which agrees fairly well with that of

A.S.T.M. standard aurichalcite from Franklin Furnace, New Jersey (Table 7.11). The zinc:copper ratio of the latter is given as 2.65:1. Semi-quantitative microchemical tests based on a technique described by Millman (1960) indicated that a specimen of the Tynagh material also contained more zinc than copper, perhaps in the ratio 6:4. Zinc and copper substitute mutually in the species over an indeterminate range (Dana, 1951).

Table 7.11 X-ray powder data for aurichalcite

1. Aurichalcite, $(Zn,Cu)_5(CO_3)_2(OH)_6$ with Zn:Cu = 2.65:1, Franklin Furnance, New Jersey (A.S.T.M. 9-492)
2. Aurichalcite, Tynagh

1		2	
dÅ (measured)	I	dÅ (measured)	I
3.70	100	3.70	vs
3.24	15	3.22	w
2.89	10	2.88	w
2.71	50	2.73	s
2.61	100	2.61	s
2.28	10	2.30	vwb
2.14	10	2.14	vw
1.939	10	1.939	vw
1.827	25	1.816	vw
1.600	25	1.591	w
1.549	20	1.547	w

vs = very strong, s = strong, w = weak, vw = very weak, b = broad

7.3 MINERALOGY OF COPPER

The minerals of copper that have been identified in the residual deposit are, in approximate order of decreasing abundance:

Primary	Secondary
Tennantite-tetrahedrite	Malachite
Chalcopyrite	Azurite
Bournonite	Chalcocite
Enargite	Covellite
Covellite	Digenite
	Cuprite
	Native copper
	Cuprite
	Bornite
	Chalcopyrite
	Aurichalcite
	Tenorite
	Bayldonite
	Chalcanthite

Minor amounts of copper have been reported in analyses of smithsonite, dundasite, allophane, cerussite, mimetite and sphalerite.

A. Tennantite, $(Cu,Zn,Fe,Ag,Hg)_{12}(As,Sb,Bi)_4S_{12-16}$[1] Tetrahedrite.

The most abundant and widespread primary mineral of copper in the residual deposit, as in protore, is a member of the tetrahedrite-tennantite series. Concentrator returns, supported by analyses given in the following text, indicate that the average atomic proportion of

---

[1] Many different formulae have been suggested for the tetrahedrite-tennantite series. The one given here expresses the divergence of opinion that exists as to the ideal atomic proportions of constituent elements and indicates the best-substantiated substitutions.

arsenic to antimony in the mineral is about 1.5:1. Throughout this thesis, therefore, the mineral is usually termed tennantite, the species name of the member of the series in which the atomic content of arsenic exceeds that of antimony.

Tennantite is found in amounts visible in hand specimen mainly in the eastern and southern parts of the residual deposit, where it is sometimes the principal constituent of protore fragments several inches in size. In these, tennantite largely occurs as 10-50μ anhedral grains in complex intergrowths with most of the other primary sulphides, with barite, and with calcite and lesser amounts of other non-opaque minerals. It forms mutual grain boundary intergrowths with enargite and primary chalcopyrite, and mutual replacements of the three minerals are quite commonly seen in polished sections. Similar textures indicate a measure of depositional overlap between galena and tennantite, though the former is usually seen to have replaced the latter in aggregates of the two.

Tennantite, generally unaccompanied by enargite and chalcopyrite, is a widespread minor constituent of copper-poor primary mineralisation, in which it typically occurs in close association with galena. Its usual occurrence in mineralisation of this type is as replacement relics marginal to galena, and as roundish inclusions in the latter.

Electron probe spot analyses of two samples of residual tennantite showed the mineral to be a zincian variety with the following approximate compositions (which correspond fairly closely to the formula $(Cu,Ag)_{10}(Zn,Fe)_2(As,Sb)_4S_{13}$ suggested by Pauling and Neumann (1934)):

	Cu%	Ag%	Zn%	Fe%	As%	Sb%	S%
Sample 1	42.0	<0.5	6.0	2.0	12.5	11.0	27.0
Sample 2	40.0	<0.5	8.5	0.5	12.0	13.0	(28.0)

Major elements ± 1%

Zinc at concentrations of about 5-9% by weight was found by semiquantitative electron probe spot analysis of four other specimens of tennantite (two residual, two protore). The high zinc content of the mineral may partly account for its deep cherry-red streak and for the blood-red internal reflections that are commonly seen in polished section in oil, occasionally in air. According to Dana (1944), the former is a characteristic of arsenic-rich, iron-poor tennantite.

The near-impossibility of obtaining monomineralic material discouraged quantitative spectrographic analysis of tennantite, but qualitative investigation of three samples with minor admixed contaminants showed that all contained silver in amounts probably not exceeding 5,000 ppm (Table 7.12). Other elements detected in all three samples included, in decreasing order of estimated average abundance, lead, zinc, barium, iron, cobalt, cadmium and nickel. That mercury was not reported may be due to the fact that low concentrations of this element (less than about 1%) are hard to detect in iron-bearing bases by spectrography in the wavelength range investigated (2,700-4,700Å).

How many of the elements detected spectrographically were wholly present in admixed minerals is problematical. It is generally agreed that tetrahedrite-tennantite can accomodate substantial amounts of iron, zinc, mercury and silver as lattice constituents, but the upper limits of their diadochic substitution in members of the series under varying conditions of temperature and pressure have yet to be established. Maxima reported by Springer (in press) for natural materials included 11% Ag and 9.6% Hg in Sb-rich tetrahedrites, 8.5% Zn and 7.0% Fe in As-rich tennantites. Springer's analyses, and others quoted by Dana (1944), suggest that As-rich members of the series are inherently less capable of incorporating available silver and mercury than Sb-rich members.

Table 7.12 Qualitative spectrographic analyses of Tynagh zincian tennantite

Element	Estimated abundance, ppm		
	1	2	3
Ag	1000 - 5000	100 - 1000	500 - 5000
Cd	500 - 5000	500 - 5000	500 - 5000
Co	100 - 1000	1000 - 10000	1000 - 100000
Ni	100 - 1000	<100	100 - 500
Hg	ND	ND	ND
Fe	Present	Present	Present
Zn	Major	Major	Major
Sb	Major	Major	Major
As	Major	Major	ND

Analyst: J.McM.Moore

ND - Not detected Major - More than 1%

Major amounts of Ba and Pb, and trace amounts of Mn and Mo, were detected in two or more samples.

Sample locations

1. Protore, 75W 50N, elevation 5098
2. Residuum, open pit, 5180E bench
3. Residuum, open pit, 5120E bench

Lead, nickel and cobalt are quite commonly reported in analyses of tetrahedrite-tennantite (Dana, 1944), but it is uncertain whether they are ever present as lattice constituents. They were not detected in any of 20 specimens from many different localities which Springer (in press) analysed by the electron probe method. Barium and cadmian varieties of the mineral are unknown.

There can be little doubt that lead and barium reported in Tynagh tennantites were contained in galena and barite respectively. Nickel, cobalt and cadmium were probably present in included minerals such as siegenite, pyrite and sphalerite, but it is possible that all three were also present as lattice constituents of tennantite.

Although one of the samples analysed spectrographically was arsenic-deficient and hence tetrahedrite, reflected light studies of material from widespread sources indicate that tennantite is far more common at Tynagh. The sulphosalt generally has a distinct green tint in polished section that is said by Uytenbogaardt (1951) to be characteristic of arsenian members of the series, while reflectivity measurements on ten specimens in yellow light were all closer to those given by Millman and Gray (1962) for tennantite than for tetrahedrite:

	Reflectivity %
Tynagh tennantite, range of 40 measurements on six specimens (λ= 589nm)	27.9$\pm$1.0 to 29.6$\pm$1.0
Tennantite (λ = 575nm) (Millman and Gray, 1962)	29.0
Tetrahedrite (λ = 575nm) (Millman and Gray, 1962)	33.7

Although it seems that Tynagh tennantite is usually rich in zinc, its minor and trace element composition may vary considerably from one part of the deposit to another. Some indication of this is that substantial variations occur in the Cu:Ag ratio of lead-deficient primary mineralisation containing tennantite as the main copper mineral. From a scientific and an economic standpoint these variations would be worth investigating further. There is no evidence that they have a measurable effect on the reflected light optics of the mineral.

B. Enargite, Cu_3AsS_3

Enargite is a minor constituent of copper-rich primary mineralisation in eastern parts of the residual deposit and of some copper-rich protore. It mainly occurs in fine- to medium-grained anhedral aggregates with tennantite, with which it has a mutual replacement relationship suggestive of penecontemporaneous deposition. It has also been observed in a simplectic intergrowth with bournonite apparently formed by replacement of tennantite (Plate 4.16). Enargite was identified on the basis of its optical properties in polished section and the x-ray diffraction pattern of selected grains.

Possible substitutions in enargite include antimony for arsenic over an indeterminate range towards stibioenargite, $Cu_3(As,Sb)S_4$, and iron and zinc in small amounts for copper. Silver is rarely present in more than minor trace amounts: Thomson (1960), for instance, found only 150-500 ppm of silver in 11 of 12 enargites from the Yauricocha district of Peru, where deposition of the mineral overlapped that of argentian tennantite. No antimony, silver or other non-essential elements were detected in one specimen of Tynagh enargite by electron probe microscanning.

C. Bournonite, $PbCuSbS_3$

See section 7.1.B.

D. Chalcopyrite, $CuFeS_2$

After tennantite, chalcopyrite is the most abundant primary mineral of copper at Tynagh. In the residual deposit, as in protore, it is a common, usually subordinate, associate of tennantite and enargite in zones of copper-rich primary mineralisation, and hence is concentrated in the south-eastern part of the deposit. Unlike tennantite, it is rarely found in copper-poor or zinc-rich residual sulphide ores.

Chalcopyrite generally occurs in complex granular intergrowths with tennantite, and sometimes enargite, as fine to coarse anhedral grains that often show lamellar twinning in polished section. It usually replaces tennantite and is replaced by galena, but chalcopyrite-tennantite mutual replacement textures are not uncommon, and mutual grain boundary intergrowths of the three minerals are occasionally seen. Except for grains that are presumed to be basal sections, the mineral displays weak to moderate reflection anistropy that demonstrates its tetragonal symmetry. The high-temperature cubic form of chalcopyrite, and cubanite, $CuFe_2S_3$, with which it forms a complete solid solution above about 547°C (Yund and Kellerud, 1966), have not been observed at Tynagh.

The minor and trace element composition of Tynagh chalcopyrite has not been investigated. Major substitution in chalcopyrite is not reported by Dana (1944), though the tetragonal $CuFeS_2$ polymorph (a_o = 5.25Å, c_o = 10.32Å) is isostructural with stannite, $CuFeSnS_4$, and is closely related and similar in structure to sphalerite (a_o = 5.41Å). Limited mutual solubility exists between sphalerite and the cubic $CuFeS_2$ polymorph (a_o = 5.26Å), which is stable in the Cu-Fe-S system above about 547°C.

Although the Ag:Cu ratio of chalcopyrite-rich mineralisation at Tynagh is typically lower than that of mineralisation rich in tennantite, indicating relative concentration of silver in the latter mineral, chalcopyrite may be a minor host of silver in the deposit. Tetragonal chalcopyrite is isostructural with $AgFeS_2$ (which apparently does not occur in nature), and trace element analyses of chalcopyrite given by Fleischer (1955) show that the mineral often contains trace amounts of silver.

(ii) Supergene occurrence

The residual deposit and the weathered rocks surrounding it contain minute quantities of chalcopyrite formed by alteration of other copper sulphides. It typically occurs in bornite (which is probably itself a supergene alteration product of primary chalcopyrite) as microscopic spindle-shaped and flame-like areas oriented in what are thought to be the crystallographic directions of original, primary chalcopyrite (Plate 7.9). Less commonly it occurs as even smaller spindle-shaped areas in binary copper sulphides formed by supergene alteration of the margins of chalcopyrite grains. Textures in supergene copper sulphides and their possible origin are discussed further in Chapter 8.

E. Bornite, Cu_5FeS_4

Bornite has not been observed in unaltered protore either by the writer or by Schultz (1968). It is, however, a common associate of demonstrably supergene copper sulphides in the residual deposit and its wallrocks, and may therefore be supergene in all its occurrences at Tynagh.

The usual occurrence of bornite is as patchy replacements of primary chalcopyrite, and as medium-grained anhedral aggregates that are thought to be pseudomorphous after chalcopyrite. As described later, incipient supergene alteration of chalcopyrite is manifest in polished section by a mottled appearance and a pinkish cast that seems to be due to the presence of numerous microscopic areas of bornite. Less commonly, bornite forms a narrow alteration selvage on grains of chalcopyrite that have been indirectly replaced by binary copper sulphide. One instance of bornite replacing an alteration rim of chalcocite or digenite on chalcopyrite has been seen.

Plate 7.9 - Flame-like replacements of supergene bornite (purple) by supergene chalcopyrite (yellow). The bornite has also suffered alteration to covellite (blue). Polished section.

Idaite, Cu_5FeS_6, which occurs intergrown with supergene chalcopyrite as a weathering product of bornite at localities in S-W Africa and Chile (Frenzel, 1959; Clark et al, 1967; Sillitoe, pers. comm.), has not been recognised at Tynagh.

F. Covellite, CuS. Digenite, $Cu_{1.76}S$. Chalcocite, Cu_2S

The three common binary sulphides of copper are widespread in small amounts in the residual deposit and the immediately surrounding rocks. None is listed as a constituent of protore by Schultz (1968), but disseminated euhedra of covellite up to 10μ across and closely associated with bournonite, enargite and pyrite were found by the writer in a veinlet of anhedral calcite walling the eastern end of the residual deposit on the 5180 bench. With this one exception they seem to be entirely supergene in origin at Tynagh.

Various aspects of the occurrence of supergene copper sulphides in the residual deposit are dealt with in Chapter 8. In summary, the three species considered here occur for the most part as replacements of chalcopyrite, galena, sphalerite, tennantite and each other. They have also been found, rarely, as replacements of pyrite, arsenopyrite and siegenite. Their paragenetic relationships with each other often vary within the area of a polished section.

It has not been possible to determine quantitatively which is the most abundant of the three in the deposit as a whole or at a particular level. Uncertainty about their relative abundance is due to the fact that in the fine-grained mixtures with other secondary copper sulphides that are usual at Tynagh, digenite and chalcocite are hard to tell apart in polished section. However, some chalcocite occurs in grains large enough to show the optical anisotry of the low-temperature form of the mineral, and fairly coarse-grained digenite is sometimes found, usually as replacement rims on primary chalcopyrite. Overall, digenite is probably the least abundant of the three sulphides.

Visual identifications of the three sulphides have been confirmed by x-ray powder photography of selected material. This shows that the chalcocite is the orthorhombic variety stable in the Cu-Fe-S system below 103°C. Covellite and low digenite are stable in the same system below about 507°C and 73°C respectively (Yund and Kullerud, 1966). Roseboom (1966) has shown that the copper content of digenite stable at 25°C is somewhat variable ($Cu_{1.765}S$ to $Cu_{1.79}S$), which may partly account for variation in the colour of Tynagh digenite from blue-grey to battleship grey. Above 25°C the copper content of low digenite increases with temperature to $Cu_{1.84}S$ at the high digenite inversion point.

Djurleite, $Cu_{1.96}S$, which is stable below about 90°C with chalcocite and digenite and may form a metastable assemblage at low temperature with covellite (Roseboom, 1966), was not observed. Nor was "blaubleibender" covellite, which has the stoichiometric composition $Cu_{1.09}S$ but may vary in composition up to $Cu_{1.45}S$ (Frenzel, 1961; Yund and Kullerud, 1966). Supergene formation of djurleite and "blaubleibender" covellite has been reported in several parts of the world, for instance by Wurzburger (1967) in the Timna copper deposit in Israel, and by Clark et al (1967) in the Copiapo region of Chile. In view of the very close similarity in their reflected light properties to those of, respectively, chalcocite and basal sections of normal covellite, there is a possibility that they are very minor associates of the three identified binary copper sulphides at Tynagh.

Considerable substitution of silver for copper is possible in chalcocite formed at high temperatures (Schwartz, 1935), but there seems to be no record of supergene formation of binary copper sulphides containing more than trace amounts of substitutional silver. No silver (<5,000 ppm) was detected in a specimen of Tynagh chalcocite by electron probe microscanning.

G. Malachite, $Cu_2(CO_3)(OH)_2$. Azurite, $Cu_3(CO_3)_2(OH)_2$

Malachite and azurite, the most abundant secondary minerals of copper at Tynagh, occur together in quantity in oxide ores in the eastern part of the deposit. They are widely distributed in small amounts in rocks surrounding the deposit, which partly owes its discovery to widespread glacial dispersion of sandstone blocks containing these minerals from the Tynagh Devonian inlier. Malachite is the commoner of the two, but in some small bodies of copper carbonate-cemented barite breccia in the NE corner of the residual deposit in upper benches it is subordinate to azurite.

Malachite usually occurs as botryoidal and spherulitic aggregates of radiating fibrous crystals, as microgranular encrustations, and in compact and powdery forms (Plates 7.4, 7.5). Rosettes of tiny acicular malachite crystals occur on joints and other surfaces in weathered rocks.

The normal occurrence of azurite is as encrusting groups of small tabular to equant crystals of complex morphology, and as open-textured crystalline and granular aggregates (Plate 7.10). It also occurs in compact granular and powdery forms.

The commonest associates of the two carbonates are cerussite and hydrated oxides of iron and manganese. Other common associates are mimetite, beudantite, native copper and cuprite. Both carbonates are frequently found in small amounts as overgrowths on mimetite and cerussite, but rarely as encrustations of native copper or cuprite. A green variety of beudantite (q.v.) seems to be a mixture of the latter with cryptogranular malachite. Azurite, in common withcerussite, more commonly veins and encrusts malachite than the reverse (Plate 7.11).

A qualitative analysis of Tynagh malachite (Table 7.5) showed numerous non-essential elements to be present. Most were probably

Plate 7.10 - Malachite and subordinate azurite cementing brecciated barite. The specimens are both about 2in. in size.

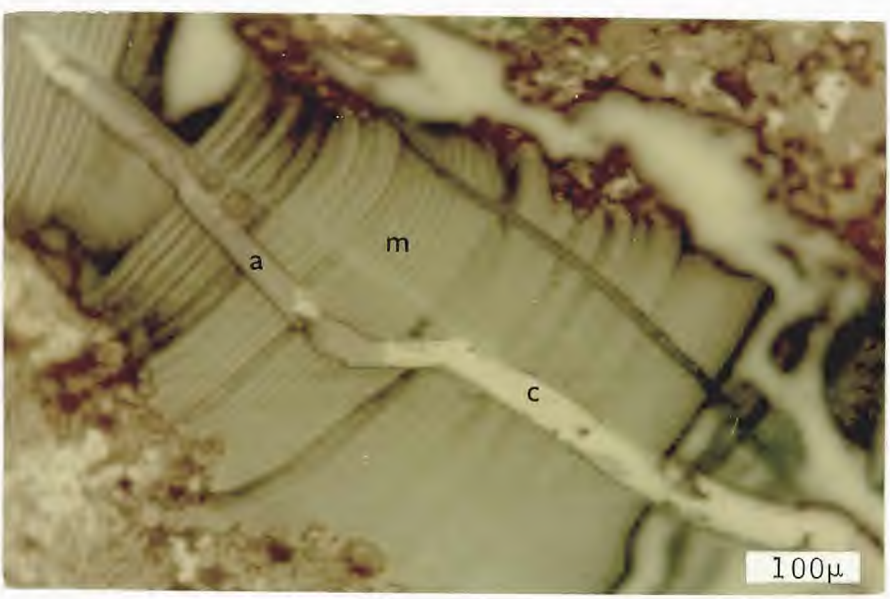


Plate 7.11 - Colloform-banded malachite (m) cut by segmented veinlet of cerussite (c) and azurite (a). Polished section.

contained in admixed minerals such as cerussite and limonite, for according to Dana (1951), the composition of natural malachite (and azurite) generally deviates very little from the theoretical. Some zinc may have been present in diadochic substitution for copper, since malachite may be isostructural with one of several basic carbonates of copper and zinc of uncertain structure and variable composition, viz. rosasite, cuprozincite and paraurichalcite (all apparently $(Cu,Zn)_2$ (CO_3) $(OH)_2$). Substitution of trace amounts of silver for copper has been reported in malachite, e.g. at Keno Hill, Alaska (Boyle, 1965), and it will be shown in the next chapter that some of the malachite at Tynagh is probably slightly argentiferous.

H. Native copper, Cu. Cuprite, Cu_2O

Small amounts of native copper and cuprite are widely distributed in oxide ores at the eastern end of the deposit. They typically occur in close association with each other as granular and crystalline growths in voids in rubble, and as disseminations in muddy materials. Native copper is commonly found as small spongy masses and in dendritic and wire-like forms that are sometimes partially pseudomorphed by cuprite. Small roundish inclusions of cuprite in native copper seen in polished section may also be of replacement origin, though textural evidence on this point is inconclusive. Replacement of native copper by cerussite, supergene barite and perhaps by chalcocite has been seen in polished section, and replacement of malachite by cuprite in hand specimen. In some parts of the deposit cuprite is closely associated with native silver (q.v.).

Information about variations in the minor and trace element composition of supergene native copper and cuprite is scarce, and the composition of Tynagh material has not been investigated. Geochemical considerations suggest that the former may contain traces

of silver (atomic radius 1.44Å) in substitution for copper (1.28Å). An arsenian variety of native copper, and natural alloys of copper and arsenic, are known, but are generally of hypogene origin.

I. Tenorite, CuO

X-ray diffraction analysis of a cryptogranular black substance apparently formed by replacement of malachite in one hand specimen showed it to be poorly crystallised tenorite. The same mineral may be a constituent of microscopic black crusts on cerussite crystals from the eastern end of the deposit, which electron probe microscanning showed to contain zonal concentrations of copper.

J. Bayldonite, $(Pb,Cu)_7(AsO_4)_4(OH)_2.2H_2O$

See section 7.1.I.

K. Aurichalcite, $(Zn,Cu)_5(CO_3)_2(OH)_6$

See section 7.2.D.

L. Chalcanthite, $CuSO_4.5H_2O$

Efflorescences of pale blue chalcanthite as small contorted fibrous crystals form on mining faces in pyritic residuum in copper-rich parts of the deposit. Chalcanthite formed before mining began has not been found.

7.4 MINERALOGY OF SILVER

The main primary hosts of silver in the residual deposit, and its main hosts in protore, are galena and, subordinately, tennantite. Silver is almost certainly present in tennantite as a lattice

constituent, but it has not been established in what form or forms silver is associated with galena. A small but economically significant proportion of the silver in primary mineralisation is associated with sphalerite, of which it may be a lattice constituent. It is possible that other identified primary minerals contain silver in trace amounts.

The only supergene host of silver that has been positively identified is the native metal, which sometimes occurs in a highly mercurian variety. Traces of silver have been detected spectrographically in cerussite, and it is possible that other oxidate minerals, notably malachite and beudantite, contain silver in trace amounts.

The present study did not confirm the presence in the deposit of the seven argentiferous minerals reported by various metallurgical consultants, namely pyrargyrite, proustite, polybasite, pearceite, bromyrite, argentojarosite, argentopyrite and argentite (presumably acanthite). Circumstantial evidence presented in Chapter 8 suggests, however, that small amounts of one or more of the last three may be present in parts of the residual body.

A. Native silver, α-(Ag,Hg)

Minute quantities of native silver were found during the present study in the heavily oxidised residuum of lead-copper protore. None was found in zinc-rich residuum, residuum classified as sulphide ore, or in Calp mud.

To judge from its few observed occurrences, the usual crystallisation habit of native silver at Tynagh is as small irregular, sometimes spongy, granules up to $\frac{1}{5}$mm. but generally less than 50μ in size. The mineral occurs in free growth forms deposited on the walls of solution voids in oxidised protore fragments, as discrete

granules in oxide mud matrices, and as granular intergrowths with supergene replacement products of primary sulphides (Plate 7.12). Its usual supergene associates are cuprite, anglesite and beudantite. In one specimen it was found with anglesite encrusting a pebble of detrital tennantite.

Tiny hexagonal plates of native silver, the largest about 100μ across and 3μ thick, were found encrusting a protore relic in oxide rubble. An electron probe microanalysis showed the silver to be alloyed with up to 30% mercury. Compositional zoning was detected, the approximate silver content of the alloy ranging from 70% to 80%. No reflection anisotropy was observed in polished sections through randomly oriented crystals, implying cubic symmetry. The x-ray diffraction pattern of the crystals agreed well with that of cubic mercurian silver (a_o=4.11Å) containing 80% Ag from British Columbia (Table 7.13). Traces of mercury were also detected in anhedral granules of silver from Tynagh in the course of this study.

Murphy (1931) found in a study of artificial silver-mercury alloys that the maximum mercury content of the cubic α-alloy (a_o=4.07-4.17Å) at room temperature is about 50%, and Dana (1944) reports mercury contents of up to 30.76% in the natural alloy corresponding to Murphy's α-phase. Moschellandsbergite, Ag_2Hg_3, which contains about 73% mercury and is the natural equivalent of Murphy's γ-alloy (a_o=10Å), has not been found at Tynagh. No natural occurrences of his hexagonal β-alloy, which contains about 60% mercury, have been reported.

The main primary source of the mercury alloyed with native silver at Tynagh was probably tennantite (q.v.). Another possible source was sphalerite. Compared with its hypogene equivalent, supergene mercurian silver is allegedly rare (Newhouse,1933).

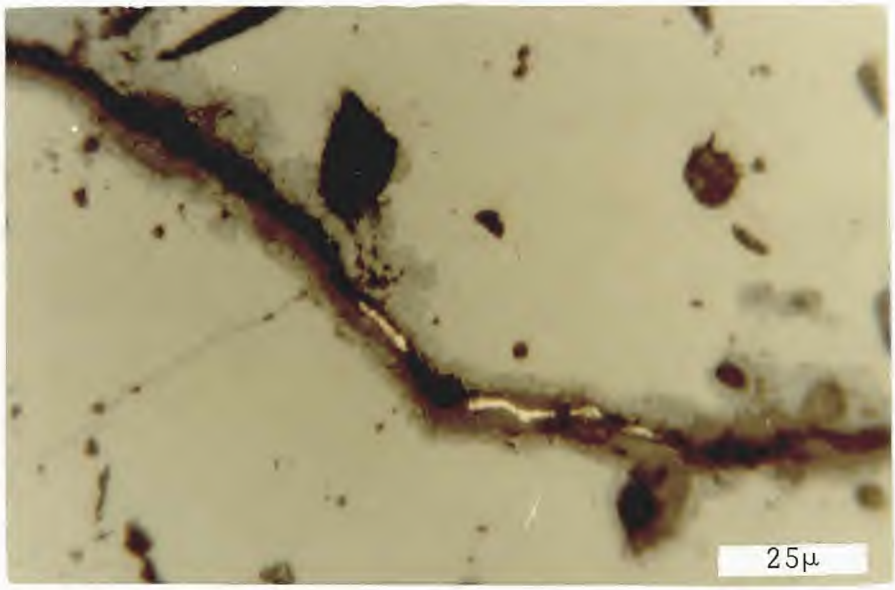


Plate 7.12 - Native silver (white) and anglesite (dark grey) in a solution-enlarged crack in tennantite. The bluish alteration product of tennantite is mainly chalcocite. Polished section.

Table 7.13 X-ray powder data for mercurian silver

1. Mercurian silver containing about 80% Ag, Omineca district, British Columbia (Berry and Thompson,1962).
2. Mercurian silver, Tynagh.

1		2	
dÅ (measured)	I	dÅ (measured)	I
2.39	10	2.39	vs
2.07	8	2.07	s
1.46	6	1.46	s
1.24	7	1.25	s
1.186	2	1.193	w
1.027	½		
0.942	3	0.946	w
0.919	3	0.924	w
0.839	3	0.843	w
0.791	3	0.792	w

vs = very strong, s = strong, w = weak

Copper, arsenic and antimony, all of which are capable of limited solid solution in native silver, were not detected in specimens of Tynagh silver investigated by electron probe techniques.

7.5 PRINCIPAL GANGUE MINERALS

A. Barite $BaSO_4$

(i) Primary occurrence

Barite is the main epigenetic gangue mineral in all ore types. Gossanised materials in the central part of the residual deposit are composed largely of barite - an analysis of gossan cored in one grade control hole showed it to contain 82% $BaSO_4$ over 17 ft - and the estimated barite content of high-grade residual sulphide ores is widely 20-30%. At the opposite extreme, large tonnages of Calp mud and zinc oxide ore contain less than 5% $BaSO_4$. Protore below the residual deposit is estimated by Schultz (1968) to have an average barite content of 15%. Locally, barite comprises over 50% by weight of 50-100 ft vertical drillhole sections of protore.

Most of the barite in the residual deposit occurs in aggregates with primary sulphides and their oxidation products that range in size from large boulders to microscopic particles. The mineral rarely occurs alone in lumps more than a couple of inches across.

The usual crystallisation habit of barite is as tabular euhedra up to 2 in in size. These occur as sheaf-like and fan-like groups, as unordered masses, and as scattered individuals in sulphide matrices (Plate 4.7). Crystalline barite tends to be euhedral against pyrite and to have irregular interfaces with lead and copper sulphides. The size of barite crystals and their geometry in aggregates is to some extent indicative of whether the mineral

formed by replacement or as a cavity filling, replacement barite tending to occur as a network of small crystals, and cavity-lining barite as large crystals in radiating bundles. Granular barite formed by replacement and as a cavity-filling material occurs in subordinate amounts.

In thin section barite is colourless (except when impregnated by limonite) and often has spectacularly undulose extinction. It is typically littered with tiny inclusions of non-opaque minerals (e.g. calcite, albite, orthoclase and quartz), sulphides (especially pyrite and sphalerite) and other substances that have not been identified. Minute (less than 2μ) vacuoles that may contain fluids are sometimes seen at high magnifications.

Analyses of barite test concentrates made from protore and oxidised residuum (Table 7.14) indicate the presence of chloride inclusions in barite, and suggest that the mineral generally contains small amounts of strontium in substitution for barium. Other contaminants reported in the concentrates, with the possible exceptions of calcium, lead and fluorine, were probably present by admixture. How the fluorine occurred is not known: the possibility that fluorite (CaF_2) may be a very minor paragenetic associate of barite has not been confirmed optically.

Barite theoretically forms complete isomorphous series with anglesite, $PbSO_4$, and celestite, $SrSO_4$, but plumbian varieties of barite are rare (Dana, 1951) and analyses show that barite normally contains only between 0.4 and 1.5% Sr (Hanor, 1968). Strontium substitution in barite tends to lower the refractive indices of the mineral, lead substitution to increase them. The refractive index maxima of specimens of Tynagh barite have not been found to differ measurably from the value for pure material (1.648, compared with 1.631 for celestite, 1.894 for anglesite).

Table 7.14 Analyses of barite concentrates

	Sulphide Ore %	Oxide Ore %
$BaSO_4$	94.90	92.95
$SrSO_4$	1.10	2.75
SiO_2	1.68	2.30
Pb	0.43	0.65
Zn	0.76	0.18
Cu	0.01	0.10
Fe	0.59	0.70
Ca	0.16	0.04
Al_2O_3	0.09	-
F	0.01	0.01
Cl	0.14	0.04
Loss on ignition	-	0.30
Total	99.87	99.92

Analyses by A.H. Knight Ltd., Liverpool
(Pb, Zn, Cu by I.B.M. Ltd)

Geochemical considerations suggest that if both elements are freely available, diadochic substitution of Sr^{+2} (ionic radius 1.27Å) for Ba^{+2} (1.43Å) will be temperature-dependent, and that the Sr:Ba ratio of barite will increase sympathetically with its depositional temperature. However, analytical evidence that tmperature is sometimes the main determinant of the strontium content of barite in mineral deposits has yet to be produced. Gough (1962) concluded that the extent of strontium substitution in barite at the Greenside Lead Mine, Derbyshire, was largely dependent on the composition of the depositing solution.

Analyses of barite concentrates made from Tynagh protore and residual materials support the evidence of refractive index measurements and x-ray powder photographs that Tynagh barite contains little substitutional strontium or lead. The strontium content of the mineral is likely to be locally variable. Gough (1962) found that that of barite in outcrop at Greenside ranged from 0.30 to 1.63%, compared with 0.24 to 1.82% Sr for the mine as a whole.

(ii) Supergene occurrence

Very small amounts of supergene barite have been identified in the residual deposit. The basis of recognition of the supergene variety of the mineral is its manner of occurrence. Tapering acicular prisms up to 1 mm long have been found lining a small void in Calp mud (Plate 7.13), and thin tabular crystals up to 3 mm in maximum dimensions as individuals and groups on partings in the residuum of argillaceous limestones in the NE quarter of the deposit, and as overgrowths on lead and copper carbonates (Plate 7.14) in oxide ores of these metals at the eastern end of the deposit.

X-ray powder photographs of supergene barite show that the structure of the mineral has not been perceptably modified by isomorphous substitution of strontium or lead for barium.

Plate 7.13a - Supergene barite as 1-2mm. acicular crystals lining a void in Calp mud.

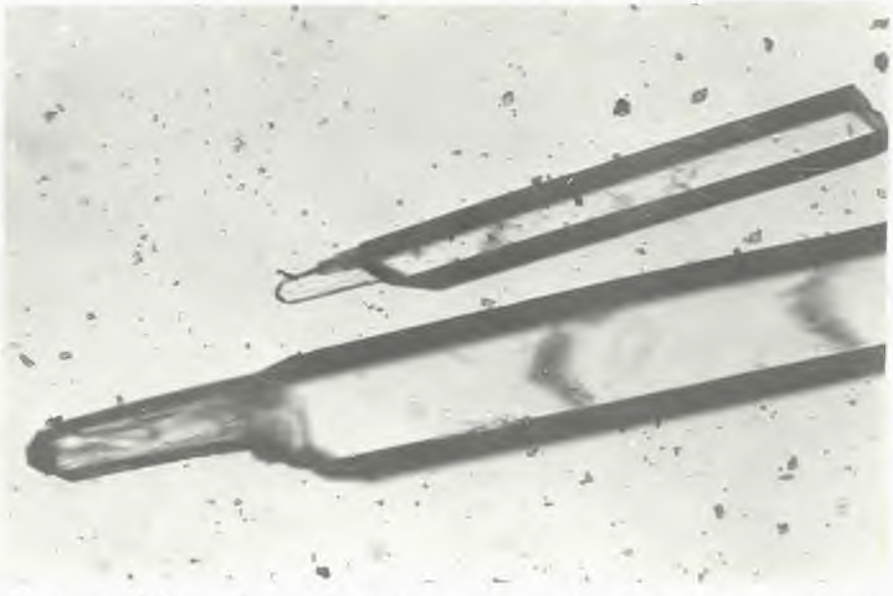


Plate 7.13b - Detail of the same crystals. Transmitted light, in air. x10.

Plate 7.14 - Supergene barite as 2-4mm. tabular crystals associated with azurite and limonite.

B. Quartz, α-SiO_2

(i) Primary occurrence

Quartz in various crystallisation habits is a constituent of all types of residuum. Its abundance ranges from over 60% in Calp mud to less than 5% in high-grade residual sulphide ores and in the central gossan.

The commonest forms of quartz in the residual deposit are: (a) silt-sized and sand-sized anhedral grains; (b) microgranular and cryptogranular aggregates (chert) as small nodules and fragments of thin bands and laminae, as the main constituent of siliceous sponge spicules, and as pseudomorphic replacments of various faunal and microfloral remains; (c) doubly-terminated authigenic microeuhedra up to about 1 mm in length. A small proportion of each occurs in aggregates with residual primary sulphides and barite.

Less common are complete and fragmental crystals of clear and milky quartz up to 5 cm in length that are virtually restricted to Calp mud and appear to have formed in fissures in Calp above the present erosion level, and fairly coarse-grained aggregates of anhedral quartz that constitute Devonian sandstone fragments in the residuum. Quartz in a microscopic fibrous habit has been observed filling a small post-mineralisation fracture in a fragment of residual primary mineralisation.

Fluid inclusions of unknown composition are occasionally seen in the relatively large euhedra of quartz referred to above. They may also be present in some of the chert that occurs at Tynagh, the mean refractive index of which is lower than that of Canada Balsam (1.540, compared with $\omega = 1.544$, $\varepsilon = 1.553$ for macrocrystalline quartz). Smith (1960) has suggested that the anomalous optics of the cryptogranular variety of quartz termed chalcedony that is a common constituent of chert is due to the presence of sub-microscopic fluid-filled cavities.

(ii) Supergene occurrence.

Supergene quartz may be present in the residual deposit in small amounts, but it has not been positively identified. Possibly supergene quartz was found as clear prismatic crystals up to 1 cm long in a small cavity in massive primary pyrite near the North Tynagh Fault, 5200 bench. The crystals were overgrown by cerussite and supergene barite. It was not possible to confirm their supergene origin, or that of a fractured overgrowth of chalcedonic silica on a single lump of residual galena found elsewhere.

C. Clay Minerals

Clay minerals are a constituent of all the residual materials, and a major constituent of some residual sulphide ores, Calp mud and in situ oxides formed by weathering of argillaceous Waulsortian limestones and Lower Muddy Limestone. They occur in local concentration as beds and lenses formed by sedimentation of residuum, and as the matrix of sulphide-barite rubble adjacent to the North Tynagh Fault.

The clay mineralogy of the deposit was investigated by x-ray diffraction analysis of specimens with randomly oriented constituents. The main aim of the investigation was to establish which clay mineral groups are represented in the deposit. Differential thermal analysis and other techniques necessary for precise identification of some clay mineral species were not used.

The most abundant and widespread clay mineral has a basal spacing of about 9Å, and distinct reflections corresponding to d-spacings of about 4.47Å, 3.33Å, 2.57Å and 1.50Å. It is evidently a hydrous mica, probably the dioctohedral variety of illite, for which Deer et al (1962) give the formula $K_yAl_4(Si_{8-y}, Al_y)O_{20}(OH)_4$,

where $y<2$. The predominant clay mineral in Lower Carboniferous rocks surrounding the deposit has the same x-ray diffraction pattern. Most of the illite in the residual deposit is probably an unaltered derivative of these rocks.

The next most abundant clay mineral in the deposit has a basal spacing of 7-7.5Å and the x-ray diffraction pattern of a mineral of the kaolinite group, which includes kaolinite itself, $Al_2(Si_2O_5)(OH)_4$, and several other hydrated silicates of aluminium. It is the main clay mineral in the residuum of some shaly phases in Calp (of which it may have been an original constituent), and occurs in supergene concentrations with allophane and a mineral tentatively identified as halloysite (see below) in the residuum of argillaceous limestones.

A common associate of kaolinite is a substance, termed "clay soap" by Blanchard (1968), that occurs as compact angular lumps up to 3 cm in size with conchoidal fracture and often with polished or slickensided surfaces. It is usually pure white, sometimes pale brown, blue or green. The last two tints tend to be lost on drying, suggesting that they are a hydration effect.

Some of this material gives poor x-ray diffraction patterns which show that the constituent mineral has a basal spacing of about 9Å. This is thought to be hydrated halloysite, a semiamorphous clay mineral compositionally related to kaolinite. Macroscopically similar material of which the main constituent has a basal spacing of about 7Å and a diffraction pattern closely resembling that of kaolinite may be its partially dehydrated equivalent, metahalloysite.

A minor associate of illite in some samples of residuum is a clay mineral with a basal spacing of about 15 Å, probably montmorillonite or a related clay mineral. The compositional range of montmorillonite is large and uncertain. Ross and Hendricks (1945) give the formula of the species as $5Al_2O_3.2MgO.24SiO_2 6H_2O(Na_2O,CaO)$, and Deer et al (1962) state that montmorillonite forms a partial solid solution series with illite. A clay mineral with a basal spacing of about 12.5Å found at Tynagh as a patchy replacement of bioclastic limestone relics in the residuum may be an illite-montmorillonite mixed layer silicate or a partly hydrated montmorillonite. The zincian montmorillonoid, sauconite, has not been identified at Tynagh.

To judge from field occurrences, the most abundant supergene clay minerals at Tynagh are of the kaolinite type and probably include kaolinite itself, halloysite and metahalloysite. The weathering conditions that favour the formation of particular clay mineral species are mentioned in Chapter 8.

D. Pyrite and Marcasite, FeS_2

Pyrite, often accompanied by lesser amounts of marcasite, is virtually ubiquitous in the residual deposit and the surrounding rocks. Dark varieties of residuum normally contain between 5% and 15% of pyrite and marcasite, and even the most heavily oxidised materials usually contain a finite amount of one or both. Stratiform concentrations of iron sulphide up to about 5 ft. thick are a widespread feature of Calp mud at the north side of the deposit, and many less extensive concentrations are known from mapping and drilling elsewhere within it. Some have been referred to in previous chapters.

Various aspects of the primary occurrence of the two sulphides have already been mentioned, and it is proposed to deal here mainly with their textural characterics and chemical variations. Their supergene occurrence is discussed in Chapter 8.

The main textural varieties of primary pyrite and marcasite are as follows:

(i) Discrete and aggregated crystals and subhedral to anhedral grains

These constitute a substantial proportion of the primary iron sulphide in the residual deposit, having formed at many stages during the diagenesis and mineralisation of its parent materials. Crystals of pyrite - cubes and pyritohedra with a normal size range of 5-50μ but exceptionally up to 3 mm. in size - are very common, crystals of marcasite comparatively rare (Plates 4.4, 7.15). Pyrite crystals often display growth zoning, and compositional differences between different growth zones that will be described later (Plate 7.17a).

(ii) Groupings of microcrystallites

Most groupings are spherical to sub-spherical in shape and consist of numerous microcrystallites that tend not to be in close contact with each other. They are covered by the term framboid as defined by Rickard (1970).

Framboids of diagenetic origin are concentrated in argillaceous rock types, rare in pure limestones, and apparently not present in Devonian sandstones (Plates 3.1, 7.16). They usually appear to have formed by replacement of non-sulphide rock-forming materials. Their size distribution in a sample of Lower Muddy Limestone was found[1] to be positively skewed unimodal (4.5μ) and their mean diameter about 26μ : 96% were less than 40μ in diameter. No general relationship could be detected between the diameter of framboids and size of their constituent microcrysts. There is

---

[1] This statistical investigation was carried out by D. Rickard, who was then studying the low-temperature formation of iron sulphides at Imperial College.

no observational evidence that these values do not apply to diagenetic framboids at other stratigraphic levels, or that the partial to near-complete ordering of microcrysts observed in 10-20% of the framboids in Lower Muddy Limestone is a stratigraphically restricted feature. Numerous ordering patterns were recorded, but is is presumed that they were based on a limited number of packing arrangements.

In many respects the diagenetic framboids at Tynagh closely resemble framboids that occur in Recent sediments and in mineral deposits and argillaceous rocks of widely differing ages (Deans, 1948; Love and Zimmerman, 1961; Love and Murray, 1963; Love and Amstutz, 1966; Kanehira and Bachinski, 1967).

Commonly associated with diagenetic framboids at Tynagh are irregular groupings of pyrite microcrystallites that can be likened to microscopic clouds of pyrite dust (Plate 7.16). A genetic affinity with the framboidal grouping referred to above is suggested by the fact that they occasionally display partial ordering. Rare microscopic (5μ) groupings of well-ordered diagenetic microcrystallites with rectangular (hexagonal) outlines have been noted in Lower Muddy Limestone. It is beyond the scope of this thesis to discuss the implications of their geometry vis-a-vis the origin of such groupings (including those covered by the term framboid).

The framboidal aggregates that were deposited from solutions responsible for primary ore mineralisation at Tynagh (Plate 4.10) differ from their diagenetic counterparts in that they typically lack internal organisation and appear to have a somewhat different size distribution, with a modal size between 15μ and 25μ. The latter point has not been established with statistical rigour but deserves investigation.

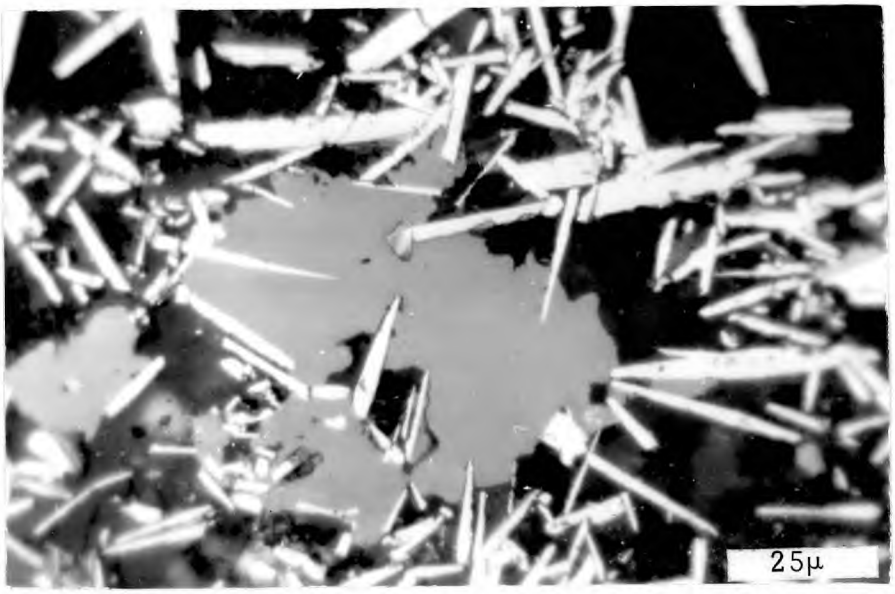


Plate 7.15 - Acicular crystals of marcasite (white) in Calp patchily replaced by sphalerite (medium grey). Polished section.

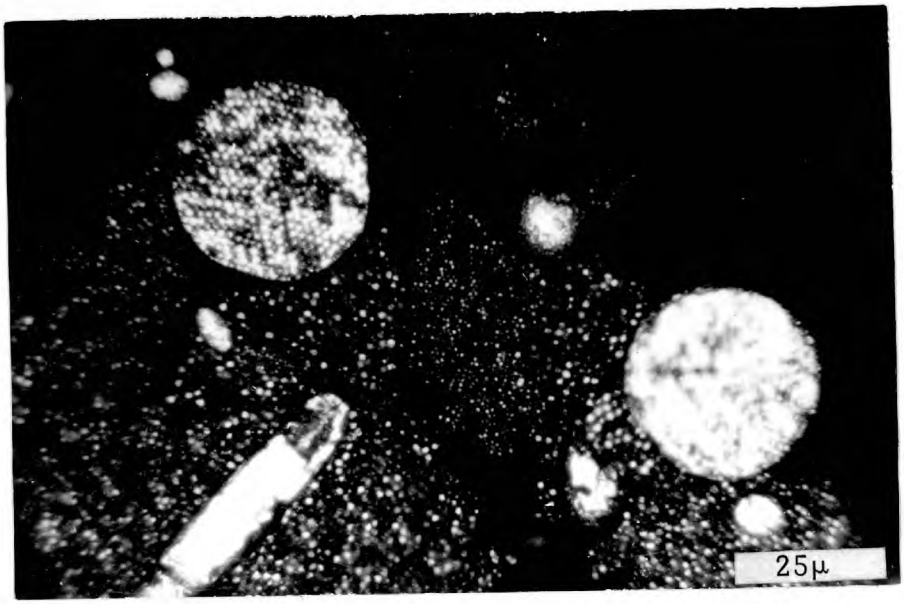
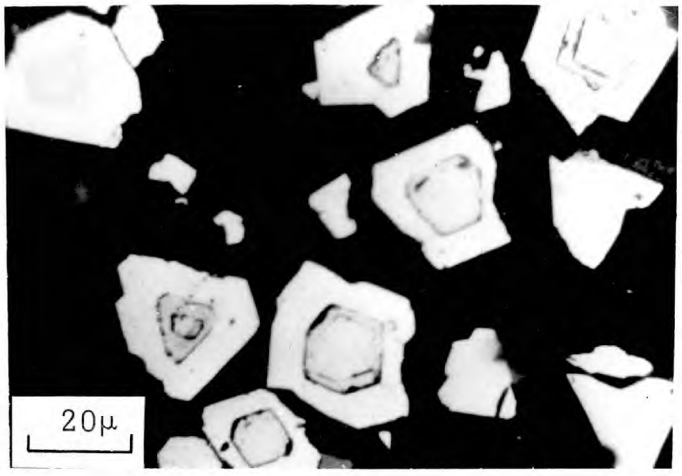
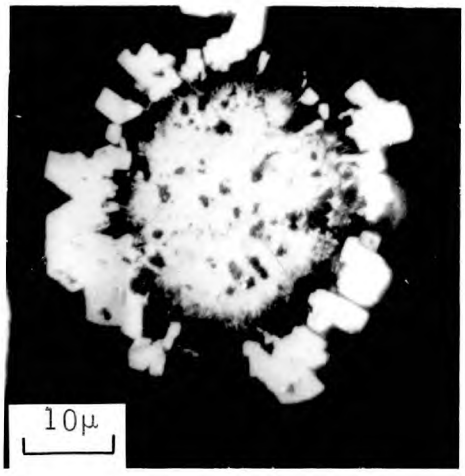


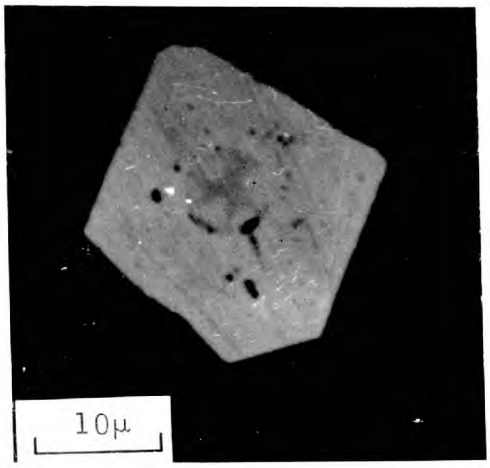
Plate 7.16 - Organised and unorganised pyrite micro-crystallites, including an ordered framboidal aggregate, in a residual Calp fragment. The cigar-shaped pyrite body is probably pseudomorphous after a sponge spicule. Polished section. Oil immersion.



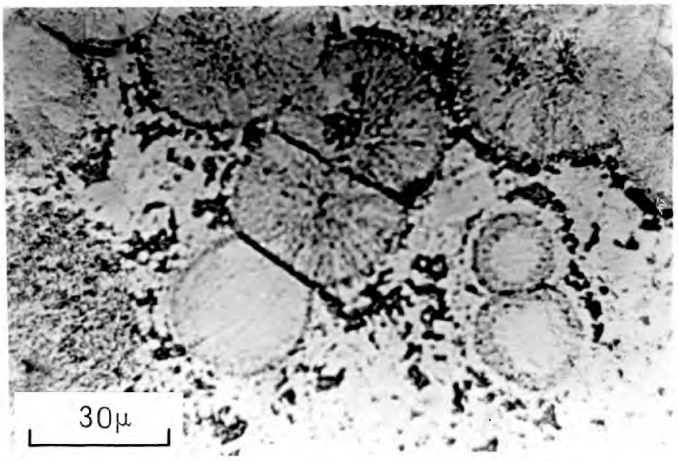
(a)



(b)



(c)



(d)

Plate 7.17 - Forms of diagenetic and epigenetic pyrite

(a) zoned pyrite-nickelian pyrite euhedra

(b) "whiskery" spheroid with euhedral overgrowth

(c) spheroid with Y-shaped area of nickelian pyrite and euhedral overgrowth

(d) pyrite "globules" with interference surfaces.

(iii) Non-framboidal spheroids

Included in this category are:

(a) diagenetic microspheroids up to 50μ in size composed of numerous radiating fibres that protrude into the surrounding sediment, giving the whole a whiskery appearance (Plate 7.17b);

(b) diagenetic microspheroids with about the same size range but lacking marginal protrusions and apparently physisically homogeneous (Plate 7.17c);

(e) hypogene spheroids with a radiating fibrous structure but fairly smooth outlines; doublets, triplets and other groupings with planar interference surfaces occur (Plate 7.17d).

(iv) Botryoidal forms

Aggregates of pyrite and marcasite consisting of numerous concentric bands of fibrous and granular sulphide, often incorporating framboidal aggregates, are one of the commonest constituents of protore (Plates 4.3, 4.5, 4.6, 5.1). Individual bands vary in width from as little as 1μ to about 1mm, usually without regard to their position in a particular aggregate. Band margins are sometimes smooth, sometimes composed of crystal faces. The morphology of the latter indicates that many bands now consisting of pyrite originally consisted of marcasite. Much pyrite that occurs in anhedral to subhedral medium-grained mosaics appears to be a recrystallisation product of concentrically banded aggregates of this type.

The only compositional variation detected visually in Tynagh primary pyrite was the presence of small amounts of nickel in

material of types (i),(iii) and (iv). This was inferred from the slightly pinkish tint and decreased reflectivity of the mineral in polished section, and confirmed by semi-quantitative electron probe microanalysis. About 2% Ni and 0.5% Co were detected in the darker area of the microspheroid shown in Plate 7.17c, compared with less than 200 ppm of either in its more highly reflecting areas. Concentrations of this order are not uncommon in pyrite, which forms limited solid solutions with isostructural vaesite (NiS_2) and cattierite (CoS_2) over a wide range of temperatures. According to Carstens (quoted by Fleischer,1955), pyrite of sedimentary origin generally contains less than 100 ppm Co and less cobalt than nickel, whereas pyrite of hydrothermal origin characteristically contains more cobalt (400-2,400 ppm) than nickel. There is no visual support for this hypothesis at Tynagh, but it has not been tested by measurement. Analyses of two samples of Tynagh hypogene pyrite are given by Schultz (1968) as follows:

	Fe%	S%	As,ppm	Co,ppm	Ni,ppm	Remainder%
1.	45.45	52.38	3,200	30	20	1.85
2.	45.39	50.32	3,200	10	20	3.77

Remainder assumed to represent admixed impurities, mainly barite and calcite.

These analyses suggest that some Tynagh pyrite has a non-stoichiometric composition, which may partly account for the variable resistance of optically identical material to chemical attack by hypogene and supergene solutions. Variations in Fe:S ratio and internal strain due to lattice-contained As are two of several suggested causes of the anomolous reflection anisotropy that pyrite commonly displays, at Tynagh as elsewhere (Deer at al, 1962). The

actual cause of the phenomenon may vary from place to place, or anisotropy may simply be, as Stanton (1957) has suggested, a consequence of the mineral's imperfectly isometric structure.

The trace element composition of Tynagh marcasite and pyrite has not been investigated in detail. Analyses of pyrite from elsewhere often show that it contains many non-essential elements other than cobalt and nickel, notably arsenic, copper, lead, zinc and silver (Fleischer, 1955). As much as 10% Cu has been reported by Frenzel and Ottemann (1967) in pyrite from Fiji, but this is probably a rare exception to the general rule that the last four elements referred to only occur in solid solution in pyrite in very small amounts.

E. Hydrated Iron Oxides

By far the commonest secondary precipitate of iron in the residual deposit and its surrounds is hydrated ferric oxide. X-ray diffraction traces usually show that it is very poorly crystallised or amorphous, while substantial variations in its reflectivity in polished section - estimated to range from about 15% to less than 10% in white light - are probably due partly to variations in its content of adsorbed water. It is best termed limonite, for which the formula $Fe_2O_3.nH_2O$ is usually given. Better crystallised material has the x-ray diffraction characteristics of goethite, $HFeO_2$ [1]. Lepidocrocite, which has the same composition and crystal symmetry as goethite but differs from it in unit cell size, has not been identified at Tynagh.

---

[1] This formula has been adopted in preference to FeO.OH to avoid the implication that the iron is in the ferrous state. Some mineralogists reserve FeO.OH for lepidocrocite, though the structural information conveyed by the formula is incorrect (Bragg, 1937).

Limonite is concentrated in in situ oxides at the margin of the residual deposit, and in the central gossan body (see Chapter 8). The limonite content of these materials widely ranges between 15% and 25% by weight. Residuum of which the dominant colour in field exposures is one of those characteristic of limonite - red, yellow, orange and brown - has been termed "oxide" in this thesis, though it is worth noting that some smithsonite ores are pale grey, and that some gossan owes its yellow colour as much to beudantite (q.v.) as to limonite.

Limonite occurs mainly in a porous cryptogranular form. In heavily oxidised materials it also occurs in botryoidal and microspheroidal habits, as clinkery aggregates and cellular boxworks, and as compact crusts and cements. For the most part it is exotic, in the sense that the iron has been reprecipitated at some indeterminate distance for its primary source, but some that occurs as a pseudomorphic replacement of primary minerals, especially pyrite and chalcopyrite, is clearly indigenous. Much of the limonite in dark Zn oxide ores is of the latter kind.

The composition of Tynagh limonite has not been fully investigated, monomineralic material being almost impossible to isolate for detailed analysis. A qualitative x-ray fluorescence analysis of material consisting largely of limonite indicated the presence of numerous admixed minerals containing Cu, Pb, Zn, Mn, Co and As.

F. Calcite, $CaCO_3$. Dolomite, $Ca(Mg,Fe,Mn)(CO_3)_2$

Very little of the residuum has been completely decalcified by weathering. Dark materials in the centre of the deposit ubiquitously contain minor to trace amounts of non-supergene calcite and dolomite, while towards the margin of the deposit there is in many places a gradational contact between largely decalcified residuum and largely unweathered limestone. Disaggre-

gation of massive dolomite and selective dissolution of calcite in limestones containing small amounts of authigenic dolomite have contributed discrete granules of slightly ferroan dolomite to residuum in the marginal zone.

Of the occurrence of calcite and dolomite in limestone relics within the residuum it need only be said that it is the same as in rocks of the same lithology bounding the deposit. Both minerals also occur in residual primary aggregates with epigenetic sulphides and barite. The typical occurrence of calcite in such aggregates is in coarse-grained intergrowths with barite as an open space filling, and alone as a granular replacement of sulphides and as replacement relics in sulphides and barite. Stain tests show that some of the calcite is iron-bearing. A ferroan variety of dolomite tending towards ankerite in composition is widespread as microscopic euhedra and replacement relics in primary mineralisation.

The residuum apparently contains no supergene calcite or dolomite.

7.6 MINOR GANGUE MINERALS

A. Arsenopyrite, FeAsS

Arsenopyrite is a very minor constituent of residual primary mineralisation, in which it generally occurs as elongated prismatic crystals up to 1 mm in length aggregated with pyrite and marcasite, or as microscopic replacement relics in primary copper minerals. Squat prismatic crystals up to 5 mm in length and often as interpenetrating twins are locally abundant in the residuum of Lower Muddy Limestone in the S.W. quarter of the deposit.

Common substitutions in the species are cobalt for iron and antimony for arsenic, arsenopyrite forming limited or extensive solid solution series with the isostructural minerals glaucodot, (Co,Fe)AsS, and gudmundite, FeSbS. Gudmundite occurs at Silvermines, Co. Tipperary, as a hydrothermal alteration product of tetrahedrite (Rhoden, 1958). The x-ray powder pattern of a specimen of Tynagh arsenopyrite indicated that the mineral was essentially pure, agreeing exactly with that of A.S.T.M. standard arsenopyrite.

B. Siegenite, $(Co,Ni)_3S_4$

Rare, microscopic (up to 30μ) grains of siegenite were found associated with arsenopyrite in two specimens of residual primary mineralisation as corroded relics in tennantite and chalcopyrite. Tentative identification of the mineral on the basis of its reflection isotropy, high reflectivity and slightly pink tint in polished section was confirmed by electron probe microanalysis of a grain, which showed the approximate composition of the mineral to be 47% Ni, 14% Co, trace Fe, 39% S.

Siegenite is the most common member of the Linnaeite Series, in which more or less complete chemical variation exists within the general formula $(Co,Ni)_2(Co,Ni,Fe,Cu)S_4$ (Dana, 1944). Other members of the series - listed by Dana as linnaeite (Co_3S_4), polydymite (Ni_3S_4), violarite (Ni_2FeS_4) and carrollite (Co_2CuS_4) - have not been identified at Tynagh.

C. Realgar, AsS. Orpiment, As_2S_3

The two sulphides of arsenic have been found in small amounts in dark argillaceous residuum containing local concentrations of arsenopyrite (see above). Realgar occurs partly as discrete anhedral grains up to about 3 mm in size disseminated in the residuum, and partly in small granular aggregates with orpiment.

The latter sometimes contain weathered relics of arsenopyrite, of which realgar is evidently a supergene alteration product. Orpiment may have formed by supergene alteration of realgar, but this is not certain. Neither has been observed in unweathered materials.

Orpiment has been reported previously in Ireland at Silvermines, Co. Tipperary, where its formation was attributed by Gages (1860) to the action of low-temperature acid waters on "arsenal pyrites". Realgar also occurs at Silvermines.

D. Native arsenic, As. Arsenolite, As_2O_3

A single 4 mm equant crystal of native arsenic was found on the wall of a diagenetic recrystallisation cavity in crinoidal limestone at 31600E 20800N, 5180 bench. Reflected light and electron probe investigations showed the metal to be essentially pure, not intergrown with native antimony or with arsenic-antimony alloys as is often the case elsewhere. Incipient cleavage-guided alteration to arsenolite was visible in polished section. The identity of both minerals was confirmed by x-ray powder photography.

It was not possible to judge from this single occurrence whether or not the native arsenic was deposited from the primary ore-forming solutions.

E. Hydrated Manganese Oxides

Hydrated manganese oxide is a widespread minor constituent of residuum in marginal parts of the deposit, and occurs in traces in weathered rocks surrounding it. Most common is the sooty x-ray amorphous variety termed wad and, more recently, manganomelane.

It also occurs in microspheroidal and dendritic forms, generally as overgrowths on other secondary minerals but sometimes as inclusions in them. The main primary sources of the manganese it contains were sphalerite and dolomite.

Manganomelane is generally a mixture of poorly crystallised manganese oxides together with hydrated ferric oxides and other minor phases. It may contain up to at least 25% adsorbed water. The manganese oxides may include, in varying proportions, manganite ($MnO.OH$), pyrolusite (MnO_2), braunite ($(Mn,Si)_2O_3$) and the complex barium-bearing manganese oxide psilomelane. Cobaltian, cuprian, ferrian and other varieties have been described: they probably represent mixtures with such minerals as heterogenite (hydrous cobalt oxide), tenorite and goethite (Dana, 1944).

The chemical and mineralogical composition of Tynagh manganomelane has not been determined, but there is some analytical evidence (e.g. Table 7.5) that it is in places the cobaltian variety known as asbolite. Possible sources of cobalt were pyrite and, more locally, tennantite.

F. Feldspars

The weathering products of mineralised and unmineralised rocks of the Tynagh area include small amounts of various types of feldspar. Albite, $NaAlSi_3O_8$, is a minor constituent of the residua of most of the Lower Carboniferous sediments, and tiny euhedra of albite and orthoclase (var. adularia), $KAlSi_3O_8$, are commonly present as inclusions in primary sulphides and barite. Microcline (also ideally $KAlSi_3O_8$) and sodic plagioclase ($(Na,Ca)AlSi_3O_8$)) are mainly present in the residuum as detrital products of Devonian sediments.

G. Allophane, $Al_2SiO_5.nH_2O$

Allophane, an amorphous mineral compositionally similar to halloysite (see Clay Minerals), is widespread in small amounts in argillaceous residuum (Fig.8.1). Its usual occurrence is as translucent granules up to 4 mm across intimately mixed with supergene kaolinite and illite. Other common associates are dundasite and cerussite. Intergrowths of allophane and microcrystalline supergene barite have been observed, and allophane alone has been found as thin botryoidal crusts on blocks of residual primary mineralisation.

Allophane was identified on the basis of its low specific gravity (about 1.9), its optical isotropy and refractive index, and its mineralogical associations. Colourless, honey-coloured, pale blue and pale green varieties occur at Tynagh. Their refractive indices range from 1.480 ± 0.002 for colourless material to 1.493 ± 0.002 for the pale blue variety.

Compositionally, allophane is a mutual solution of silica, alumina, water, minor bases and accessory acid radicals in varying proportions. Qualitative analyses (Table 7.5) show that Tynagh allophane commonly contains zinc, copper and/or lead. The first two elements may be present largely as admixed silicates, most probably hemimorphite and chrysocolla respectively. Up to 3.7% Zn and 1.3% Cu have been reported in pale blue allophane with a refractive index of 1.496 from Montevecchio, Sardinia (Ross and Kerr, 1936). Plumbian allophane has been reported from the same locality, but it has not been established how lead occurs in allophane.

H. Rozenite, $FeSO_4 \cdot 4H_2O$

A colourless mineral that occurs widely in small amounts as an efflorescence of contorted fibrous crystals on pyritiferous residuum has been identified from its x-ray powder pattern as rozenite. Like chalcanthite (q.v.) it seems to have formed entirely since stripping of the deposit's overburden. **Melanterite**, $FeSO_4 \cdot 5H_2O$, from which rozenite may form by dehydration (Boyle, 1965) has not been recognised at Tynagh.

I. Hydrocarbons and Graphite

A lustrous jet-black brittle substance with a conchoidal fracture that occurs mainly as free angular grains up to 1 cm in size in Calp mud has been identified as a solid hydrocarbon, chiefly on the basis of its low specific gravity (about 1.2). It is x-ray amorphous, non-radioactive, insoluble in benzene and ether, and does not burn or melt perceptibly in a bunsen flame. These properties resemble those of the hydrocarbon albertite, which has been found as a fissure-filling in the Lower Carboniferous rocks of Nova Scotia (Dana, 1932). It has been observed in crinoidal limestones walling the residual deposit as angular grains, fragmental in appearance, associated with coarse-grained sphalerite in veinlets and patches of sparry calcite.

Small amounts of the same or a similar hydrocarbon occur in residual aggregates of primary mineralisation. In these it usually forms microscopic crusts on botryoidal pyrite, but sometimes encrusts granular sphalerite and crystalline barite, or occurs as uncorroded fragments in galena.

Partially graphitised organic substances (macerals) occur as irregular grains and in microscopic cellular forms with complicated geometries in the residuum of all the darker limestones

at Tynagh. They and carbonaceous particles of sub-micron size are thought to be the main colouring agent of the dark grey and black muds.

J. Minor Detrital Minerals

Weathering of Lower Carboniferous and Devonian sediments has contributed volumetrically insignificant amounts of the following identified resistate minerals to the residual deposit: magnetite, Fe_3O_4; hematite, Fe_2O_3; rutile, TiO_2; ilmenite, $FeTiO_3$; fluorite, CaF_2; apatite, $Ca_5(PO_4)_3(F,Cl,OH)$; zircon, $ZrSiO_4$; chlorite, epidote, garnet and tourmaline.

CHAPTER EIGHT

CHEMICAL WEATHERING OF THE RESIDUUM

Chemical weathering of the residuum deposit has been going on more or less continuously since it started to form. Consequently, although a large proportion of the residuum is classified as sulphide ore, it is oxidised to some extent throughout, and there are few if any of its primary constituents that have not been affected by supergene chemical activity. The main chemical effects of weathering have been the alteration of primary sulphides to numerous secondary species, and the gradual enlargement of the residual body by alteration of the surrounding limestones. Large quantities of metal leached from primary sulphides have been reprecipitated within the residual body in extensive zones of supergene enrichment.

It should be understood from the outset that no clear division exists in time or kind between chemical weathering events responsible for the formation of the residuum and those responsible for its alteration. However, since chemical weathering of the residuum has had major, definable effects on its mineralogy and on metal distribution within the deposit it can justifiably be made the subject of a separate chapter. The origin of the deposit is discussed in Chapter 9.

8.1 ALTERATION OF PRIMARY MINERALS

A. Galena

The commonest alterations of galena are corrosion (see footnote), replacement by cerussite, and replacement by secondary

Footnote: The term corrosion is applied in this chapter to dissolution of a mineral without precipitation of another in its place.

sulphides of copper. Direct replacement of galena by anglesite is comparatively rare, and replacements of galena by secondary zinc minerals, secondary copper minerals other than sulphides, and by complex secondary minerals of lead such as mimetite and beudantite apparently do not occur. Variations in the predominant style of alteration from one part of the deposit to another are described later.

Corrosion of galena is commonly guided by the sulphide's cleavages or grain boundaries, and initiated at the margins of inclusions, especially inclusions of pyrite (Plates 8.1, 8.2). An early effect of corrosion is sometimes to bring out the triple-junction geometry of galena aggregates.

A widespread corrosion effect is internal breakdown of galena grains, which imprints on them a filigree-like decomposition pattern (Plate 8.3). The onset of this form of alteration is indicated by darkening of lobate areas of the sulphide in polished section. At high magnifications this darkening is seen to be due to the presence of numerous anastomosing voids, some of which have preferred orientations that correspond to the cleavage directions of the sulphide. No elements other than lead and sulphur were detected by electron probe microanalysis of darkened areas, and x-ray powder photographs of affected grains showed that they had no crystalline constituent other than galena. In individual grains, intensely corroded galena may be separated from virtually unaltered galena by a single cleavage.

Replacement of galena by cerussite appears to have been essentially volume-for-volume (Plate 8.4). Many of the resulting textures are identical to those described by Anderson (1930) as typical of replacements of galena by anglesite. This textural similarity may indicate that the original metasome of galena in

Tynagh ores was usually or always anglesite. Alternatively, it may simply reflect the control that the sulphide's structure has on the geometry of its replacements by either mineral. This subject is taken up again in a later section, but it should be mentioned here that if anglesite was generally the original metasome of galena its subsequent replacement by cerussite appears to have been virtually complete in most parts of the deposit.

Anglesite has been observed as a direct replacement of galena in a few places (Plate 8.5), and x-ray diffraction traces of galena-bearing residuum commonly indicate the presence of minor amounts of anglesite, but no instances of partial replacement of anglesite by cerussite have been seen. The converse, on the other hand, is locally common.

Replacement of galena by supergene copper sulphides is common in some parts of the deposit. Examples are shown in Plates 8.6 and 8.7. The most usual replacement products are chalcocite, covellite, mixtures of the two that probably resulted from mutual replacement of the copper sulphides, and chalcocite-limonite intergrowths. Copper-rich oxide ores sometimes contain microscopic aggregates of anglesite and covellite formed by replacement of galena.

B. Sphalerite

The most noticeable supergene alteration of sphalerite is replacement by galena. Almost all the supergene galena in the deposit has formed at the expense of sphalerite. Its occurrence was described in Chapter 7 and is illustrated by Plates 7.2 and 7.3.

Replacements of sphalerite by supergene copper sulphides are common in some parts of the deposit. The usual metasome is

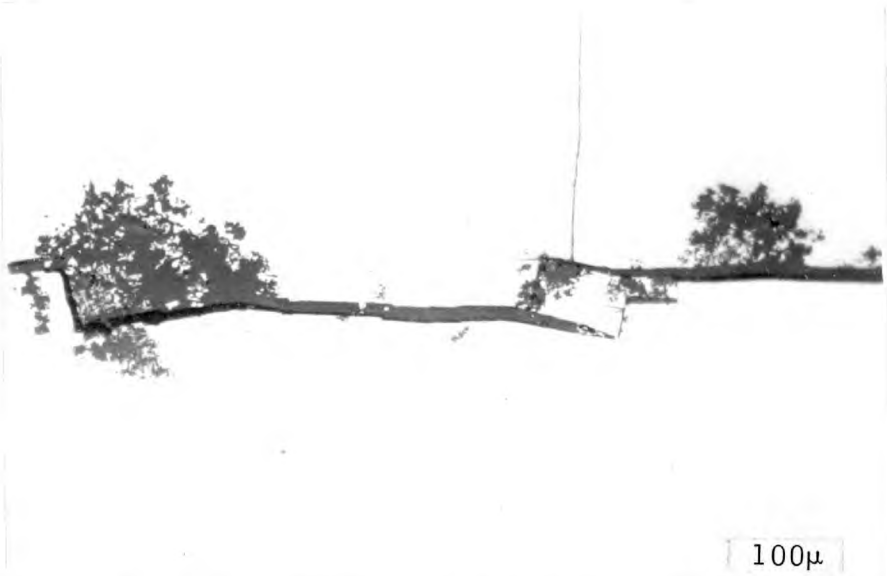


Plate 8.1 - Cleavage-guided alteration of galena (white) to cerussite (medium grey). Polished section.

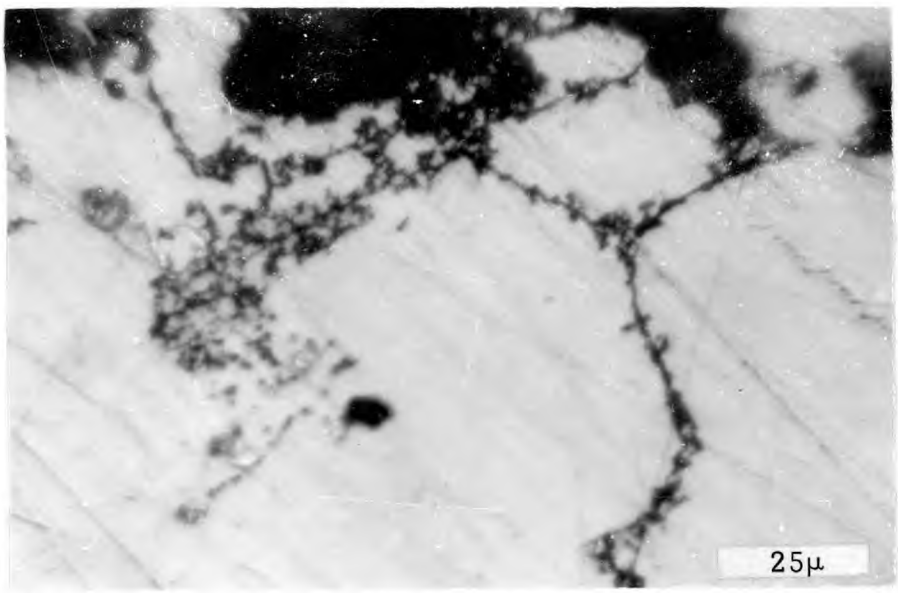


Plate 8.2 - Grain boundary control of galena alteration. Polished section. Oil immersion.

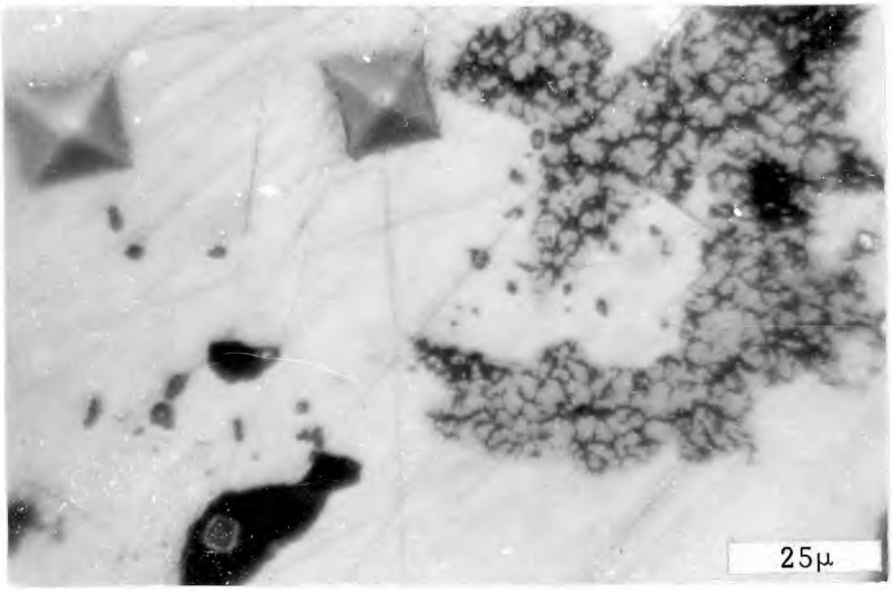


Plate 8.3 - Patchy alteration of galena (containing microhardness indentations). Polished section. Oil immersion.

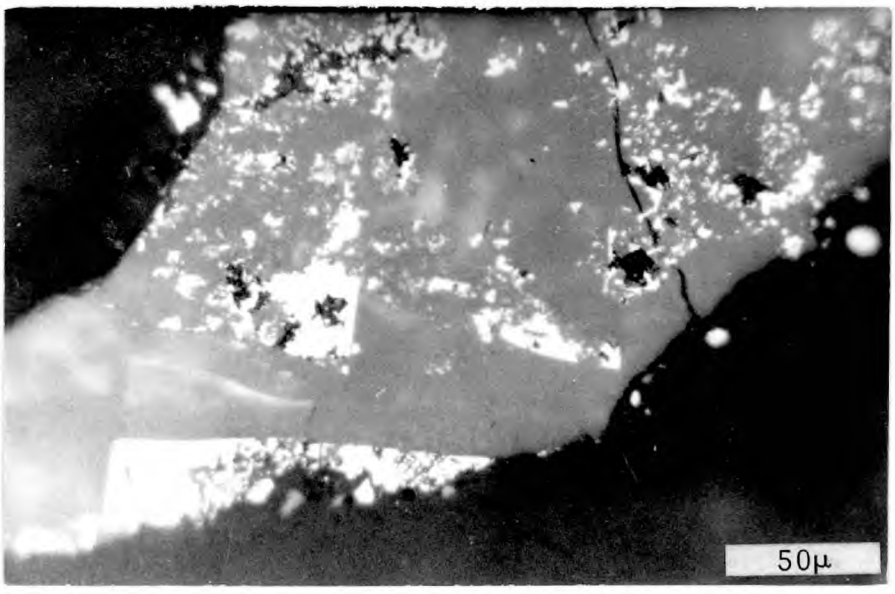


Plate 8.4 - Replacement relics of galena (white) in cerussite. Polished section.

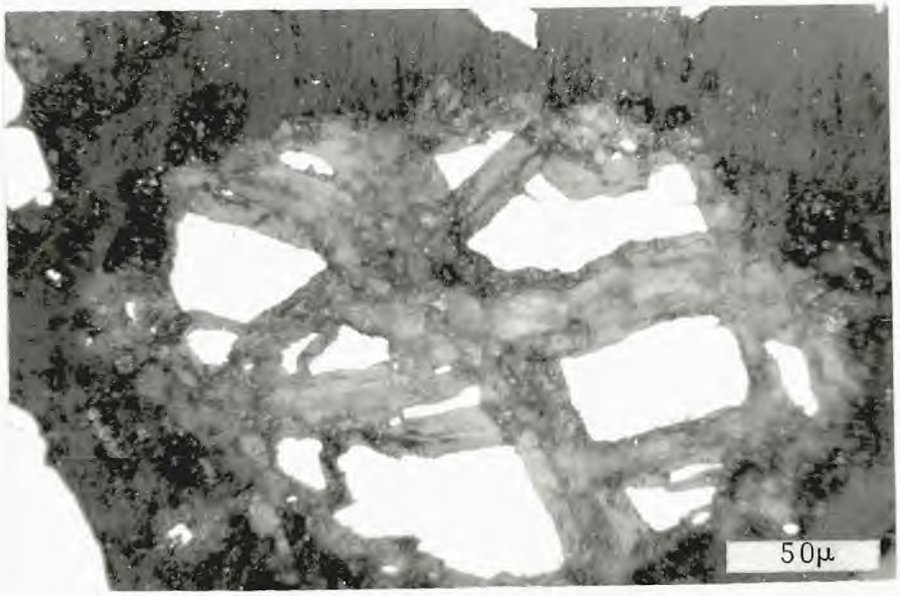


Plate 8.5 - Residual primary galena grain veined and marginally replaced by anglesite. Polished section.

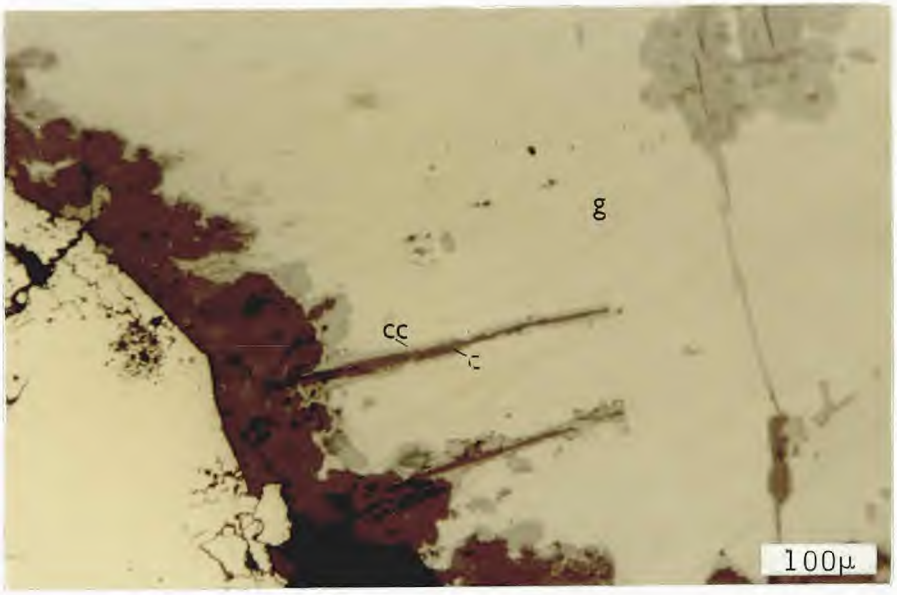


Plate 8.6 - Chalcocite (cc) replacement of galena (g). The replacement was guided by galena cleavages and grain boundaries. Alteration of the galena involved a loss in volume, which was largely compensated for by precipitation of cerussite (c). More advanced alteration of this kind yields a network of ragged cerussite blades in supergene copper sulphides. Polished section.

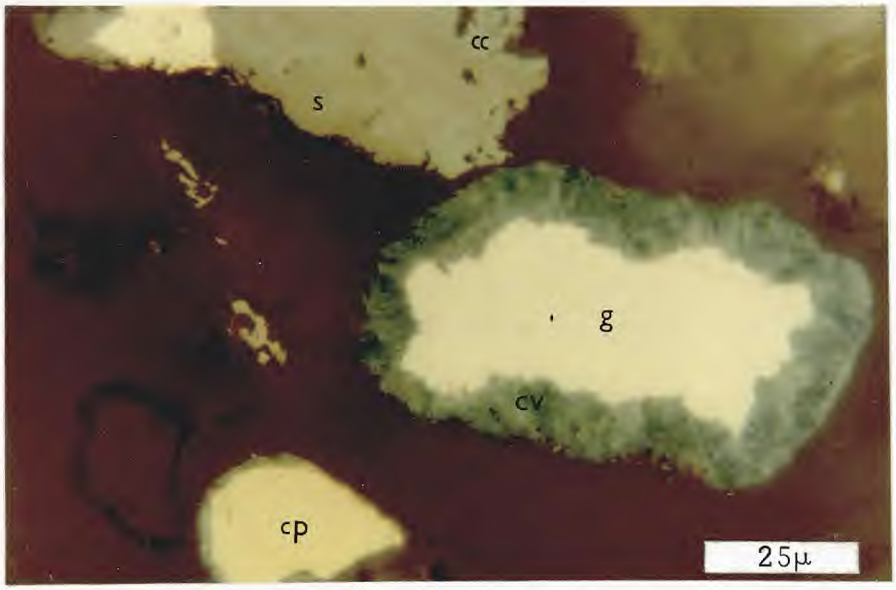


Plate 8.7 - Replacement of primary galena (g), sphalerite (s) and chalcopyrite (cp) by supergene copper sulphides, including covellite (cv) and chalcocite (cc). Polished section.

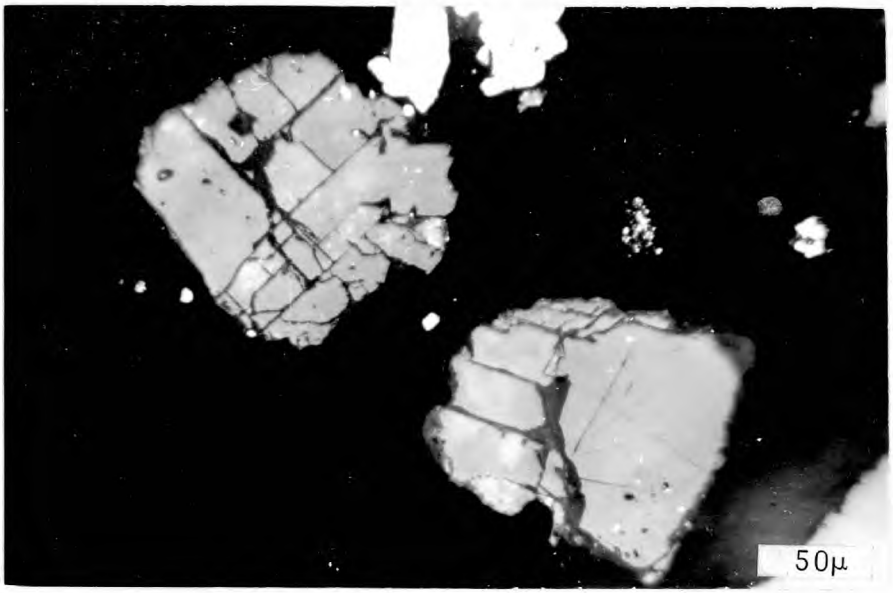


Plate 8.8a - Cleavage-guided dissolution of grains of residual primary sphalerite. Polished section. Oil immersion.

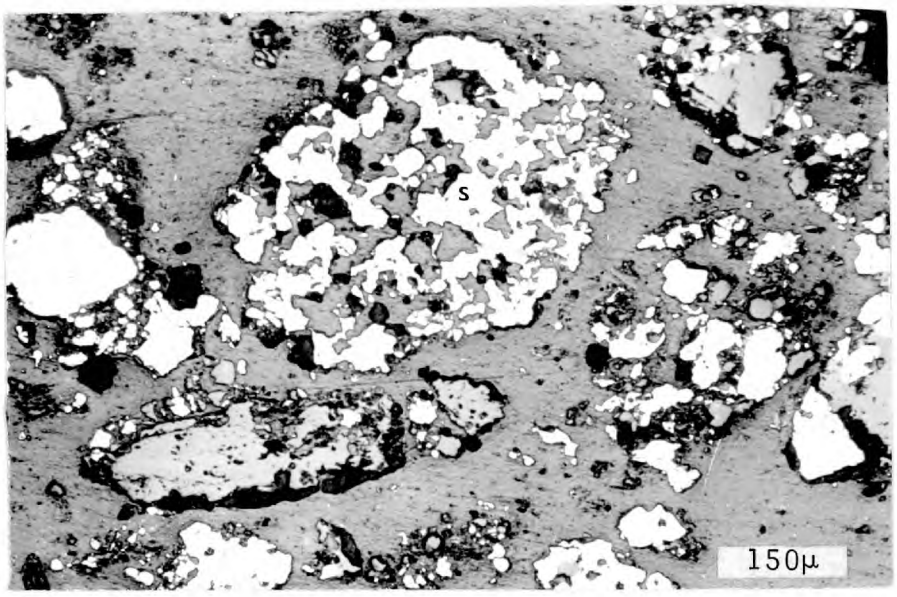


Plate 8.8b - Partially dissolved aggregate of microgranular primary sphalerite (s). Polished section.

covellite, though chalcocite and intergrowths of two or more copper sulphides also occur in this way (Plate 8.7). Preferential replacement of alternate sphalerite twin lamellae by chalcocite has been observed.

Probably more common than either type of replacement is corrosion (Plate 8.8). This affects sphalerite grains peripherally, and solutional enlargement of the mineral's excellent cleavages is quite often seen in coarser-grained material. It does not produce the complicated internal decay textures seen in galena, and is not as noticeable in polished section.

Replacements of sphalerite by supergene minerals other than the sulphides referred to above are uncommon, but peripheral alteration of sphalerite grains to limonite and unidentified non-opaque minerals is occasionally seen. Even in smithsonite-rich ores it seems to be rare for the zinc carbonate to replace the sulphide directly.

C. Pyrite and marcasite

Pyrite and marcasite generally weather by corrosion or by replacement by hydrated ferric oxide. In alkaline environments pseudomorphic replacements of this kind are common (Plate 8.22), and excess iron tends to be reprecipitated as limonite close to its primary source, e.g. as fringes around limonite pseudomorphs of pyrite in limestone. More rarely the two sulphides are replaced by covellite and chalcocite. Replacement by supergene galena is very uncommon.

D. Chalcopyrite, tennantite and enargite

Supergene alteration of the main primary copper minerals generally takes the form of corrosion or replacement by secondary

copper sulphides, limonite and cerussite. None of the three primary species appears to have been replaced directly by supergene zinc minerals, supergene sulphides of metals other than copper, copper carbonates, cuprite or native copper in any part of the deposit.

Bornite, covellite, digenite and chalcocite are the usual supergene replacements of chalcopyrite. Textural evidence of their crystallisation sequence is often ambiguous. All occur as the only existing metasome of chalcopyrite in particular grains, and mutual replacements involving most of their possible combinations have been observed.

An incipient alteration effect quite commonly seen in polished sections of primary chalcopyrite is a brownish to pinkish cast that varies in intensity between adjacent grains or twin lamellae. At high magnifications this is seen to be due to the formation at discrete centres of a mineral phase or mixture that is purple to brown in colour and not detectably anisotropic in reflected white light. This is probably bornite, though x-ray powder photographs of slightly mottled grains failed to confirm the presence of a phase other than chalcopyrite. The incipient alteration product occurs in areas too small to be effectively analysed by electron probe techniques, and separation of a sufficient quantity of affected material for analysis by other methods is impossible. The composition of this alteration product of chalcopyrite is therefore uncertain. It may, to judge from the colour of the mineral, be variable, probably within the range $CuFeS_2$-Cu_5FeS_4. Alternatively, the colour differences may reflect differences in the proportion of bornite to relict chalcopyrite within the altered areas.

At a more advanced stage of alteration the centres coalesce to give bornite pseudomorphs or irregular replacements of chalco-

pyrite grains. This apparently involves little or no volume change. Rim replacements of chalcopyrite grains by bornite also occur.

More common alteration products of chalcopyrite are chalcocite, covellite and digenite in that order of abundance (Plates 8.9, 8.10). The sulphides usually appear to have formed by direct replacement of chalcopyrite though it is not uncommon for covellite to form by replacement of bornite after chalcopyrite. Direct replacement of chalcopyrite by secondary copper sulphides usually appears to involve a volume loss, particularly when the metasome is covellite.

Chalcopyrite is replaced by mixtures of secondary copper sulphides and limonite in all proportions and sometimes in microscopic vermicular intergrowths (Plate 8.11). Colloform aggregates of limonite containing minor amounts of secondary copper sulphide as scalloped strings arranged concordantly with the outlines of chalcopyrite relics are occasionally found.

Direct replacement of chalcopyrite by cerussite is comparatively uncommon. It is best discussed in the context of the environment in which it takes place.

Tennantite and enargite are relatively more prone to simple corrosion than chalcopyrite. Bornite has not been observed replacing either of the sulphosalts, but otherwise their alteration products are the same as those of chalcopyrite. Zinc and silver released by weathering of tennantite generally seem to have migrated in solution from alteration sites, for no supergene precipitates of these metals have been found replacing the sulphosalt, and electron probe investigations have not shown that silver is a lattice constituent of any supergene copper sulphide formed by replacement of tennantite. Replacements of primary sulphosalts by secondary minerals of arsenic or antimony have not been observed.

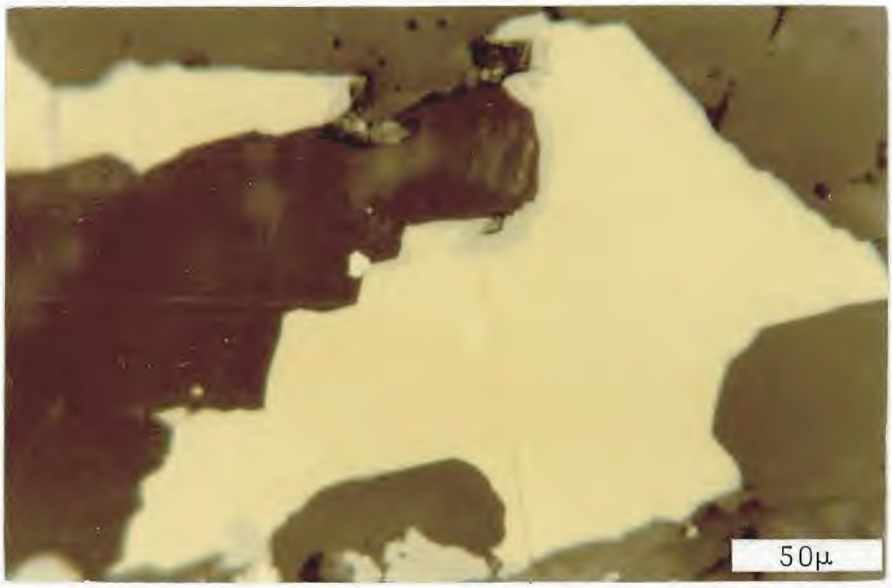


Plate 8.9 - Marginal replacement of primary chalcopyrite (yellow) by chalcocite (grey). Polished section.

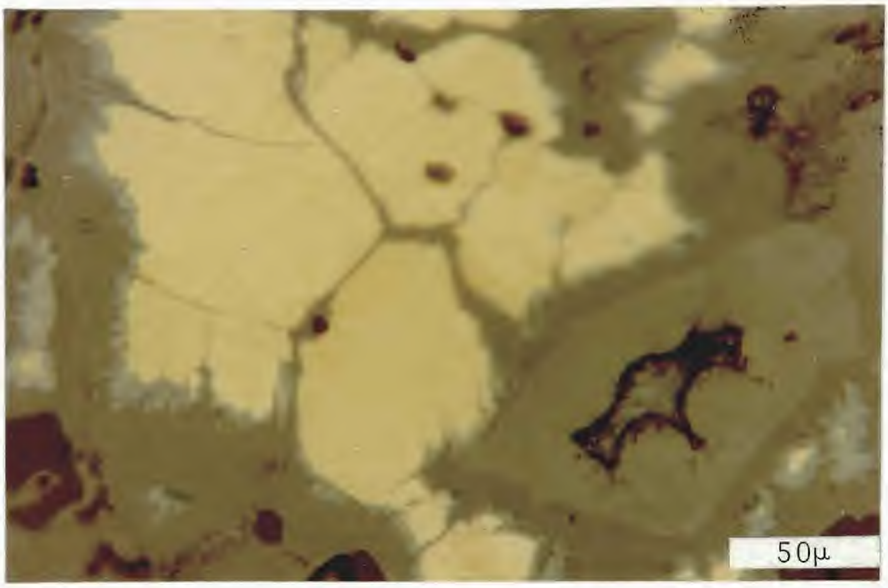


Plate 8.10 - Sequential replacement of primary chalcopyrite by a covellite-chalcocite intergrowth (blue) and colloform limonite (brown). Polished section.

Plate 8.11 - Replacement of primary chalcopyrite (yellow) by chalcocite (blue) containing a vermicular intergrowth of limonite (brown).

E. Barite

In all parts of the deposit barite has suffered some degree of corrosion. Plate 8.12 illustrates cleavage-guided corrosion of a residual barite grain. In certain types of weathering environment to be described later, it is not uncommon for barite to be replaced by cerussite, malachite, azurite and limonite. The first of these sometimes forms as idioblastic replacements of barite, and the last as microscopic spheroids and microbotryoidal aggregates with radiating fibrous structure.

Weathering apparently tends to purge barite of included chlorides. Analytical evidence to this effect is that a trial concentrate of barite from heavily oxidised ores contained three and a half time less chlorine than a concentrate of barite from sulphide ores (Table 7.14). Both concentrates contained 95.9 ± 0.1 per cent $BaSO_4+SrSO_4$, and the main contaminant in both was silica. Since the chlorine-deficient concentrate was made from residuum that may well have contained some mimetite it is possible that the barite itself may have been virtually chlorine-free. Conversely, primary sulphide contaminants in the other concentrate may have contained some of the chlorine, and in any case it is possible that the difference in the chlorine content of the two concentrates could reflect differences in the primary distribution of included chlorides. Barite must, nevertheless, be considered as a potential source of chloride ion during weathering.

F. Other Minerals

Many of the primary constituents of the residuum not already discussed have been affected to some degree by supergene chemical activity. Dissolution of calcite and dolomite is virtually complete in dark granular and blocky ores in the centre of the deposit.

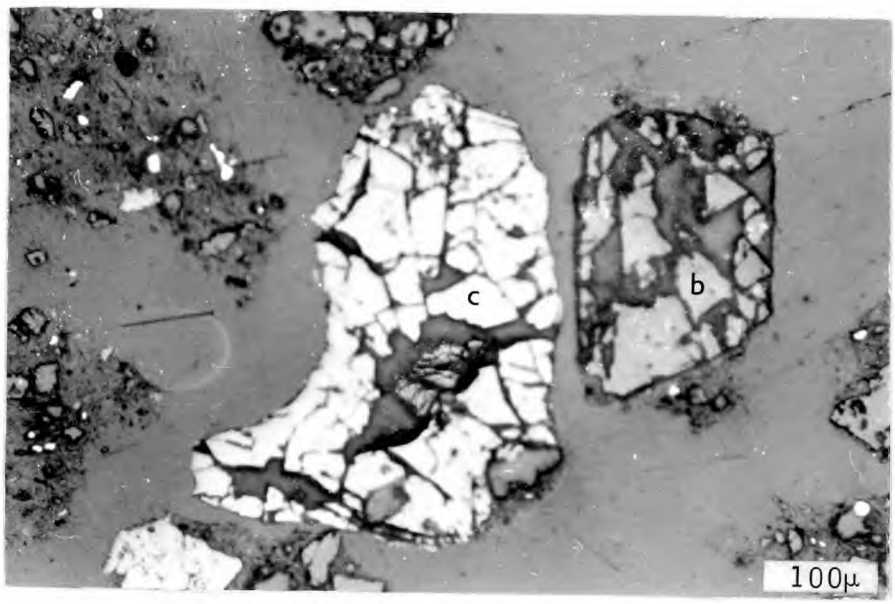


Plate 8.12 - Cleavage-guided dissolution of cerussite (c) and barite (b). Polished section.

Towards its edges and in residuum consisting largely of Calp mud marginally decomposed blocks of bioclastic limestone and partially decalcified Calp fragments persist. Quartz and feldspar have been relatively little affected by weathering of the residuum, though corrosion of both is sometimes detectable in thin sections of residuum. Detrital magnetite, rutile and ilmenite do not appear to have been altered, but some limonitisation of hematite in the residuum of the Calp ironstone horizon has occurred.

8.2 RELATIVE WEATHERING RATES OF PRIMARY MINERALS

Some residual primary minerals are typically more intensely weathered than close associates, irrespective of grain size, crystallisation habit, the character of their matrix or their position in the deposit. The relative susceptibility of others to weathering appears to have been partly controlled by one or more of these variables. It may also have been influenced by the stoichiometry and minor and trace element chemistry of the minerals concerned, and by the anion composition of the solvent. In the following account of the observed weathering resistance of the main primary constituents of the residuum, comparison is only made between minerals in grains that are thought to have been equally and simultaneously accessible to weathering agents.

Residual galena is almost invariably more intensely weathered than associated primary minerals other than carbonates (Plates 8.13, 8.14). In particular, it appears to have been much more susceptible to alteration than sphalerite in all parts of the deposit, and it is not uncommon for galena to be replaced by cerussite without the slightest alteration effect being discernible in original inclusions of sphalerite, which are inherited by the carbonate metasome.

A peculiar feature of galena alteration is the wide variation in its apparent intensity between essentially monomineralic fragments of equivalent size in small samples of residuum. This is

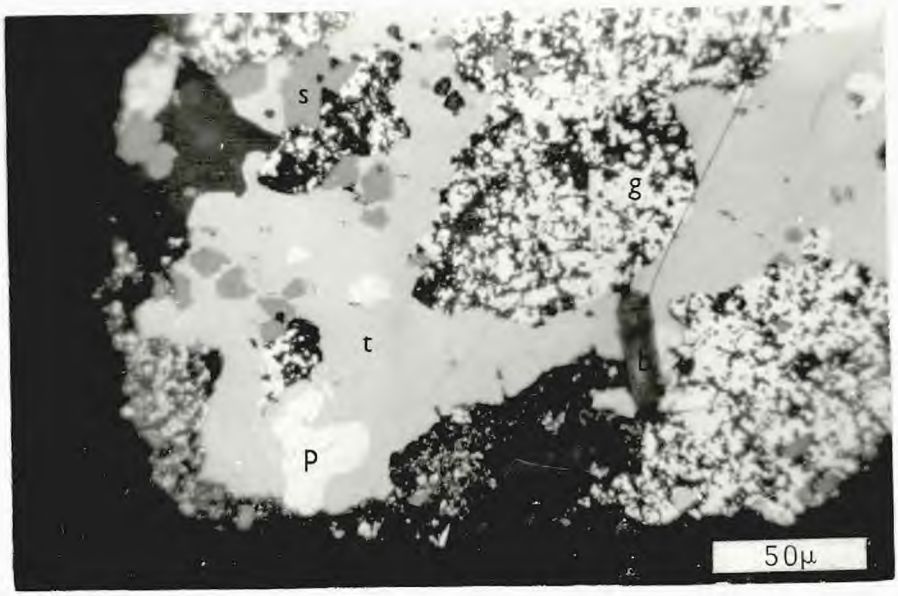


Plate 8.13 - Selective alteration of galena (g) aggregated with tennantite (t), sphalerite (s), pyrite (p) and barite (b). Polished section.

Plate 8.14 - Selective alteration of galena in tennantite to a mixture of chalcocite (blue) and limonite (brown). Polished section.

common in residuum from all depths in the deposit, and applies equally to materials that have clearly been transported and to those that have undergone little or no transport. In some cases it may be partly due to physical mixing of materials with a different weathering history. More generally it may reflect differences in the style rather than the rate of alteration of grains: the grains of fresh galena, in other words, may be corroded relics of larger grains that, for structural or compositional reasons, were not as amenable to internal decay as their associates. Alternatively, it may indicate that water circulation in the residual mass was so sluggish that the weathering regime varied on a microenvironmental scale. Many other local variations in the rate and effect of alteration processes, such as the complicated paragenesis of the secondary copper sulphides, are open to the same interpretation.

Relative to that of sulphides other than galena, the weathering resistance of sphalerite is variable. In aggregates with primary sulphides of copper and iron, sphalerite is commonly less weathered than both. It has a marked tendency to corrosion at interfaces with pyrite. The proneness of sphalerite grains to peripheral attack, allied with the small size of typical grains and the irregularity of their original outlines, makes it hard to assess the extent to which free microgranules of sphalerite have been corroded.

No clear relationship has been observed at Tynagh between the iron content of sphalerite and the mineral's susceptibility to weathering, and the effect on the latter of variations in the trace element chemistry of the sulphide has not been investigated.

Tennantite and enargite have been weathered less intensely than associated chalcopyrite, and in places resisted alteration

almost entirely while chalcopyrite was largely replaced by bornite or a secondary copper sulphide. Very rarely the converse is true, but this is probably an aggregation effect. Differences in the weathering behaviour of chalcopyrite and tennantite are illustrated in Plate 8.15.

Iron sulphides have resisted alteration better than other sulphides with which they are aggregated, though it has already been mentioned that their oxidation has clearly enhanced the rate of alteration of associated sulphides. There is no observational evidence of a marked difference in solubility between optically isotropic, optically anisotopic and visibly nickeliferous pyrite. Marcasite has apparently been slightly more susceptible to alteration than pyrite with the same crystallisation habit. The susceptibility of pyrite to weathering was to some extent dependent on its habit: euhedra have generally resisted weathering better than framboidal aggregates, the latter better than intermicrocryst pyrite and their fibrous pyrite overgrowths. Marked differences are apparent between the alteration rate of different growth zones of pyrite in colloform-banded aggregates and zoned euhedra.

Barite has generally resisted weathering better, and calcite and dolomite less well, than all the sulphides referred to above (Plate 8.16). In the rare cases in which barite appears to have been more intensely altered than associated sulphides, its corroded appearance is probably due largely to the dissolution of intergrowths and inclusions of calcite and dolomite.

Discussion

There is no general agreement about the relative importance of solvent chemistry, mineral chemistry and aggregation effects in

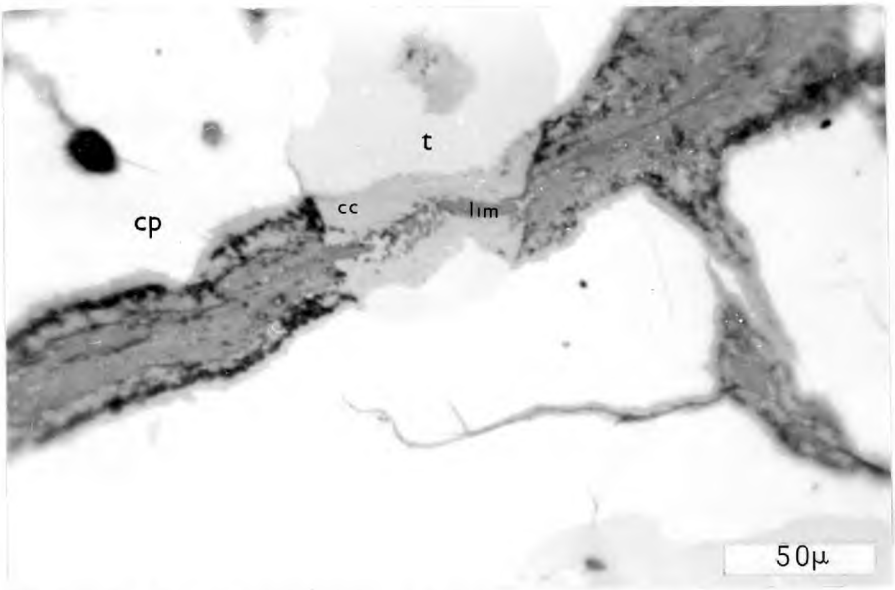


Plate 8.15 - Supergene replacement of chalcopyrite (cp) and tennantite (t) by an intergrowth of chalcocite (cc) and limonite (lim). Polished section.

Plate 8.16 - Voids in galena (white) due to selective dissolution of dolomite. Smaller voids in the associated barite and sphalerite may have resulted from dissolution of included calcite/dolomite. Polished section.

determining the solubility order of the common sulphides in natural weathering systems. In particular, it is far from clear why sphalerite, which has a greater calculated solubility in pure water at atmospheric temperatures and pressures than galena (Verhoogen, 1938) but a lesser empirical solubility under laboratory conditions (Table 8.1), weathers more rapidly than galena in some deposits and less rapidly in others. Some authors, among them Grondijs and Schouten (1937) and Garretty and Blanchard (1942), have explained the variation in terms of the abundance of associated pyrite, arguing that where pyrite is scarse oxidation of galena is not retarded by the formation of protective coatings of anglesite. No evidence has been found at Tynagh that the solubility order of the two sulphides varies with the pyrite content of the residuum.

Other suggested explanations for the superior solubility of galena relative to sphalerite in some deposits include the presence in the former of readily oxidised manganese sulphide in solid solution (Nishihara, 1914), and complexing of ions of the two metals with dissolved chloride ion (Garrels, 1941). Spectrographic analyses of Tynagh galena (Table 7.2) show that it contains little or no manganese, while the chloride ion concentration and temperature required to effect solubility reversal by the second mechanism are too high for it to operate under weathering conditions.

Another possibility is that galena weathers more rapidly than sphalerite when some peculiarity of the aqueous environment encourages complexing of their respective metal ions with one or more of the intermediate oxidation products of sulphide ion, e.g. thiosulphate ion. Listova (1966) has demonstrated the effectiveness of this mechanism in increasing the solubility of Pb^{++} in oxidising aqueous solutions of intermediate pH (Eh +3.35 mV, pH 5.5-8.3), and Cloke (1961) has suggested that lead is more soluble than zinc in some ore-forming fluids because the metals are transported as poly-

Table 8.1 Solubility of some sulphides and chlorides in water (gm/100gm H_2O at approx.25°C, 1atm.)

	Sulphide	Chloride
Zn	0.000065 (sphalerite)	432
	0.00069 (wurtzite)	
Cd	0.00013 (greenockite)	140
Fe^{++}	0.00049 (pyrite,marcasite)	
Pb	0.01244	0.99
Ag	insoluble	0.000089

Source: Handbook of Chemistry and Physics,45th edition,1964.

sulphide complexes. Though complexes of this kind are readily destroyed by physico-chemical changes in their aqueous medium, their formation may be the usual or inevitable first stage in natural oxidation of sulphides, and some may be capable of prolonged metastable existence in slow-moving anoxic solutions. Granger and Warren (1969) have recently suggested that intermediate sulphur species play an important part in supergene sulphide enrichment.

Observed variation in the relative solubilities of other Tynagh sulphides may be partly accounted for by differences in their structure and in the permeability of their matrices, and partly by compositional variations that do not have a distinct effect on the reflected light optics of the species concerned. Marked differences in the oxidation rate of artificial lead sulphides differing in Pb:S ratio have been reported by Eadington and Prosser (1969), and non-stoichiometry is presumably a contributory cause of variation in the alteration rate of natural sulphides. The significance (if any) of variations observed at Tynagh vis-a-vis the anion composition of weathering agents is unknown.

8.3 DISTRIBUTION OF SUPERGENE ALTERATION EFFECTS

The residual materials can be broadly divided on the basis of their supergene mineralogy into those in which more metals are represented by supergene sulphides than by carbonates, those of which the reverse is true, and those in which supergene carbonates of certain metals have been replaced by arsenates and oxides. Materials of the first type are invariably dark in colour and occur mainly in the central part of the deposit. Carbonates of lead and zinc are ubiquitous in dark and limonitic materials, but they and carbonates of copper are most strongly concentrated in oxide

ores at the deposit's periphery. Residuum of the third type ("gossan") is widely distributed. Fig. 8.1 shows in simplified form, the distribution of some primary and secondary minerals in a horizontal section through the deposit.

For present purposes the deposit can be considered as having a central supergene sulphide zone and a peripheral supergene carbonate zone. In fact, the distribution of the first two types of material is very much more complicated than that, partly due to physical reworking of residuum, which has in places caused mixing or interstratification of materials with a different weathering history, and partly due to local variations in the character and intensity of weathering processes. In addition, progressive weathering of the residuum has caused partial to complete gossanisation of many small bodies of residuum in the supergene sulphide and carbonate zones.

In this section the effects of chemical weathering on the mineralogy and metal content of different parts of the deposit are first described and then discussed in relation to the physical chemistry of weathering processes. The weathering history of the deposit as a whole is summarised on page 335.

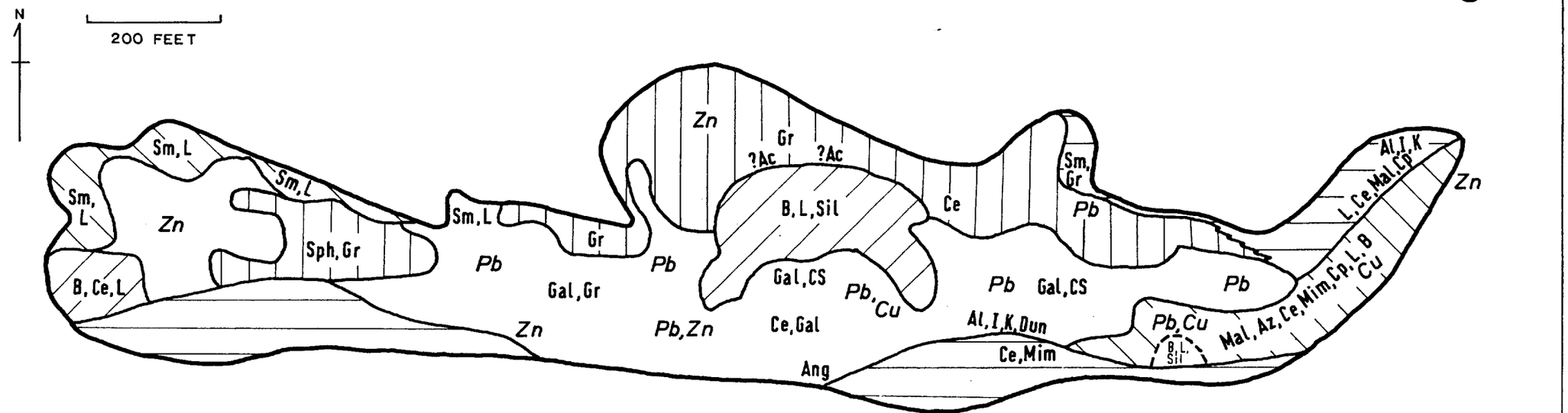
A. The Supergene Sulphide Zone

(i) Mineral distribution

At least six metals are represented in the residuum by supergene sulphides. To recapitulate, they are:

	Metal	Supergene sulphide species
	Lead	Galena
	Zinc	Sphalerite and perhaps wurtzite
	Copper	Chalcocite digenite, covellite, bornite, chalcopyrite
	Cadmium	Greenockite, hawleyite
	Iron	Pyrite and probably marcasite
	Arsenic	Realgar, orpiment
and probably	Silver	Acanthite

Fig. 8.1



Residuum type

- Calp mud
- Dark sulphide-rich rubble and mud
- Gossan of massive protore
- Oxidised argillaceous limestone
- Oxidised Waulsortian bank and bank-cover limestone

Pb, Zn, Cu Main primary ore metal

Supergene minerals

Ac	Acanthite	**Cp**	Cuprite, native copper	**K**	Kaolinite, halloysite
Al	Allophane	**CS**	Copper sulphides	**L**	Limonite, goethite
Ang	Anglesite	**Dun**	Dundasite	**Mal**	Malachite
Az	Azurite	**Gal**	Galena	**Mim**	Mimetite
B	Beudantite	**Gr**	Greenockite, hawleyite	**Sil**	Native silver
Ce	Cerussite	**I**	Illite	**Sm**	Smithsonite
				Sph	Sphalerite

Tynagh residual deposit - AREAS OF CONCENTRATION OF SOME SUPERGENE MINERALS

(5160 bench, diagrammatic)

Supergene sulphides of lead, zinc and arsenic are largely restricted to dark varieties of residuum, and hence occur mainly in the central part of the deposit. Features of the assay distribution of silver described later in this section suggest that the supergene sulphide of this metal is also commonest in dark residuum in the core of the deposit. Most iron sulphide that is thought or known to be supergene in origin occurs in dark residuum containing supergene sulphides of several other metals.

Copper and cadmium differ from the other metals in that while their supergene sulphides are most widespread in the dark materials of the deposit's core, they are also fairly common in visibly limonitised residuum.

The distribution of particular supergene sulphide species is erratic, and not always closely related to that of primary hosts of the metal concerned. That of galena has been studied in some detail. Points of particular interest are that:

(i) supergene galena occurs at all levels in the deposit;

(ii) its abundance in small samples of residuum, and its abundance relative to that of primary galena, vary considerably in horizontal and vertical sections through the deposit;

(iii) in some places its abundance seems to be positively related to that of primary galena, in others to that of primary sphalerite;

(iv) supergene galena has not been found in what are thought to be the most recently formed bodies of Calp mud, though this may be simply a reflection of the low lead content of the parent rock;

(v) it is rarely unaltered, and is sometimes overgrown by crystalline cerussite (Plate 8.17).

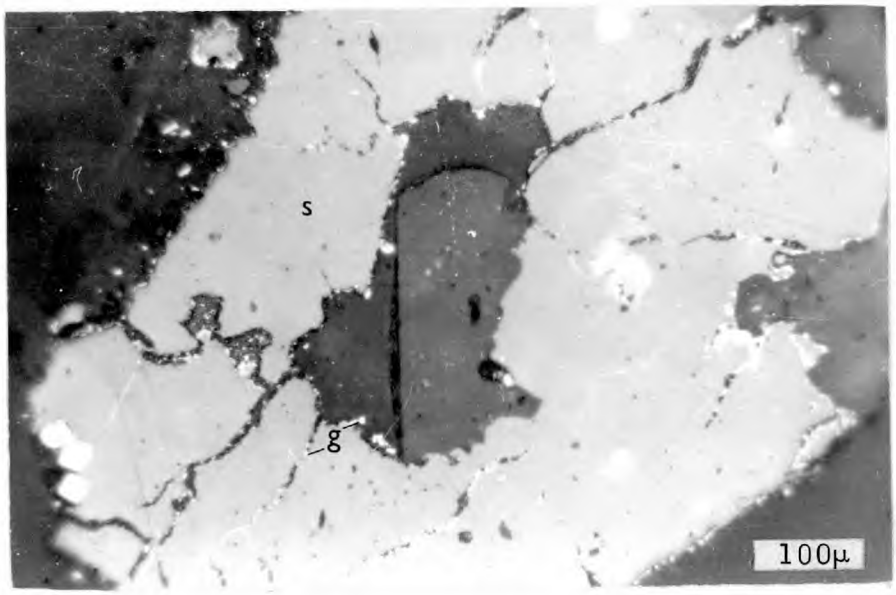


Plate 8.17 - Corroded primary sphalerite (s) veined and encrusted by supergene galena (g). The central cavity contains a crystal of cerussite. Polished section.

Supergene sphalerite that has been recognised as such occurs largely as a replacement of fossil wood in the western part of the deposit's core, where much of the residuum is rich in primary sphalerite. Fossil wood is probably present at all levels in the deposit in this area, but it is not known whether it is ubiquitously replaced by sphalerite. Variations in the specific gravity of wood from parts of the Collapse Breccia above elevation 5160 suggest that its sulphide content varies considerably. This has been confirmed analytically by the mine assay department. The variation is not related to depth or to the zinc content of the surrounding residuum. The highest zinc assay recorded on wood to date was on a sample from the uppermost bench of the deposit.

In the eastern part of the deposit supergene sphalerite has only been found as a replacement of fossil wood in an area where limestones bounding the residuum are in places unusually rich in primary sphalerite.

As previously mentioned, it is possible that zinc sulphide formed by replacement of wood was originally deposited as wurtzite, most of which subsequently inverted to sphalerite.

Cadmium sulphides, also occur in close association with fossil wood. Analyses suggest that the wood generally contains less cadmium than zinc, but cadmium sulphides alone occur as powdery coatings on wood fragments and as impregnations in the surrounding residuum.

Cadmium sulphides are widespread in inorganic materials. This is probably reflected in the fact that Zn:Cd ratios are usually higher in zinc sulphide sands concentrates than in bulk (slimes) concentrates, for cadmium sulphides in the Tynagh residuum are typically microgranular. They are markedly concentrated in and close to pyritiferous clay bands in dark residuum west of

about 32200E (Fig. 8.1). Concentration is thought to have resulted from impounding of cadmium-bearing groundwaters by these relatively less permeable horizons, and from inorganic or bacterial generation of reducing agents within them.

The two sulphides of cadmium that occur in the residuum, greenockite and hawleyite, cannot be distinguished from each other in the field, and it has not been possible to establish whether the distribution and mode of occurrence of the two species differ. They occur too sporadically for their distribution below present mining levels to be determined by examining drill cores, and the latter are not usually assayed for cadmium. Mining and drilling to date have not shown that they are concentrated at a particular level in the deposit, or that their abundance varies systematically with depth in any part of it.

The same is true of the supergene sulphides of copper. These are strongly concentrated in the eastern half of the deposit, where they are common both in dark residuum and in limonitic materials at the margin of the deposit. Since they generally occur as replacements of primary copper sulphides and of primary galena and sphalerite associated with the latter, their spatial distribution is essentially the same as that of primary copper sulphides.

Other than on a very local scale, enrichment of residuum in copper by the formation of supergene sulphides is very hard to demonstrate. Certainly, no part of the deposit has been substantially enriched in copper in this way. Small samples of dark residuum examined in polished section often seem to contain somewhat more copper as supergene sulphide than appears to have been leached from associated primary minerals. This may be a local redistribution effect, or it may reflect slight but widespread copper enrichment, particularly of the eastern half of the deposit's core.

Because primary iron sulphides occur in so many habits and associations, recognition difficulties make the distribution of supergene varieties uncertain. Supergene marcasite has not been specifically identified. Most of the pyrite that is thought to be supergene in origin occurs in a friable microgranular form as patchy concentrations and as thin incomplete encrustations of protore fragments (Plate 7.1) in dark residuum in the central part of the deposit. Botryoidal pyrite partially altered to goethite and overgrown by supergene sphalerite crystals was found lining a small cavity formed by weathering of limestones at the margin of the Collapse Breccia. Only slight replacement of fossil wood by supergene iron sulphide has taken place.

A bizarre occurrence of undisputably supergene pyrite at Tynagh illustrates the speed with which sulphides can form from weathering solutions. In mid-1964 the writer found several dead newts, identified as belonging to the species Titurus vulgaris Limna, which occurs widely in Ireland at the present time, in an exploration trench in Calp mud dug 18 months or so previously. All were dehydrated but otherwise well-preserved (Plate 8.18). No newts or casts of newts were found in residuum walling the trench, and since the species is not known in the pre-Pleistocene (Charrig, pers. comm.), their demise was almost certainly of very recent date. Polished sections of two newts showed that they had been replaced by small amounts of pyrite as disseminated grains and framboidal aggregates (Plate 8.19). The absence of other supergene sulphides is probably accounted for by the preponderance of iron in the residuum of the area in which the cacases were found. Enigmatic aspects of the matter are why the creatures chose to assemble in the trench, and what causedtheir death.

Plate 8.18 - Carcase of a newt, 1.5in. long, found in a trench in Calp mud.

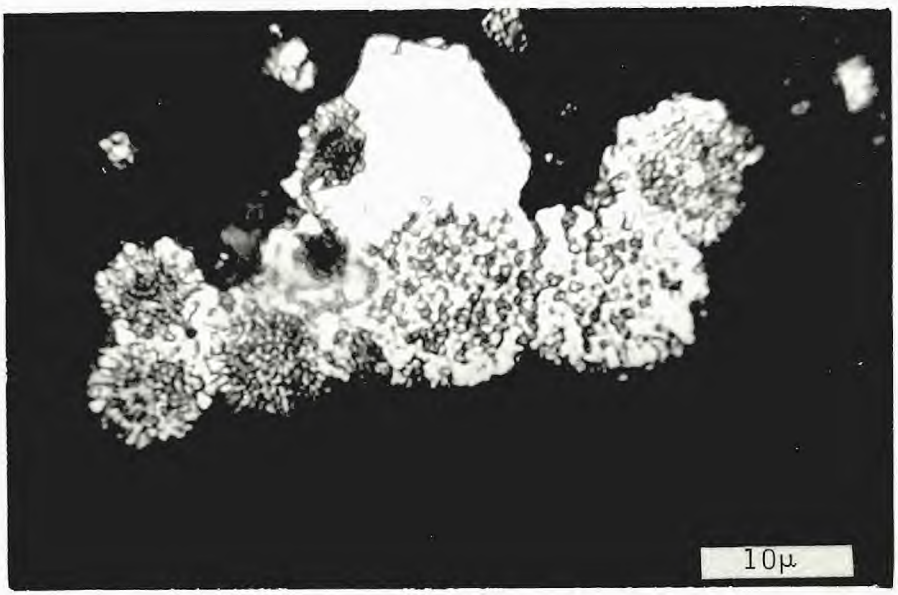


Plate 8.19 - Framboidal and granular pyrite formed by replacement of a newt carcase. Polished section. Oil immersion.

(ii) Theory of supergene sulphide formation

Formation of sulphides from aqueous solutions takes place by reactions between dissolved metal ion and reduced or partially reduced sulphur species in gaseous, solid or ionic form. The sulphur species concerned include H_2S, elemental sulphur and bisulphide ion, all of which are stable in water at atmospheric temperatures and pressures. They also include such relatively unstable species as sulphite, bisulphite, thiosulphate and polysulphide ion. Rickard (1968) has shown that polysulphide anions are involved in the formation of pyrite from aqueous solution under low temperature and pressure conditions. Other workers have synthesised pyrite from thiosulphate solutions (Browne, 1969).

Reduced sulphur species may be produced inorganically, for instance by the action of sulphuric acid on pre-existing sulphides, or biochemically, as a byproduct of the metabolic reactions of sulphate-reducing bacteria (see Chapter 9).

The conditions under which sulphides form as stable or metastable phases during weathering are limited by other reactions that take place in natural environments, in particular oxidation of reduced sulphur species to sulphate ion. In strongly oxidising environments this takes place almost immediately, and redox potentials exceeding +0.4mV effectively prohibit sulphide formation. Only fresh rainwater, free-flowing surface waters, and atmospheric solutions percolating through well-drained parts of oxidising sulphide deposits characteristically have an Eh of +0.4mV or more (Baas Becking et al, 1960). At positive Ehs below that value, sulphides may be precipitated from solutions with a pH of less than about $4\frac{1}{2}$, while in reduced environments they may form solutions of any pH.

Natural aqueous environments in which the rate of generation of reduced sulphur species commonly exceeds the rate of supply of dissolved oxygen to the system include stagnant surface and underground waters, and waters moving slowly either through organic materials in which sulphate-reducing bacteria are active or through inorganic materials that include sulphides. Granger and Warren (1969) have recently emphasised the importance of unstable reduced sulphur species resulting from limited oxidation of pre-existing sulphides in the non-biologic formation of supergene sulphides, and shown that this can take place well below the water table.

The tendency that the sulphides of some metals have to crystallise from polymetallic solutions before the sulphides of others is expressed by the Schurmann Series, which is in part: Hg, Ag, Cu, Cd, Sb, Pb, Zn, Ni, Co, Fe, As. Metals higher in the series tend to be precipitated as sulphides more readily than metals lower in the series. Their sulphides tend to replace those of metals lower in the series, and to do so more completely the farther the two metals are apart in the series. Since it is by no means certain exactly how the sulphides of most metals form under low temperature and pressure conditions, let alone how such environmental factors as the activity of extraneous ions in the crystallisation medium affect their solubility, it is not surprising that the observed crystallisation behaviour of supergene sulphides does not always conform to that predicted by the Schurmann Series. In particular, it is common for supergene sulphides formed in pyritic materials to selectively replace sulphides of metals closer than iron in the series.

Many factors determine which of two or more possible sulphides of a particular metal form during weathering. Marcasite, for instance, is more likely to form from strongly acid solutions than pyrite, though either may form from solutions with a wide

range of pH (Rickard, 1968). The structure of zinc sulphide precipitated from low-temperature aqueous solutions may also be primarily pH-dependent, wurtzite (the high-temperature ZnS dimorph) forming metastably in preference to sphalerite from acid solutions (Allen et al, 1914). Several investigators cited by Deer at al (1962) have found that preferential formation of wurtzite is favoured from solutions with a high Mn or Cd content.

Similar uncertainty exists about the factors that control the structure of cadmium sulphide precipitated from low-temperature solutions. According to Traill and Boyle (1955), the cubic dimorph hawleyite is likely to be precipitated from acid sulphate solutions. The experimental work of Sato (1959) suggests, however, that if they contained even small amounts of chloride ion, such solutions would tend to precipitate instead the hexagonal dimorph greenockite.

The case of copper is very much more complicated, since at least four binary copper sulphides and two copper-iron sulphides are capable of stable formation from low-temperature aqueous solutions. Even in oxidising macroenvironments it is usual for some metal ion released during weathering of copper or copper-iron sulphides to be immediately reprecipitated as sulphide by reduced sulphur species generated at alteration fronts. In this way chalcopyrite may alter sequentially through bornite, covellite (CuS), various copper sulphides with the general formula $Cu_{x>1<2}S$, to chalcocite (Cu_2S). Conversely, where Eh considerations prohibit reprecipitation of dissolved copper as sulphide, chalcocite alters through digenite to covellite by step-wise release of copper ion into solution (Sato, 1960). Exactly how bornite and chalcopyrite form mutual replacements during weathering is not understood.

Differences in Eh and metal ion activity from one part of the weathering environment to another can give considerable diversity to paragenetic relationships between secondary sulphides of copper. This is particularly to be expected in poorly-drained materials in zones of partial oxidation.

(iii) The natural occurrence of some supergene sulphides

Against the theoretical background given in the previous section, it is worth briefly reviewing the occurrence and tendency to concentration of some supergene sulphides that occur at Tynagh in base metal deposits elsewhere.

By far the most common are supergene sulphides of copper, which are almost invariably present in the weathered zone of cupriferous sulphide deposits, irrespective of host-rock lithology. The latter is, however, a major determinant of whether or not copper is substantially concentrated in supergene sulphide form. Concentration is severely inhibited in calcareous environments, dissolved copper being readily reprecipitated by ionic carbonate species to form the fairly insoluble carbonates malachite and azurite. In non-calcareous environments, prolonged weathering of pyritiferous copper mineralisation by meteoric waters percolating towards a gradually receding or deep static water table tends to concentrate copper in sulphide form at a level equatable with the water table controlling the process.

Silver is less commonly concentrated as supergene sulphide than copper, partly because silver forms highly insoluble halides, and partly because silver mineralisation is relatively less common in non-calcareous environments.

As for cadmium, which follows silver and copper in the Schurmann Series, it is probably true to say that weathering of cadmiferous sphalerite generally yields some cadmium sulphide, though this is never concentrated by weathering processes to an extent that would make it worth working for its own account. Cadmium and silver taken into solution during weathering of lead-zinc-copper sulphide mineralisation in calcareous rocks tend to be partially reprecipitated as lattice constituents of carbonates of other metals.

Supergene sulphides of lead and zinc, metals intermediate in the Schurmann Series and usually associated with each other in mineral deposits, have been identified with varying degrees of certainty at many places, some of which were referred to in Chapter 7. There are no authenticated cases of supergene enrichment of orebodies by lead or zinc sulphides. Brown (1936) estimates that supergene galena and sphalerite together comprised 8% of mill heads at Balmat, New York, in 1933, but does not refer to their formation as an enrichment process.

There is no general agreement about the conditions under which supergene sulphides of lead and zinc form from weathering solutions. Supergene formation of wurtzite has not, to the best of the writer's knowledge, been authenticated, though analogy with marcasite suggests that it may occur by replacement of plant debris in, for instance, brown coals and lignites.

Taylor (1938) considers that supergene galena at Broken Hill, Zambia, formed above the water table near an advancing front of oxidation. It should be added, however, that there is some uncertainty about the history of water table movements in the region. Supergene galena at Abenab West, South-West Africa, and Broken Hill, New South Wales, he believes to have formed in the zone of deep oxidation due to prolonged weathering under hot, arid conditions and perhaps because of the scarcity of pyrite. Different conditions of formation are indicated at Balmat, where supergene galena and sphalerite occur over 1,000 vertical feet in limestone terrain deeply affected by pre-glacial karstic weathering. Here the sulphides are thought to have formed below the water table from slowly circulating groundwaters with a high metal content (Brown, 1936). Both occur from near outcrop to 660 ft. below present sea level - a vertical range of about 1,600 ft. - in Sardinia (Zuffardi and Salvadori, 1964). Perhaps significantly, Sardinia

contains geomorphological evidence of strong and repeated rejuvenation of the drainage.

(iv) Supergene sulphide formation at Tynagh

Turning now to the Tynagh residuum, it is clear that there has not been a historically distinct phase of supergene sulphide formation in the deposit as a whole. Rather, it seems that supergene sulphides have formed in different places at different times as part of the mineralogical evolution of particular bodies of residuum during chemical weathering. At all times their formation in what has been termed the supergene sulphide zone was probably encouraged chiefly by a combination of sluggish drainage and limited oxidation of pre-existing sulphides. Although, in the main, they formed non-biologically, bacterial activity may have played some part in lowering the Eh of pore fluids in residuum containing limestone-derived organic matter. It was certainly instrumental in the sulphidation of fossil wood and the newt carcases referred to earlier.

Supergene sulphides of metals high the Schurmann Series began to form at an early stage of rock weathering; those of metals lower in the Series at a stage when decalcification was well advanced and oxidising agents were concentrating their attack on sulphides. In both cases sulphide formation mainly occurred in comparatively strongly reduced microenvironments in the immediate vicinity of oxidising sulphide grains. The apparent paucity of supergene sulphides of zinc and iron, and the fact that silver, cadmium and perhaps copper were able to migrate for tens of feet through pyritic residuum before being reprecipitated as sulphide suggests that strongly reducing conditions were not widespread in any part of the deposit at any time.

Small zones of strong reduction were set up by bacterially-assisted decomposition of wood fragments. This process depressed the Eh of pore fluids in the surrounding residuum sufficiently for cadmium, but apparently not zinc, to be preferentially precipitated in the inorganic materials. Variations in the Zn:Cd ratio of wood from different parts of the deposit may be a reflection of this, or it may reflect variations in the cadmium content of primary sphalerite. The low iron sulphide content of fossil wood is attributed partly to the slow oxidation rate of pyrite in poorly drained materials, and partly to successful competition by zinc for available sulphide ion.

The presence of hawleyite in some of the residuum may indicate that dissolved metals were locally transported as chlorides, but analogy with the ZnS dimorphs makes it equally likely that the structure of CdS precipitates was determined by the cationic rather than the anionic composition of cadmium-bearing solutions.

The widespread oxidation of supergene sulphides was due to physicochemical variations in both space and time. Because pore fluids were not stagnant at any time, the stability of sulphides was at all times limited by macroenvironmental Eh-pH conditions, which were permanently inimicable to the survival of sulphides as such in all but the most poorly drained materials (in practice, the interior of compact aggregates). Thus at all times supergene sulphides were inherently subject to alteration. The rate at which this took place at a particular time depended partly on the drainage characteristics of their matrix and partly on the intrinsic and/or extrinsic factors that have caused differential solubility among sulphide species in the Tynagh residuum.

A time-dependent contributory factor was alkalinisation of pore fluids due to progressive decomposition of the deposit's

limestone wallrocks. This effect which is dealt with more fully in the next section, probably became more marked with time because of denudation of the Tynagh area, and it has been reinforced in the upper parts of the deposit by the superimposition of a calcareous till.

It is doubtful whether sulphides of metals lower than cadmium in the Schurmann Series are capable of forming in the residuum at the present time, except in such exceptional milieu as decomposing animal tissue. The characteristic smell of H_2S is not detectable in the open pit.

B. The Supergene Carbonate Zone

(i) Mineral distribution

Carbonates of lead and zinc are almost ubiquitous in dark residuum referred to the supergene sulphide environment, and there has been some replacement of supergene galena by cerussite. They are, however, most strongly concentrated at the periphery of the deposit, especially in its partial envelope of in situ oxides (Figs. 8.1 and 8.2). Malachite and azurite, which are absent from typical dark residuum, are locally very abundant in the peripheral oxide zone. Other supergene carbonates that it contains are dundasite (Pb) and aurichalcite (Cu, Zn).

In general, smithsonite is most strongly concentrated at the margin of sphalerite-rich portions of the Collapse Breccia, and carbonates of lead and copper at the margins of the eastern sulphide rubble body, which contains much more galena than sphalerite and is locally rich in primary copper sulphides. Exceptions to this general scheme arise largely from the imperfection of the pattern of primary metal zonation, e.g. local concentrations of zinc-rich mineralisation in the "copper-lead zone".

The peripheral carbonate zone has been strongly enriched in lead, zinc and copper. In the western half of the deposit about 100,000 tons of smithsonite ore, much of it containing over 30% Zn, has been formed by replacement of barren and sparsely mineralised limestone. In the eastern half, assay sections containing as much as 60% Pb or 15% Cu occur in oxide ores formed by supergene alteration of limestones that generally contain less than a quarter of these amounts of primary metal. In places there has been marked enrichment of the carbonate zone in silver.

Fig. 8.3 shows vertical assay profiles that exemplify supergene concentration of lead, copper and silver in the carbonate zone, the first two metals mainly as cerussite and malachite respectively. The mineralogy of silver in this environment will be discussed later. In both sections the in situ oxides are a residuum of Waulsortian micrites that contained some primary mineralisation. It is not possible to say what the zinc content of the primary mineralisation was, or what proportion of the reprecipitated lead, copper and silver originated in the altered limestones.

Significant features of metal distribution in the two sections are that:

(i) copper is concentrated closer to the rock-residuum contact than lead;

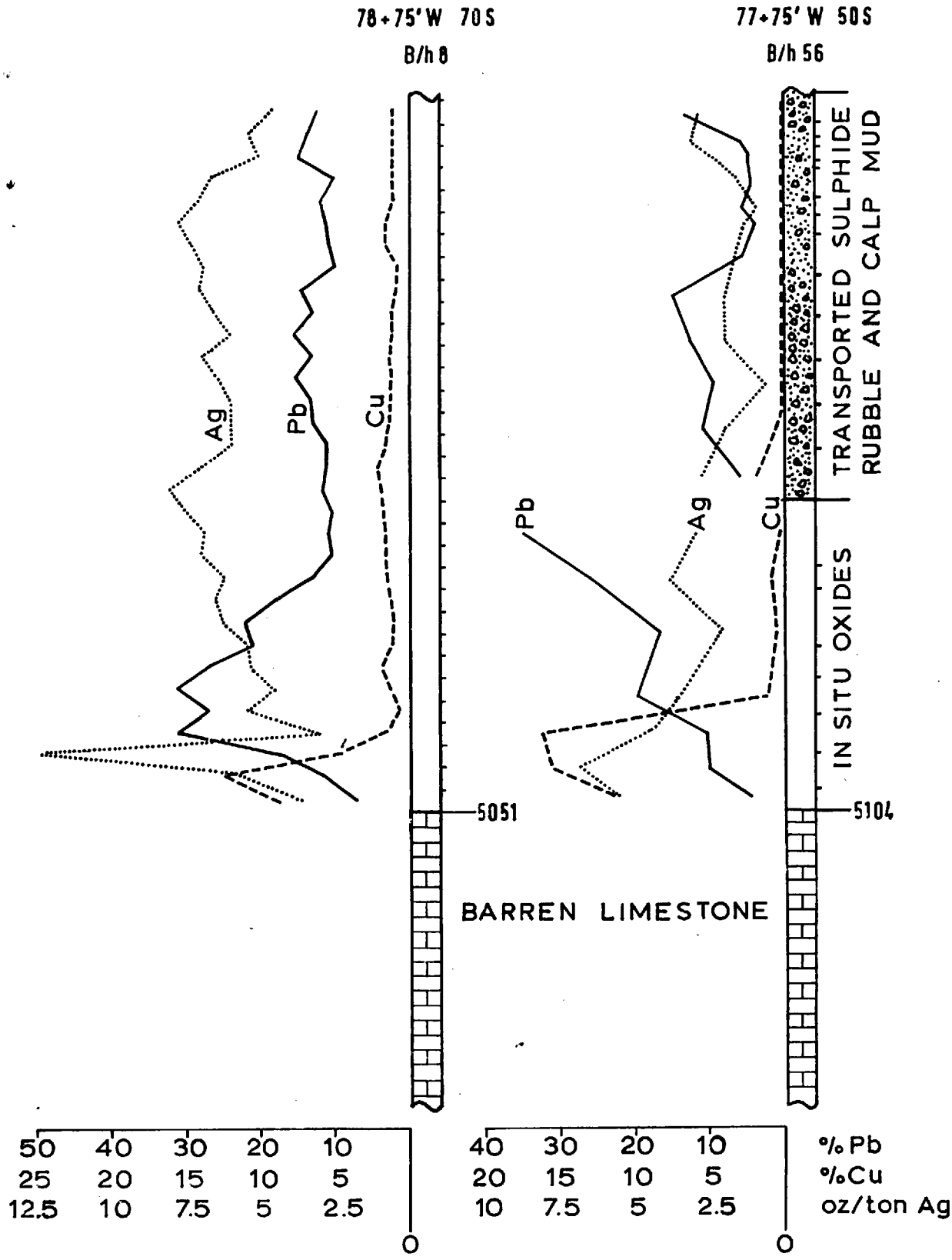
(ii) silver follows copper more closely than lead;

(iii) Ag:Cu ratios vary considerably, and in both profiles silver does not peak in the same assay section as copper.

The width and metal tenor of lead/copper carbonate zone vary considerably. Where the carbonate-rich materials are an in situ residuum of limestones, both are more closely related to the lithology and primary grade of the altered limestones than to the

VERTICAL SCALE 1in = 20ft

Fig. 8.3



thickness or grade of overlying detritus or to the attitude of the latter's lower contact. The residuum of well-mineralised micrites has been more substantially and extensively enriched than that of barren or poorly mineralised micrites. Enrichment is widespread but less pronounced in the residuum of more argillaceous limestones, while in grey and black residuum types it tends to be localised still more, and to result from the formation of lead and zinc but not copper carbonates. Where the enriched materials contained little primary copper, deposition of exogenic lead as carbonate is accompanied by a decrease in silver:lead ratios. It is not known whether this decrease is proportional to the amount of introduced lead.

The distribution of zinc in two vertical borehole sections through the western part of the deposit is shown in Fig. 8.4. In both there is a marked increase in the metal in the lower 40-60 ft. of the section. Analyses supported by field and laboratory investigations show that virtually all the additional zinc is present as smithsonite. The enriched zone comprises an upper part (A) in which dark transported residuum rich in primary sphalerite has been augmented by a granular, largely non-replacive precipitate of smithsonite (Plate 8.20); an intermediate part (B) in which the enriched material is a limonitised version of A, and a lower part (C) in which smithsonite has formed by direct replacement of limestone (Plate 8.21). The upper contact of B has been placed where the borehole logs first record "oxidised" (i.e. limonitic) residuum, and the lower contact where lead:silver ratios first fall well below the normal range for the transported residuum of this area (0.35-0.80 oz. Ag/% Pb). In one section C is sub-divided into an upper part in which smithsonite is accompanied by much limonite, and a lower iron-poor part with a zinc content of 43%. This compares with 52% in pure smithsonite, the balance being represented mainly by limestone relics and cerussite. It is not uncommon for limestone fragments in the zone of zinc enrichment to

VERTICAL SCALE 1 in = 20 ft

Fig. 8.4

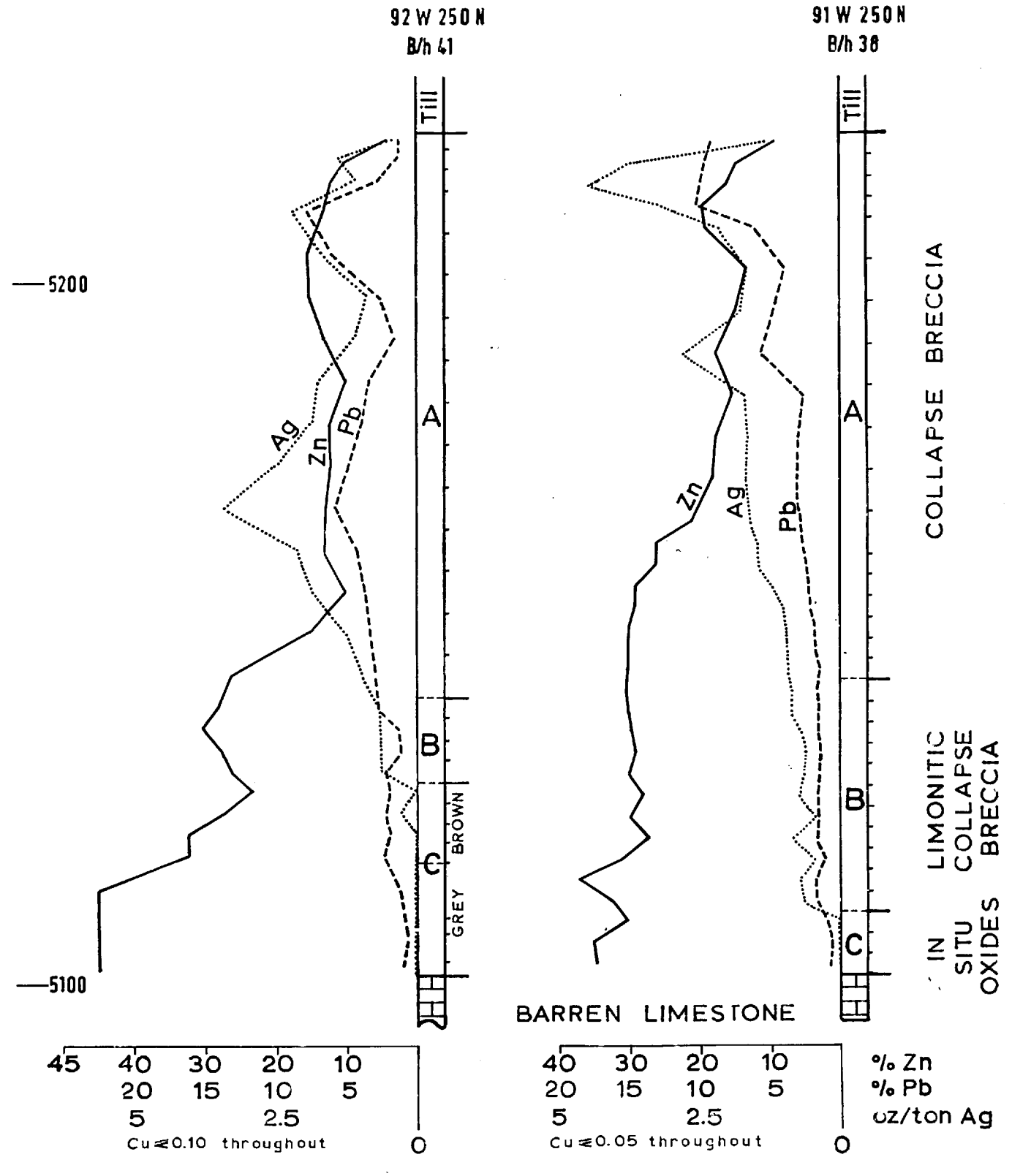


Plate 8.20 - Crinoidal biomicrite partially pseudomorphed by smithsonite. The coarse-grained calcite of the crinoid stem fragments resisted replacement by smithsonite and was subsequently dissolved, yielding smithsonite casts of the bioclasts. Specimen size 3in.x2.5in.

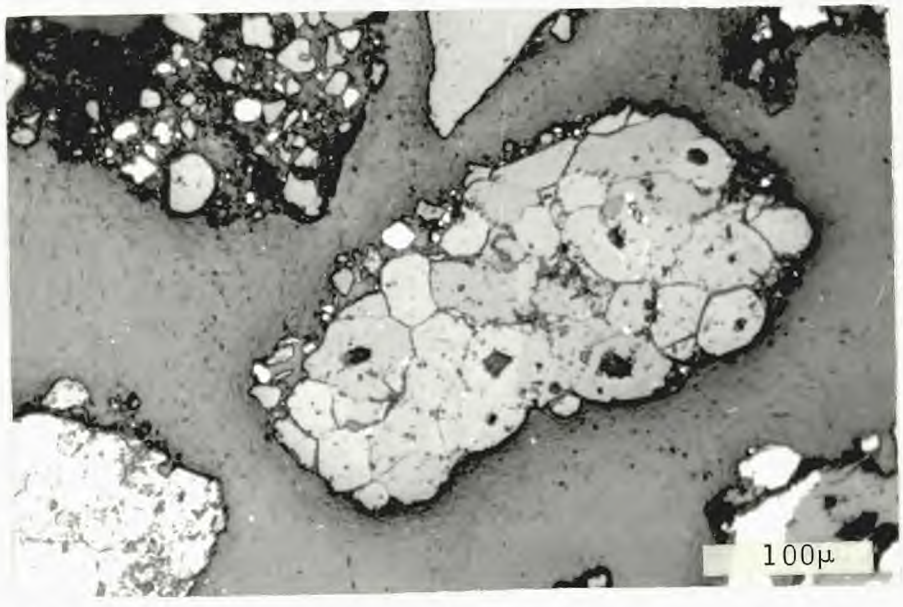


Plate 8.21 - Grain (central) consisting of an anhedral mosaic of smithsonite. Polished section.

be wholly replaced by limonitic smithsonite without substantial alteration of contained veinlets of primary galena, and it will be noted that lead: zinc ratios are much lower in sub-zone C than they are in the overlying detritus.

Varying amounts of limonite, generally accompanied by hydrated manganese oxides and sometimes by a little barite that may be of supergene origin occur in sub-zone C, indicating supergene enrichment in iron, manganese and perhaps barium. Most of the manganese is thought to have been derived from weathering of primary sphalerite. Cadmium occurs locally as supergene sulphide, but is probably more abundant overall as a lattice constituent of smithsonite.

Considered as a whole, the zone of demonstrable zinc enrichment varies in width from less than 1ft. to more than 60 ft. These figures relate to its extent measured normal to the rock-residuum contact. It is best developed in and below the north-west quarter of the Collapse Breccia and on the deposit's northern margin. The widths of constituent sub-zones A, B and C vary independently of each other and of the total width of the enriched zone. The combined width of A and B is greatest in the lower parts of the deposit. Sub-zone C tends to be narrow where the margin of the Collapse Breccia is steep and the wallrocks are poorly bedded, but neither this relationship nor its converse is without many exceptions.

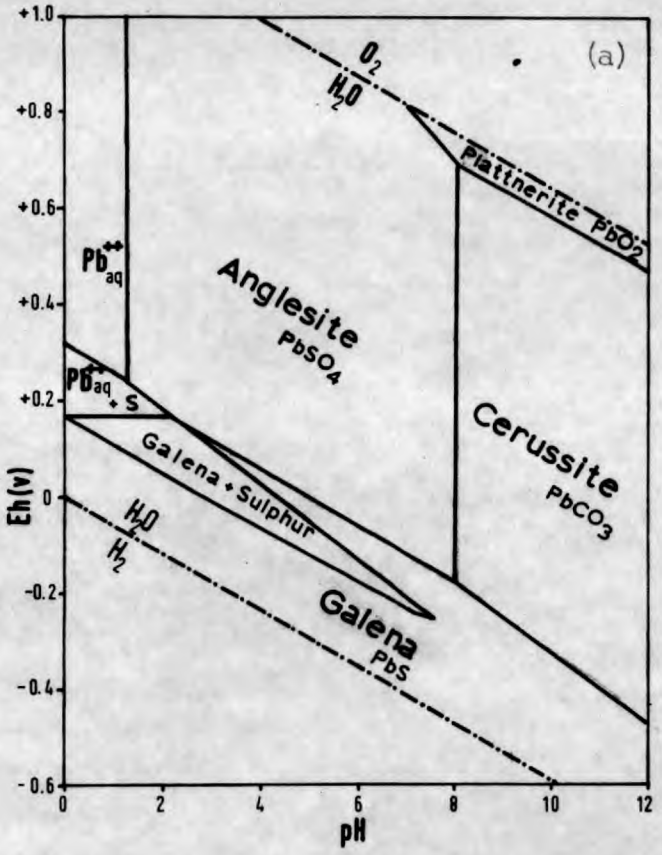
More zinc has been deposited as smithsonite than seems to have been leached from residual primary sphalerite. This may be a false impression arising from the difficulty of recognising supergene alteration in fine-grained primary sphalerite. Alternatively, the excess zinc may have been derived from residuum since removed by erosion.

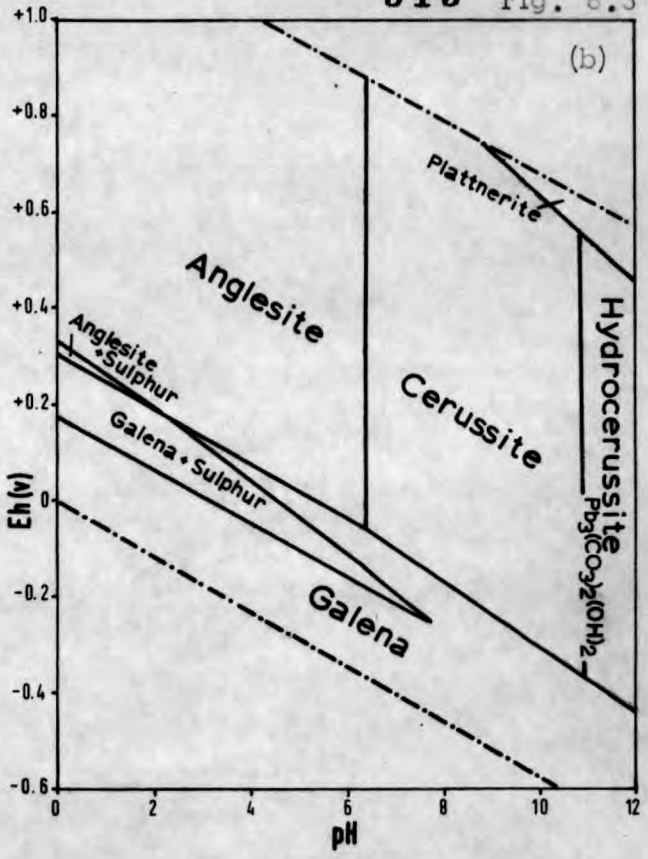
Small amounts of lead, zinc and copper have been reprecipitated in the carbonate zone as dundasite, aurichalcite and hemimorphite. Beudantite, cuprite and native copper are widespread, but are considered to be products of the gossan-forming weathering regime discussed in the next section. Other supergene minerals present in the carbonate zone are barite, manganomelane, allophane and various clay minerals.

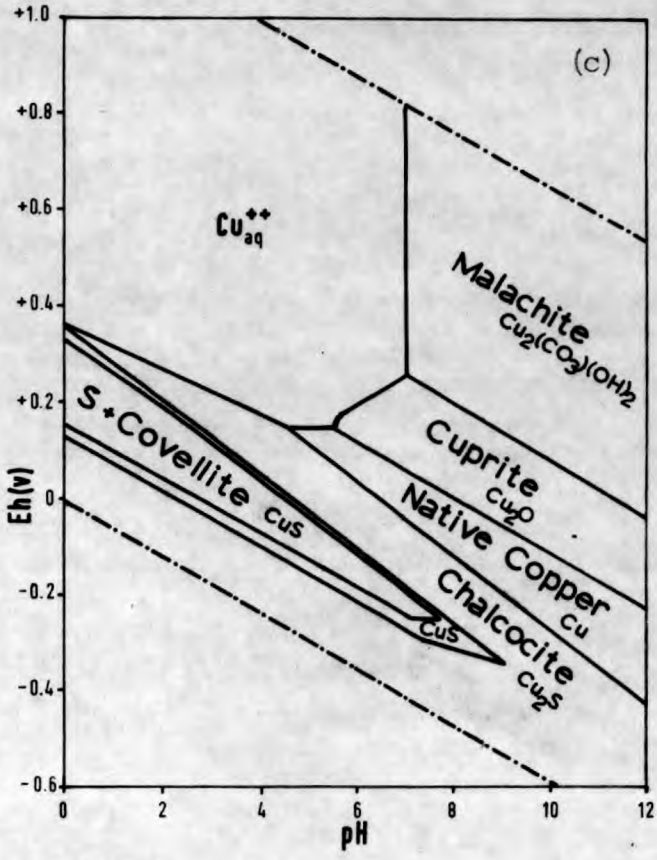
(ii) Theory of supergene carbonate formation

Base metal carbonates form from aqueous solution by reaction between metal ion and a dissolved carbonate species, usually bicarbonate ion. Experimental and thermodynamic data from various sources, especially Garrels (1954) and Garrels and Christ (1965), indicate that the stable precipitates of copper and lead from dilute solutions of their sulphates acting on calcite are malachite and cerussite respectively. Concentrated cupric sulphate solutions acting on calcite tend to precipitate basic copper sulphates such as brochantite and antlerite (Garrels and Dreyer, 1952), and concentrated lead sulphate solutions anglesite.

The stability field of malachite and cerussite in aqueous solutions that have features in common with those that occur in near-surface weathering environments are shown in Fig. 8.5. Where weathering solutions are in equilibrium with the atmosphere, cerussite is unstable with respect to anglesite in oxidising solutions with $pH < 8$. Where slow overturn of waters inhibits their equilibration with the atmosphere, or rapid bacterial generation of CO_2 is taking place, increasing CO_2 partial pressures favour its stable formation from neutral and slightly acid oxidising solutions. Under these circumstances, too, the field of malachite tends to eliminate that of cuprite, and malachite may form stably







(a) The system $Pb-H_2O-O_2-S-CO_2$

Total dissolved sulphur = 10^{-1}

CO_2 partial pressure = 10^{-4}

Total ionic activity = 10^{-6}

(b) The system $Pb-H_2O-O_2-S-CO_2$

Total dissolved sulphur = $10^{-1.5}$

Total dissolved carbonate = 10^{-1}

(c) The system $Cu-H_2O-O_2-S-CO_2$

Total dissolved sulphur = 10^{-1}

CO_2 partial pressure = $10^{-3.5}$

STABILITY FIELDS OF SOME LEAD AND COPPER COMPOUNDS IN WATER AT 25°C AND 1atm. TOTAL PRESSURE. After Garrels and Christ, 1965.

from slightly reducing alkaline solutions. (Cerussite, by comparison, may be precipitated from slightly to moderately alkaline solutions that are in equilibrium with atmospheric CO_2.) High CO_2 partial pressures are reputed to favour the formation of azurite.

Zinc is not directly influenced by Eh, being bivalent in all its salts and compounds. Smithsonite is the most stable zinc mineral in solutions saturated with atmospheric CO_2 and in the pH range 6.1-8.2. In solutions with pH >8.1 in equilibrium with the atmosphere it is less stable than hydrozincite, $Zn_5(OH)_6(CO_3)_2$, while hemimorphite may form from solutions with pH< 6.2 if the Si-O radical is available (Takahashi, 1960). Kelly et al (1958) have shown that climate has a considerable influence on the mineralogy of oxidation products of zinc, aridity favouring the formation of hydrozincite in relative abundance, and humid conditions the formation of hemimorphite or smithsonite, depending on the pH of groundwaters. A change from arid to humid conditions would be expected to cause partial to complete dissolution of pre-existing hydrozincite, and reprecipitation of zinc as hemimorphite or smithsonite. In humid regions, hydrozincite generally does not form below the water table (Takahashi, 1960).

The stability fields of aurichalcite and dundasite have not been established, but the field relationships of these minerals generally indicate that they form under oxidising conditions by neutralisation of acid sulphate solutions of their constituent metals (Boyle, 1965).

(iii) Supergene carbonate formation at Tynagh

Applying the data reviewed in the previous section to the situation at Tynagh leads to the conclusion that the residual deposit's peripheral carbonate zone resulted from reactions between rock-forming calcite and dilute, polymetallic sulphate

solutions migrating through pre-existing residuum. The shape of the zone shows that it was formed by solutions migrating in various directions, but chiefly downwards and northwards. Assay profiles do not suggest that the zone has ever been "stranded" by a sharp, general fall in the local water table. Had this happened, it is doubtful whether there would now be such simple patterns of supergene metal distribution within it.

The Tynagh carbonate zone is an exceptionally good example of fractional precipitation of metals from weathering solutions. This phenomenon is well-known in lead-zinc deposits in calcareous rocks, notably those of the Tintic district, Utah (Loughlin, 1914, 1918). Morris and Lovering (1952) have shown that post-mining groundwater dispersion of metals in this district has been Zn> Cu > Pb. Little migration of silver has taken place in carbonate rocks and in rocks containing sulphides.

The main cause of fractional precipitation at Tynagh was a progressive increase in the pH of solutions towards the limestone decomposition front. The maximum mean pH value attained was probably about 9 at reaction fronts in pure limestone, somewhat less in argillaceous limestone.

Those metals for which assay data are available - lead, zinc, copper and silver - were precipitated in order of decreasing sulphate solubility (Table 8.2), confirming that sulphate was probably the dominant ionic sulphur species in the migrating solutions. Where the latter acted on pure limestones, the main precipitate from the strongly alkaline solutions at the reaction front was malachite or smithsonite, depending on the cation composition of the solutions. Cerussite was precipitated in greatest quantity from somewhat less alkaline solutions at a variable distance from the reaction front. Where the latter was in argillaceous limestones, the formation of copper carbonates tended

Table 8.2 Solubility of some sulphates and carbonates in water
(gm/100gm H_2O at approx.25°C, 1atm.)

	Sulphate	Carbonate
Ca	209	0.0013
Cd	75.5	insoluble
Zn	53.18	0.001
Fe^{++}	23.00	0.073*
Cu^{++}	19.30	insoluble
Ag	0.57	0.032
Pb	0.00425	0.0001
Ba	0.00022	0.0022

*Saturated with CO_2 at 7atm.

Source: Handbook of Chemistry and Physics,45th edition,1964; Lindgren,1933.

to be inhibited, and some cerussite-enriched materials in parts of the deposit where dissolved copper was certainly not in short supply contain little or no malachite (see below).

Silver appears to have been precipitated in the carbonate zone chiefly as a lattice constituent of malachite and, subordinately, cerussite. It is evident that its incorporation by malachite was not favoured by pH conditions close to the reaction front. Some silver may have been reprecipitated as a lattice constituent of binary copper sulphides formed by local reduction effects in the carbonate zone. Reduction of dissolved cadmium sulphate certainly occurred in the carbonate zone, though more cadmium was probably reprecipitated in it as a lattice constituent of smithsonite. Cadmium substitution in smithsonite was probably limited by widespread reprecipitation of cadmium as sulphide elsewhere in the deposit, and by the greater solubility of its sulphate compared to that of zinc sulphate.

Field evidence does not suggest that iron has been selectively precipitated in a particular part of the carbonate zone, though the latter has in most places been enriched in iron as limonite and goethite. There is commonly a limonite-deficient zone close to the rock-residuum contact. In some places this contains massive malachite or smithsonite, in others friable material resulting from partial to thorough disaggregation of limestone.

It is conjectured that iron migrating out of dark residuum was chiefly in the ferrous state, oxidation of Fe^{++} to Fe^{+++} having been inhibited by the acidity and generally anoxic character of the solutions.[1] Their increasing pH towards the

---

[1] An indication of the acidity of waters now draining from Calp mud is that in places they precipitate a greenish-yellow substance presumed, from the fact that it alters to limonite in a matter of hours, to be a ferroso-ferric compound, probably one of the "green rusts" referred to by Rickard (1968). Donovon (1965) recorded a pH of 3.9 for pore waters in pyritic Calp mud.

margin of the deposit increased both the rate of oxidation of ferrous iron and the rate of hydrolysis of ferric sulphate to form ferric hydroxide. Under the saturated conditions prevailing, the latter was converted by partial loss of water to goethite, which tended to adsorb water and yield limonite.

Wells (1910) has shown that oxidation of Fe^{++} to Fe^{+++} is accelerated by the presence of Cu^{++} ion in sulphate solutions, but it is not known whether this was a factor in limonite formation at Tynagh. Some ferrous iron was precipitated in the carbonate zone as a lattice constituent of smithsonite. The apparent absence of supergene siderite at Tynagh suggests that solutions in the carbonate zone were not, in general, strongly reduced.

Decomposition of limestone at the deposit's margin, supplemented to some extent by continuing dissolution of limestone relics elsewhere, by introduction of atmospheric and soil-derived CO_2, and perhaps by bacterial generation of CO_2 within the residuum, caused widespread precipitation of base metal carbonates in the interior of the deposit. During its later history, alkalinisation of pore fluids in the upper part of the deposit resulted from drainage of surface waters through calcareous glacial tills (though this effect has evidently been very limited both in depth and in extent since the superimposition of the existing till (Donovon, 1965)).

Counter-flow diffusion of bicarbonate ion from the limestone alteration front progressively increased the pH of pore fluids in detrital materials to a value at which migrant zinc could be reprecipitated as carbonate, and the zone of smithsonite enrichment gradually expanded towards the centre of the deposit. In doing so it encroached on materials containing supergene sulphides of several metals, and in places on transported gossan. A concommitant of the process was accelerated oxidation of pyrite in the areas most

affected (Plate 8.22), and substantial reprecipitation of migrant iron within them as limonite. Local variations in the width of the smithsonite-enriched zone and in the relative widths of its main subdivisions (B and C in Fig. 8.4) are attributed to variations in (a) the attitude of the rock-residuum contact, (b) the main flow direction of migrating solutions, (c) the purity, texture and structure of limestone wallrocks, (d) the permeability and primary zinc content of pre-existing residuum. The composition of solutions in the wallrock alteration zone evidently varied considerably from place to place, causing wide variation in the volumetric ratio of limestone dissolved to supergene minerals precipitated. In some places, limestones acted on by metal-deficient solutions were simply dissolved.

Widespread precipitation of cerussite, partly as a replacement of primary and secondary galena, occurred in the same way. Even if the visual impression that galena in dark residuum was replaced directly by cerussite is false, the probability remains that formation of cerussite in this type of material took place under slightly reducing conditions. It is not impossible that, except in zones of relatively rapid water circulation that are discussed in the next section, reducing conditions prevailed throughout the deposit while the processes outlined above were going on. This is suggested by the failure of malachite to form in dark residuum and its relative paucity in the cerussite-enriched residuum of argillaceous limestones, and by the common occurrence of cadmium sulphides in the carbonate zone. Large-scale replacement of limestone by smithsonite has taken place below the water table in the Tintic district (Loughlin, 1914): it may, in fact, only be possible where water circulation is severely restricted.

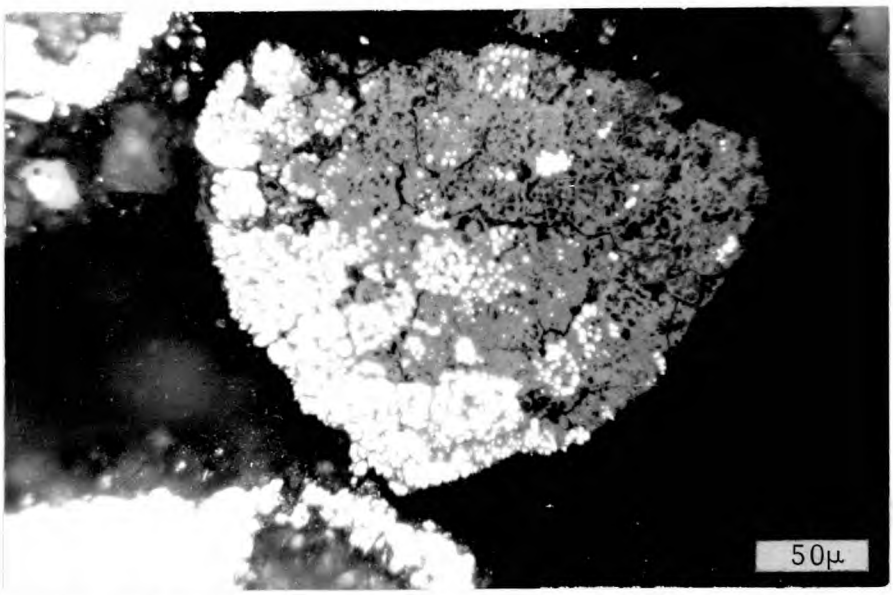


Plate 8.22 - Replacement of framboidal pyrite aggregate by limonite. Polished section. Oil immersion.

Field relationships indicate that aurichalcite and hemimorphite were formed in the carbonate zone as a direct result of reactions between rock-forming calcite and solutions containing dissolved copper, zinc and silica of very local origin. Some aluminium leached from the residuum of argillaceous limestones was reprecipitated within it as a constituent of dundasite. On the southern margin of the deposit fairly substantial amounts of dundasite formed as an alteration product of cerussite, probably as a result of northward migration into pre-existing residuum of slightly acid solutions charged with aluminium by progressive decay of Lower Muddy Limestone.

Local variations in the supergene clay mineralogy of the carbonate zone, in particular variations in the relative abundance of illite and kaolinite/halloysite, probably resulted chiefly from local variations in the non-carbonate mineralogy of the weathered rocks and in their rate of weathering. Kaolinite and halloysite form preferentially from acid solutions deficient in Ca, Mg and Fe^{++}, and are likely to have been precipitated at Tynagh from oxidising and slightly reducing solutions of their constituents acting on pyritiferous residuum that had been strongly leached of rock-forming carbonates (Ross and Hendrix, 1945). Illite and montmorillonite form from alkaline solutions, and tend to be the dominant clay minerals formed by partial decomposition of argillaceous limestones containing pyrite under waterlogged conditions (Keller, 1957). Climatic conditions were of subordinate importance in determining the supergene clay mineralogy of the deposit.

C. Gossan Zones

(i) Distribution and mineralogy

Mineralogically distinct from the oxides just described are the Fossil Gossan and its associated talus, and some of the in situ

oxides in the SE quarter of the deposit. These materials consist predominantly of barite and limonite, and contain a characteristic assemblage of oxidation products that includes beudantite, anglesite and native silver. They typically have a low content of lead, zinc and copper, but their average silver content of 10 oz/ton makes them economically mineable for that metal alone. Geochemical investigations by Donovon (1965) suggest that, relative to other types of residuum, they are enriched in mercury. In several of these respects they closely resemble the gossans of many other base metal sulphide deposits, and are named accordingly.

Two features of the Tynagh gossan zones that are particularly pertinent to their origin are their distribution in space, and the distinctive patterns of secondary mineral and metal zonation that are associated with them.

An important aspect of their distribution is that the gossan zones as a whole do not bottom at a uniform elevation, and that they have a vertical overlap of more than 150 ft. with dark residuum of the supergene sulphide zone. Locally, in situ oxides with the characteristics summarised above form the floor of the eastern core deposits and are closely overlain by protore detritus containing abundant supergene galena, while the Fossil Gossan is partially overlapped by Calp mud containing supergene sulphides of several metals. Arrangements of this kind suggest that either gossanisation took place during intermittent depressions of the general water table of the area and before the formation of the sulphide-rich residuum, or that it took place largely below the general water table. The first alternative is impossible to reconcile with evidence presented in Chapter 6 that accumulation of the core materials and the formation of the cavities that they occupy occurred penecontemporaneously.

Mineralogical zoning around gossan zones is best seen in the SE quarter of the deposit. Here, gossanised materials occur in irregular and steep pipe-like zones up to 100ft. across and grade mineralogically into rich lead/copper carbonate ores. Zones of transition between the two types of material are up to about 50ft. wide and vary in attitude from vertical to horizontal. Within them, mimetite is unusually abundant and in places occurs as a pseudomorphic replacement of cerussite. Native copper and cuprite (the latter sometimes as a replacement of malachite) are common in partially gossanised materials. Beudantite, accompanied by lesser amounts of anglesite, tends to become more abundant than cerussite towards centres of gossanisation, and the width of replacement rims of supergene copper sulphide on grains of primary sulphide to decrease in the same direction. Limonite is the main host of iron in both types of material, which have approximately the same range of iron content (5-15%).

Noteworthy features of the distribution of ore metals in and around the central gossan are exemplified by the assay profiles shown in Fig. 8.6. Fig 8.6a relates to a part of the gossan that is underlain (below about 5130) by little-altered protore rubble that is thought to be a physically diluted version of the parent material of the gossan at this point. If so, it would seem that lead has been twice as strongly leached from the gossanised material as zinc. The wide and abrupt variations in lead:zinc ratios that are characteristic of Tynagh protore do, of course, reduce the likelihood that this impression is correct. Assay profiles through similar arrangements of gossan and sulphide rubble elsewhere in the centre of the residual deposit in some cases indicate stronger leaching of lead than zinc from the gossan, in others the reverse.

Irrespective of the assumed abundances of the two metals in the parent material, gossanisation tends to yield a residuum containing neither in amounts greater than 2%. (That the upper few feet of the gossan in Fig. 8.6a appears to contain 15% of the two metals combined probably reflects mis-logging of a thin sulphide-bearing cover).

Copper generally seems to have been less strongly leached from gossanised materials than lead or zinc, but because of its very variable content in protore this impression is hard to substantiate. Its apparent enrichment in the gossan section in Fig. 8.6b is due to physical superimposition of gossan on Calp mud of even lower grade in the area concerned.

The mineralogy of copper in parts of the central gossan from which lead and zinc have been almost entirely leached is uncertain, but it is known to include malachite, native copper, cuprite and probably tenorite. The main host of lead in materials of this kind is apprently beudantite; that of zinc is uncertain. Both metals are present in very small amounts as carbonates, and zinc (in particular) as sulphide inclusions in residual barite.

The distribution of silver in and around the central gossan body is particularly interesting. Within the Fossil Gossan, silver values tend to decrease irregularly with depth from a maximum that usually does not exceed 30 oz/ton over 3 ft. Fig. 8.6a shows a typical example. It will be noted that, if the underlying sulphide rubble is representative in grade of the gossan's parent material, lead has been more strongly depleted in gossan than silver has been enriched.

In some assay profiles through the Fossil Gossan silver values vary unsystematically with depth. Unsystematic variation is a characteristic of silver distribution in the Gossan Talus, which contains, on average, about 35% less silver per ton than its in situ equivalent (see Table 6.1).

VERTICAL SCALE 1in = 30ft

Fig.8.6

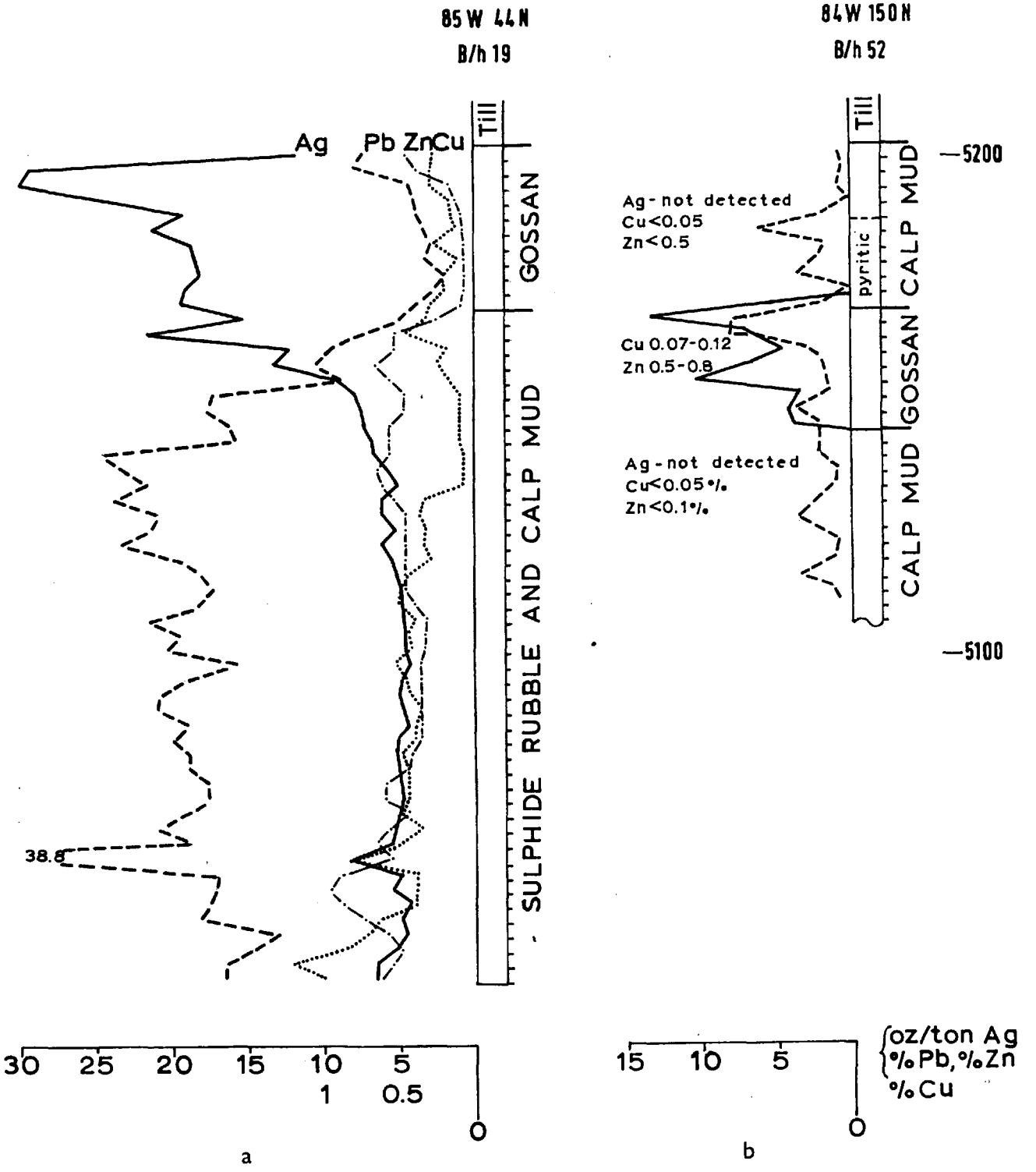


Fig. 8.6aprovides compelling statistical evidence that some silver leached from gossanised materials has been reprecipitated in underlying dark residuum. This borehole is one of several in which, over vertical distances of up to 30 ft., the silver content of copper-poor residuum overlain by in situ or transported gossan exceeds 1 oz per per cent of lead - a value that is rarely attained in copper-poor protore. The fact that residuum underlying gossan talus has been affected by this form of enrichment has important implications concerning the weathering history of the deposit.

Not only residuum overlain by gossan has been enriched in silver. Fig. 8.6b exemplifies enrichment of a body of transported Calp mud that has a southward overlap on the central gossan body. A substantial volume of the (usually) highly pyritic Calp mud that overlaps gossan in this area is classified as silver ore (Table 6.1). Silver does not vary sympathetically with copper or lead in this situation. How it occurs is not known, but since the enriched residuum contains supergene sulphides of several metals that are lower than silver in the Schurmann Series, namely lead, copper and iron, it may be present as acanthite. Alternatively, or additionally, it may occur as a lattice constituent of supergene copper sulphide.

To test the possibility that acanthite formed by replacement of the metal furthest removed from silver in the Schurmann Series a grab sample of pyrite from silver-enriched Calp mud was assayed. The silver assay - 2.3 oz/ton - was not high enough to be regarded as proof of the association, but this may reflect the erratic distribution of acanthite. It is worth noting in this context that no silver was detected in pyrite test concentrates made from residual sulphide ores from other parts of the deposit, and that a marked association between silver and pyrite has been reported in mill tailings of silver ore.

A further point of interest about the distribution of silver in and around the central gossan is that it supports other evidence of northward as well as downward transport of dissolved metals. For silver enrichment of the overlapping Calp mud to have occurred, solutions moving out of the gossan must in places have had a flow component inclined at not more than 55° from the horizontal.

Microscopic and assay evidence as to whether dark residuum underlying gossan has been selectively enriched or depleted in base metals is generally inconclusive. Fig. 8.6a for instance, suggests on the one hand leaching of copper and lead (but not zinc) over a vertical distance of about 30 ft. from the base of the gossan, and on the other copper enrichment of residuum lying immediately below the gossan. Environmental changes could, in fact, have caused leaching of both metals at one time and subsequently more localised enrichment in copper, probably in supergene sulphide form. But in this case as in many others, it is hard to distinguish between variations in the metal tenor of polymict residuum that arise from physical dilution of protore and irregularities in its primary metal content and variations that are of supergene chemical origin.

There is, nonetheless, ample evidence that superimposition of transported gossan on sulphide rubble has had some chemical effect on the latter apart from enriching it in silver. This is usually manifest in an increase in the proportion of cerussite to primary galena and a corresponding decrease in the abundance of supergene galena over vertical distances of up to 30 ft. In places the sulphide rubble has been partially gossanised over a few feet from the contact between the two structural units.

(ii) Processes of gossan formation at Tynagh.

The distribution of gossan zones can be largely accounted for in terms of local differences in the permeability of pre-existing residuum and protore. In the SE quarter of the deposit, gossanisation evidently resulted from "streaming" of groundwaters through particularly porous materials formed by weathering of barite-rich mineralisation in the deposit's original wallrocks. Similarly, the central gossan originated by selective oxidation of parts of a body of massive protore that consisted chiefly of relatively permeable galena-barite mineralisation. Some of the smaller gossan bodies in the first area may owe their position to northward discharge of groundwaters from the Devonian inlier.

The mineralogy of gossan zones reflects the passage through them of carbonate-deficient solutions with a high oxidation potential. In respect of Eh and CO_2 partial pressure, they can have differed little from atmospheric solutions, though in most places they are thought to have been phreatic in character. Structural considerations suggest that only parts of the central gossan now represented by talus may have originated by vadose weathering.

In zones of relatively rapid water percolation the solutions were potent solvents of sulphides and tended to be acid. For this reason they were also effective solvents of pre-existing base metal carbonates, and tended to reprecipitate base metals in non-carbonate minerals.

Because of the high solubility of their sulphates, copper and zinc were strongly leached from such zones. Some zinc persisted in gossanised materials as sphalerite inclusions in residual barite, and small amounts of both metals were presumably coprecipitated with hydrated iron and manganese oxides by adsorbtion and/or by the formation of independent mineral species such as tenorite, hemimorphite and chrysocolla.

Lead is considerably less mobile than either copper or zinc in acid sulphate solutions, from which it tends to be precipitated

as anglesite. Anglesite is a characteristic minor constituent of gossanised and partially gossanised materials at Tynagh, but apparently not as abundant in either as beudantite. Beudantite typically forms from mildly acid solutions of its constituents as a metastable product of the hydrolysis of ferric sulphate (Boyle, 1965). Its persistence in the most strongly gossanised materials, and the apparent absence in them of plattnerite, indicate that the pH of solutions that have passed through gossan zones has generally exceeded 4, and their Eh generally not exceeded +0.7mV. The apparent absence of mineral sulphates of copper, and the abundance of what Borchert (1968) terms "fluffy" limonite, both indicate that the solutions tended to be dilute.

Mineral zonation around gossan bodies in the SE quarter of the deposit reflects a decrease in the pH of gossan-forming solutions as they migrated into carbonate-bearing residuum. Cerussite was more soluble than malachite or smithsonite in near-neutral sulphate solutions at the gossanisation forefront, and dissolved lead tended to be reprecipitated in combination with migrant arsenic and chlorine as mimetite and beudantite. Exceptionally, copper and lead were reprecipitated as bayldonite, but the usual precipitates of copper from carbonate-deficient solutions were cuprite and native metal. Local variations in the rate of discharge of water from gossan zones, the composition of the surrounding residuum, and many other parameters caused reprecipitation of migrant metals by many different mechanisms, and the formation of an extensive semi-gossan mineral assemblage. This assemblage probably includes basic arsenates of the olivenite group, the hydrous lead antimonate bindheimite, and a number of other species that have not so far been recognised.

Turning now to silver, although supergene concentration of this metal during oxidation of argentiferous sulphide deposits is a fairly common phenomenon (see, for instance, Olson (1966) and Solomon (1967)), its geochemical behaviour during weathering is problematical. At Tynagh, as elsewhere, concentration of silver in heavily oxidised

materials presumably involved both precipitation and dissolution of a number of supergene hosts of the metal. Paragenetically the earliest of these were probably base metal carbonates (especially malachite), and perhaps supergene sulphides of copper and silver, but as gossanisation proceeded and hosts of this kind were progressively dissolved, silver tended to be reprecipitated in species stable in neutral and acid oxidising solutions. The most important of these was native silver, which was probably precipitated from acid sulphate waters by the reversible reaction:

$$Ag_2SO_4 + 2FeSO_4 = 2Ag + Fe_2(SO_4)_3$$

Native silver is usually concentrated in the intermediate and lower parts of oxidation zones, where Eh-pH conditions inhibit the formation of strongly solvent ferric sulphate (Boyle, 1968). The fact that it is the chief silver mineral in the Fossil Gossan and, in lesser amounts, in the associated talus deposits lends weight to other evidence that the two together do not comprise the entirety of the original gossan.

Several other silver minerals are likely to have been formed during gossanisation at Tynagh, including cerargyrite (AgCl) and argentojarosite (a relative of beudantite with the formula $AgFe_3(SO_4)_2(OH)_6$). The probability that silver migrating in solution from gossan zones was locally reprecipitated at their margins as acanthite has already been mentioned. That diligent searching for these minerals did not bring them to light does not, of course, guarantee their absence. If cerargyrite is present, it may have been concentrated at the margins of gossan zones in the SE quarter of the deposit by reaction between base metal carbonates and acid chlorine-bearing solutions migrating out of heavily oxidised materials in which barite was being actively decomposed.

Considering the deposit as a whole, no clear division in time can be drawn between gossan formation and chemical weathering effects described earlier in this chapter. Gossanisation was evidently not brought about by a general change in the weathering regime at a particular time, but took place simultaneously both with continuing expansion of the supergene carbonate zone and with the formation of various supergene sulphides in dark residuum. Nevertheless, it seems to have become progressively more widespread during the later weathering history of the deposit, affecting materials that would formerly have been assigned to the supergene sulphide or supergene carbonate zones.

8.4 WEATHERING OF ROCKS BOUNDING THE RESIDUAL DEPOSIT

The rocks that bound the residual deposit have been chemically weathered to depths below surface of more than 650 ft. The main effects of weathering have been those characteristic of the supergene carbonate zone of the residual deposit, namely dissolution and disaggregation of limestones, oxidation of sulphides, and the formation of a secondary mineral assemblage dominated by base metal carbonates and limonite. Mineralised limestones, and crinoidal and micritic limestones of the Waulsortian Bank Formation, are the rock types most widely affected. Except in the immediate vicinity of the residual deposit, Calp has suffered little subsurface weathering, though there are known to be local bodies of in situ Calp mud below the till to the north of the deposit (Fig.3.3). Limited borehole information suggests that the Devonian rocks on its southern side are pervasively weathered to 50ft. or so below outcrop, but that at greater depths weathering is largely restricted to the North Tynagh Fault zone.

Rock weathering is particularly intense in mineralised limestones within 200 ft. of the residual deposit. Where the latter is immediately underlain by protore its boundary tends to be indefinite, and has been

mapped arbitrarily. This is the case in the centre of the open pit area where massive protore has been pervasively weathered to a depth of about 100 ft. below the base of the residual deposit. Heavily weathered protore also underlies the S.E. part of the open pit.

The main supergene alterations of protore below the central part of the deposit are corrosion of primary sulphides and barite, replacement of galena by cerussite, and replacement of galena, sphalerite and primary copper minerals by supergene copper sulphides. Limonite is conspicuously scarce, and copper carbonates apparently absent in this area, but the first is abundant and the second fairly common in protore alteration zones below the eastern part of the deposit. Supergene galena has not been observed in weathered protore outside the limits of the residual deposit, nor have the more complex secondary minerals that occur in the latter, such as pyromorphite and dundasite.

Supergene alteration of primary sulphides becomes progressively less intense and less widespread with depth. The only weathering effects seen to date in primary mineralisation cored from below 600 ft. are minor oxidation of pyrite and pitting of galena in specimens from near the North Tynagh Fault. At depth, weathering is apparently localised along the North Tynagh Fault and shear zones in its immediate hanging wall.

An important effect of weathering has been widespread alteration of Waulsortian limestones flanking the northwestern part of the residual deposit to incoherent mixtures of smithsonite and limonite in varying proportions. Near the deposit these minerals are generally accompanied by small amounts of cerussite and sometimes by traces of apparently supergene barite. The extent and shape of the alteration zones (some or most of which are connected to the residual deposit proper, and simply extensions of its peripheral carbonate

zone) are uncertain. The zones are most numerous in an area extending up to 250 ft. northwards from the residual deposit, and open pit exposures suggest that the majority are tabular in shape and localised along bedding planes, joints and other fractures. They are more numerous in the well-bedded crinoidal limestones and biomicrites flanking the deposit than in the comparatively massive micritic limestones underlying it.

They clearly owe their origin chiefly to migration of agreressive, metal-bearing solutions out of the residual deposit proper. The latter must have been the main source of metals precipitated in the alteration zones, for the affected limestones contained little primary mineralisation. At times, probably at all times, the solutions were slow-moving enough to accept the guidance of such subtle discontinuities in the limestone as stylolitic sutures.

The East Extension Orebody is virtually unweathered and, except for local decomposition of suboutcropping Calp, there is little evidence of subterranean weathering on a significant scale outside areas of known mineralisation in the Tynagh district.

8.5 SUMMARY OF WEATHERING HISTORY

In essence, the weathering history of the deposit has been one of progressive leaching of metals from the predominantly dark residuum that forms the core of the deposit, and cumulative reprecipitation of some of them at the deposit's margin, chiefly as carbonates and oxides, by reactions between migrating solutions and limestone wallrocks. These processes have probably been going on simultaneously since the deposit began to form. Weathering of its walls has considerably enlarged the deposit, and supergene concentration of metals at its margins has yielded extremely rich carbonate ores.

Water circulation has, in general, been sluggish, and there is evidence that the bulk of the existing residuum has been permanently waterlogged. Reducing conditions have prevailed continuously in many parts of the deposit, and metals leached from residual primary mineralisation have been partly reprecipitated within the residuum as supergene sulphides. This has taken place particularly in dark residuum, where it was promoted locally or generally by bacterial activity.

Decomposition of limestones at the deposit's margin raised the pH of pore fluids in its interior, and the supergene carbonate zone progressively encroached on the supergene carbonate zone. Fewer metals were reprecipitated as sulphides, and sulphides are now in disequilibrium with pore fluids throughout the deposit. A contributory factor was superimposition on the residuum of calcareous glacial tills.

In addition to the processes just outlined, but to a large extent contemporaneous with them, channelling of strongly oxidising carbonate-deficient solutions through particularly permeable residuum caused the formation of numerous gossan bodies. Below the present erosion level the solutions are thought to have been phreatic in character, though the deposit probably contains transported products of vadose weathering, e.g. the gossan talus.

For reasons connected with the denudation history of the area and with changes in climate during the period of the residual deposit's existence, both of which are discussed in Chapter 9, oxidation of residual sulphides, and the other weathering effects stemmed from it, became more widespread and intense with time.

CHAPTER NINE

ORIGIN AND AGE OF THE RESIDUAL DEPOSIT

The Tynagh residual deposit clearly owes its existence to an extraordinary combination of circumstances, for in the normal course of events concentration of lead, zinc and copper by weathering takes place almost entirely by the formation of chemically precipitated supergene minerals. There are, in fact, few recorded instances of mechanical concentration of sulphides by weathering, and no known deposits of residual primary sulphides that are comparable in size to that at Tynagh.

Before discussing the factors that promoted the formation of a sulphide-rich residuum at Tynagh, it would be as well to establish in general terms the physico-chemical characteristics of solutions in which calcite is subject to chemical decomposition but sulphides are relatively stable. Of the other minerals that occur in the sulphidised limestones at Tynagh - chiefly barite, quartz and illite - it need only be said at this stage that they are more stable than both calcite and sulphides in all weathering environments.

9.1 RELATIVE SOLUBILITY OF CALCITE AND SULPHIDES

The solubility of calcite in aqueous solutions is largely controlled by five almost independent variables, namely environmental temperature and pressure, and the pH, ionic strength and dissolved carbonate ($HCO_3^- + H_2CO_3 + CO_3^{--}$) content of the solution (Garrels and Dreyer, 1952). The most important of these variables is pH, for, as Fig. 9.1 indicates, the solubility of calcite in acid solutions increases approximately

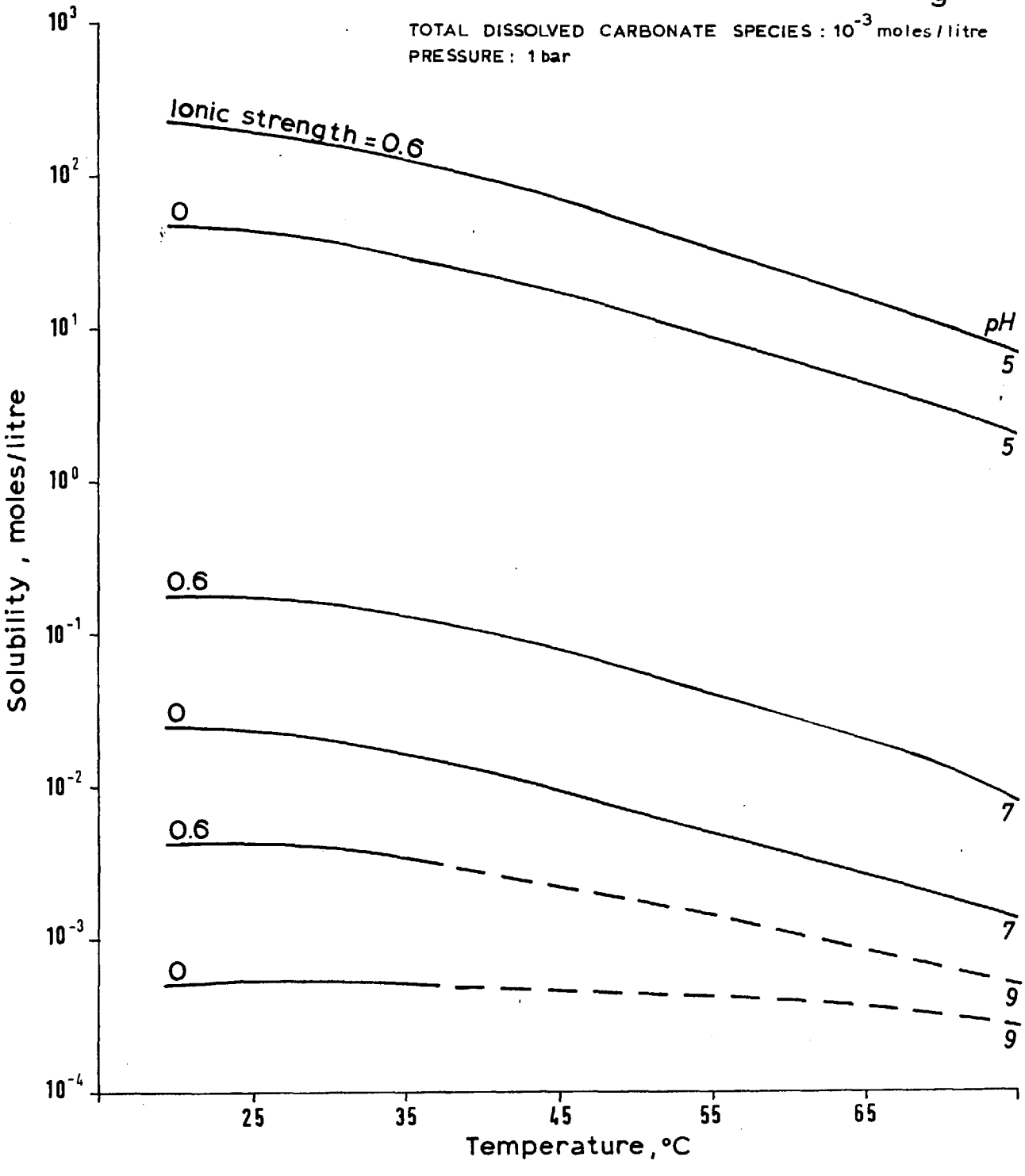
100-fold for every unit of decreasing pH. In neutral and slightly alkaline solutions the effect of a decrease in pH is less but still appreciable, and at pH 10 and above calcite has a constant solubility of about 10mg/l (10 ppm). The solubility of calcite also increases with the ionic strength of the solution and with decreasing temperature, though the latter effect is not marked at low temperatures ($\lesssim 25^{\circ}C$). The effect of an increase in pressure is to increase calcite solubility.

At constant pH, an increase in the dissolved carbonate content of a solution decreases the amount of free Ca^{+2} and hence the solvent potential of the solution with respect to calcite. Empirically, however, the net effect of an addition of dissolved carbonate species to solution is to increase its solvent capacity due to lowering of its pH.

Substitution of iron and manganese for calcium in the calcite lattice decrease the solubility of the mineral, and because of the high stability of the ion pair formed by Mg^{++} and CO_3^{--}, magnesian calcite is less soluble, and dolomite very much less soluble, than pure calcite (Garrels et al, 1960, 1961).

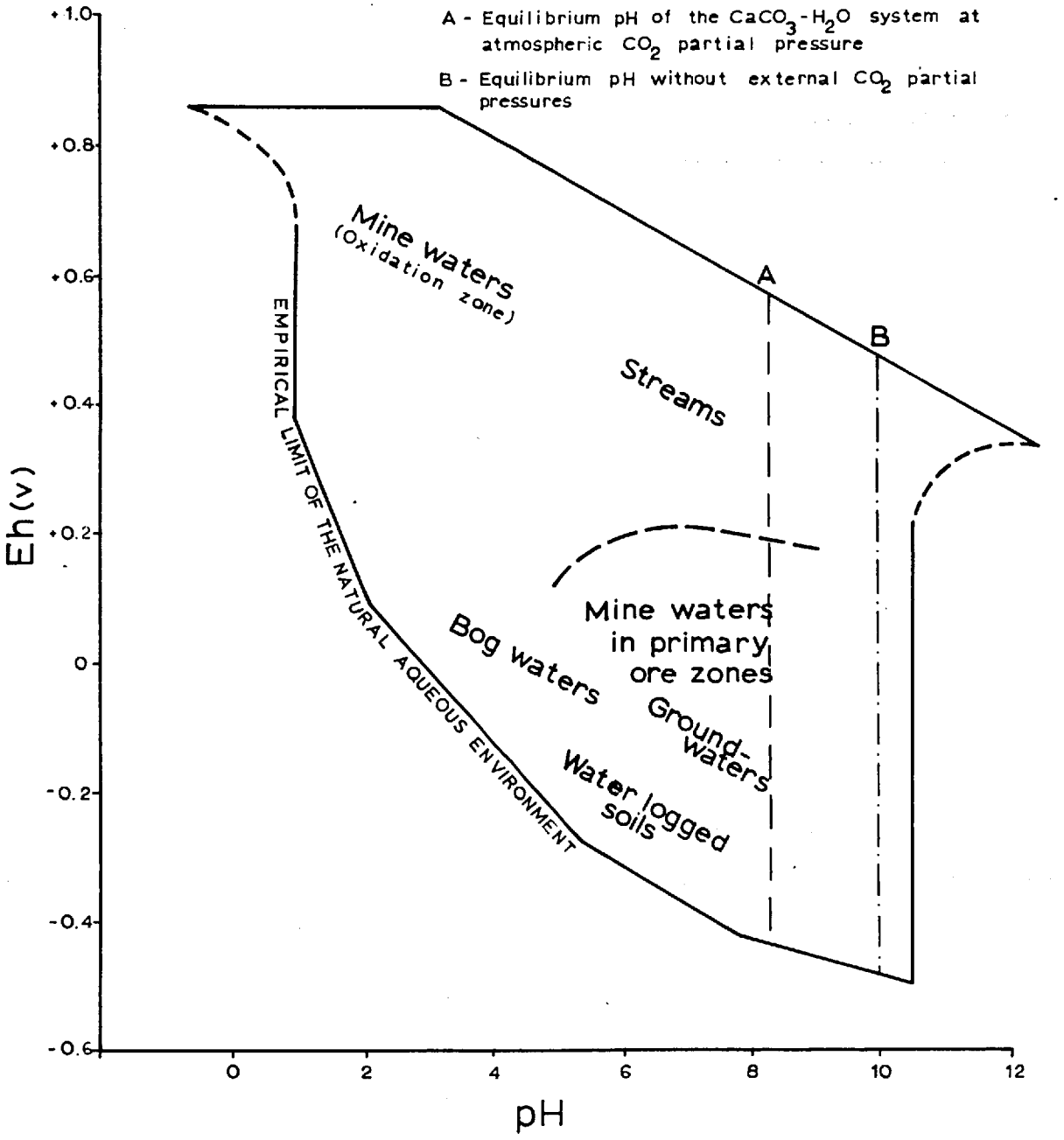
Dissolution of calcite is not an Eh-dependent reaction. Sulphides, on the other hand, depend for their stable existence in aqueous environments on the maintenance of a negative Eh or, in acid solutions, a low positive Eh. Extrinsic and intrinsic determinants of the relative solubilities of some of the common primary sulphides at Tynagh were outlined in Chapter 8, and it need only be reiterated here that their oxidation products include sulphuric acid and various soluble salts. It is also germane to what follows that oxidation of sulphide to sulphate involves the formation of several unstable soluble sulphur

Fig. 9.1



EFFECT OF TEMPERATURE, pH AND SALINITY ON THE CALCULATED SOLUBILITY OF CALCITE. After Garrels and Dreyer, 1952.

Fig. 9.2



Eh-pH CHARACTERISTICS OF SOME NATURAL AQUEOUS ENVIRONMENTS
After Baas Becking et al., 1960; Sato, 1960; Garrels and Christ, 1965.

species, such as bisulphite ion (HSO_3^-) and thiosulphate ion (SO_3^{--}), that are strong reducing agents. Where the supply of oxygen is limited they may be capable of fairly prolonged metastable persistence. Under conditions of slow phreatic circulation, the net effect of limited oxidation of pyrite may be to produce a strongly reducing environment (Granger and Warren, 1969).

Stability relations between sulphides and calcite in natural aqueous environments are summarised diagramatically in Fig. 9.2. Selective decomposition of the latter is likely to be accomplished most rapidly by acid solutions with a negative Eh. Natural solutions with these pH-Eh characteristics occur in certain poorly drained surficial environments where biochemical deoxygenation and bacterial generation of H_2S and CO_2 play an important part in maintaining a depressed pH and negative Eh (Baas Becking et al, 1960). It will also be noted that normal (alkaline) groundwaters, which are probably the main agency of cavern formation in limestones (Davis, 1930), typically have negative oxidation potentials.

9.2 CONTROLS OF RESIDUUM FORMATION

The shape and situation of the residual deposit point to a causal relationship between weathering of sulphides and selective dissolution of the mineralised limestones. Conversely, they belie the possibility that the high sulphide content of the residuum is fortuitous consequence of normal processes of cavern formation in limestones. The Tynagh solution structure has no known parallel of comparable size and shape in the sulphide-deficient limestones of the area.

Features of the deposit's structure described in Chapter 6 suggest that residuum formation began on a major scale when the

upper part of the Main Orebody was subjected to oxidation in or just below an erosion surface not more than 150 ft. above that of the present. At whatever level this took place, the affected protore was certainly pyritic, and may, due to mineralogical zoning, have been richly so. There is, further, a possibility that some of the Calp overlying the ore zone was as rich in pyrite as it is in bank-marginal positions below the present erosion level.

A necessary condition for the deposit's formation was a plentiful supply of water. Material evidence that much of the sulphide-bearing residuum formed at a time of high seasonal or perennial rainfall is the presence in it of taxodiaceous wood probably belonging to the genus Sequoia. The modern representatives of the genus are largely restricted to an area on the west coast of N.America with a Mediterranean-type climate, characterised by high winter rainfall and semi-arid conditions during the summer. Ancestral Sequoia evidently fluorished under similar climatic conditions, for its remains are abundant in plant beds in N.Ireland that were deposited at a time when the climate was warm and humid enough for bauxitisation to take place (Cole, 1912; Eyles, 1952). High humidity, heavy seasonal rainfall and winter temperatures above freezing point are climatic elements deduced by Schloemer-Jäger (quoted by Schwarzbach, 1963) from the presence of a floral assemblage including Sequoia in the Tertiary plant beds of Spitzbergen. Of the genera with which Sequoia might be confused in poorly-preserved material, none is known to have fluorished in cold or arid regions. A living species that closely resembles Sequoia is Taxodium distichum, the swamp cypress (Andrews,1947).

The climatic conditions of the time are likely to have promoted intense oxidation of sulphides in the zone of aeration and, chiefly by virtue of the assumed abundance of sulphides of iron among those that were so affected, extreme acidification of percolating waters. If, as seems likely, oxidation took place in the presence of ferrobacteria (which oxidise ferrous to ferric iron) and/or thiobacteria (which oxidise intermediate sulphur species), the pH of solutions descending towards the water table may have been as low as 2 (Baas Becking et al, 1960). Even without bacterial intervention, oxidation of pyrite might have depressed their pH to about 3.

At this point the most critical factor of all came into play, namely the closeness to surface of the local water table. It has already been shown by reference to the mineralogy of the residual deposit that the water table of the Tynagh area has probably never been more than a few feet below present ground level.

In this connection a slight digression is necessary, for it has been suggested that the glacial deposits of the Central Plain obscure a karstic topography, including rubble-filled gulleys or caverns that formed at some time in the Tertiary when the sea level was about 500 ft. below that of the present (Murphy, 1962). Drilling and mining in other mineralised areas in the central lowland have shown, however, that although oxidation effects persist to depths of at least 400 ft. below present sea level, in no case does the zone of demonstrably vadose weathering extend below +300 I.O.D. As Blanchard (1968) points out, and experience in many parts of the world confirms, groundwaters may carry dissolved oxygen several hundred feet down into the zone of

saturation if well-developed conduits - faults and joints for example - are available. Furthermore, the existence of large flooded caverns in the lowland limestones underlying the Central Plain is not proof of a depressed water table in former times, for according to the widely accepted theories of Davis (1930) and the observations of Bretz (1942) and others, cavern formation is particularly active in the upper part of the zone of saturation. So far as the writer has been able to discover, no limestone caverns containing dripstone deposits, current-bedded sediments or other evidence of vadose activity, have been penetrated more tham a few feet below surface in any of the many quarries and mines scattered throughout the central lowland. The fact that certain rivers in counties Cork and Waterford are evidently entrenched to depths of as much as 500 ft. below present sea level is of doubtful relevance to the subject of ancient water tables in the interior of the country, for as Farrington (1929) has suggested, entrenchment probably resulted from discharge of glacial meltwater into an ephemerally depressed sea.

The situation envisaged at Tynagh during the earlier stages of residuum formation was therefore such that extremely acid waters percolated almost immediately into the zone of saturation, where they encountered rocks consisting partly of pyritiferous sulphide-barite mineralisation and partly (in places very much subordinately) of high-purity calcitic limestones. On doing so they lost acidity by reaction with rock carbonates and entered a reducing alkaline environment in which they had only a vestigial capacity to oxidise sulphides. Oxidation of sulphides took place at a multitude of advancing interfaces (see below) and under conditions of severely restricted water circulation. At

interfaces its most important effect was to depress the pH of solutions and hence increase their solvent capacity with respect to calcite. This effect was widespread on a microenvironmental scale, though the degree of undersaturation may at most points have been small.

Other than at oxidation interfaces, a complementary effect of the process was the preservation of sulphides, and to some extent the reconstitution of dissolved metals in sulphide form, by the formation of various reducing agents. As discussed later this could have been a biochemical effect, but it was not necessarily so. The most important reducing agents may have been the unstable intermediate sulphur species referred to earlier. These play an essential part in the low temperature aqueous formation of at least one of the supergene sulphides present in the residuum, namely pyrite (Rickard, 1968, 1969; Granger and Warren, 1969).

Once the Calp cover of the mineralised limestones had been breached, decalcification was propagated not only by the dispersal of meteoric solutions along joints, faults and bedding planes, but also by their capillary movement along grain boundaries. The latter was particularly effective in the more loosely aggregated rock types, such as bioclastic limestones and coarse-grained protore. It is worth repeating here that much of the disaggregated mineralisation was not in micritic limestone - the host of about 90% of the mineralisation that remains unweathered - but in crinoidal limestones and biomicrites. Because of their compactness, unmineralised micritic limestones were relatively resistant to decalcification.

Major tectonic structures that promoted residuum formation were the North Tynagh Fault and the synclinal fold in its immediate

hanging wall. "Streaming" of groundwaters through fault zones is a common hydrological phenomenon, especially in limestone terrains (Davis and DeWeist, 1966). At Tynagh, it may have been accompanied by subterranean drainage towards the fault zone of the (pyritiferous) Devonian sediments of the footwall block. This was certainly a consequence of residuum formation, and it may have been a contributory cause. Initially the main contribution of the footwall block was probably to impound waters moving downwards, and perhaps southwards, into the ore zone. The possibility that channelling of meteoric waters towards the axis of the main hanging wall fold contributed to deep decalcification of the central part of the Main Orebody was referred to in Chapter 6.

While it is not known for certain how much pyrite existed in the 100 ft. or so of rock between the present erosion level and that from which residuum formation was initiated, it is not beyond the bounds of possibility that addition of soluble oxidation products of sulphides to the local drainage system could alone have been responsible for the formation of the residual deposit. This contention is supported by circumstantial evidence that conditions in the zone of aeration favoured ready hydrolysis of dissolved salts, and that oxidation of sulphides below the water table was an integral part of residuum formation at all stages in the deposit's history (see Chapter 8). In this connection it is interesting to note that thiobacteria, referred to earlier as possible promoters of acidity in solutions descending to the water table, are capable of persisting in aqueous environments with an Eh as low as -190mV (Baas Beckinget al, 1960).

Nevertheless, it seems likely that one or more of the normal causes of cavern formation in limestone contributed to the formation of the residual deposit, in particular enrichment of meteoric

waters in soil-derived CO_2. This effect is generally held to be of great importance in the chemical weathering of limestone, both at the soil-rock interface and below it (Davis, 1930; Swinnerton, 1932; Williams, 1964). It is particularly effective in temperate and humid sub-tropical climatic zones, where the CO_2 partial pressure of pore fluids in organic soils has been found to be 50 to 100 times greater than it is in the atmosphere (Adams and Swinnerton, 1937; Russell, 1950). Normally the uptake of CO_2 from soil is expended in the vadose zone, and descending waters are saturated or supersaturated with respect to calcite by the time they reach the water table (Thrailkill, 1968), but at Tynagh the closeness of the latter to surface may well have allowed the flushing into the groundwater system of solutions fortified by CO_2 derived from the organic cover that evidently existed in the surrounding area during the early stages of residuum formation. Organic acids, which Fetzer (1946) has shown to be active solvents of calcite, could have been derived from the same source.

The organic cover of the area may also have supplied nutrients to heterotrophic sulphate-reducing bacteria within the zone of residuum formation. The activity of bacteria of this kind (which will be described more fully in a later section) could have assisted both the dissolution of calcite and the preservation of sulphides, since their metabolic reactions involve the generation of both CO_2 and H_2S.

Finally, some small contribution to the undersaturation of descending waters with respect to calcite may have been made by cooling as they entered the zone of saturation. This effect is probably not significant in normal processes of cavern formation (Stringfield and LeGrand, 1969), but it may have been more so than usual at Tynagh, where atmospheric heating of

meteoric waters was supplemented by strongly exothermic reactions in the zone of vadose sulphide oxidation. The increase in hydrostatic pressure with depth was probably a negligible factor in residuum formation.

A point that needs to be emphasised is that solutions capable of liberating little-altered sulphides from a limestone matrix have probably been circulating more or less continuously in the vicinity of the deposit since its formation began. The structure of the residual mass leaves little doubt that Calp mud containing unaltered primary sulphide formed throughout the pre-glacial history of the deposit, and though residuum that can definitely be said to have formed in post-glacial times contains little fresh sulphide, it is probable that some northward expansion of the deposit by the formation in situ of sulphide-bearing Calp mud has taken place in the last 10,000 years. In any case, the implication is that over a long period of time dark sulphide-bearing residuum and heavily limonitised materials were forming simultaneously at the same elevation, the former mainly by decalcification of Calp. The slow rate of oxidation of pyrite in Calp mud formed by phreatic solutions is probably due partly to the relatively low permeability of this type of residuum and partly to the activity of sulphate-reducing bacteria within it.

SUMMARY

The formation of a sulphide-rich residuum at Tynagh resulted from chemical weathering of pyritic mineralisation in rocks otherwise consisting largely of calcite at a time when the local water table was persistently close to surface. Meteoric waters penetrated deeply and dispersed widely through the mineralised zone along joints, faults, bedding planes and grain boundaries. Their solvent effect on calcite was chiefly enhanced by oxidation of pyrite, which took place above and below the water table. Biochemical processes may have played an important part both in the decalcification of the mineralised limestones and in the preservation of residual sulphides.

9.3 THE AGE OF THE RESIDUAL DEPOSIT

It is important to establish when residuum formation began at Tynagh, partly to give a time perspective to subsequent weathering events, and partly because the residuum is one of only two known pre-glacial deposits in central Ireland containing post-Carboniferous organisms, and hence a potential source of much-needed evidence about the evolution of the Central Plain. In this section an attempt is made to deduce the age of the deposit from the sparse fossil record, and by considering at what period or periods in geological time residuum formation in the way outlined in the previous section could have began.

A. The fossil record

The only post-Carboniferous organic remains that have been found in the residuum are chunks of timber. Pollen were unsuccessfully sought by Professor W.A. Watts in six samples of residuum taken by the writer from parts of the deposit in which timber occurs, and it is presumed that they and any other vegetable debris that accompanied the timber into the residuum have suffered selective decomposition - a fairly common occurrence. In their absence it has only been possible to obtain tentative generic identifications of the plants represented. These identifications were made by Mr. J. van der Burgh at the Botanical Museum of the University of Utrecht, Holland.

Two types of wood have been recognised - Sequoia (redwood) or a closely related member of the Taxodiaceae, and Abies (fir) or a closely related member of the Pinacae. From the field relations of the enclosing residua and differences in their state of preservation it seems that the first type of wood is older than the second, but probably somewhat younger than the deposit

as a whole. The two have not been found together in any part of the deposit.

The fossil range of the Taxodiaceae in N.W. Europe extends from the late Mesozoic on the one hand to the early Pleistocene on the other. Fossil remains of Sequoia and of its close relatives Metasequoia and Taxodium are, however, typically found in Tertiary deposits (Andrews, 1947). Relative to those of other plants, the remains of Sequoia are fairly common in the Eocene deposits of the London and Hampshire Basins (Chaloner and Boulter, 1966), and they are very abundant in the Bovey Tracey Beds of S. Devon, which are probably Oligocene in age (Chandler, 1957). Sequoia, Metasequoia and Taxodium occur in N.E. Ireland in interbasaltic plant beds that Watts (1962) considers to be of late Eocene or early Oligocene age. An Oligocene age is generally accepted for the Lough Neagh Clays of N.E. Ireland, which also contain Sequoia remains (Cole and Hallissy, 1924; Watts, 1962). There are no deposits of undisputed Miocene age in the British Isles, but Sequoia and other taxodiaceous woods are abundant in Miocene deposits elsewhere in N.W. Europe. Boulter and Chaloner (in press) have recently described Pliocene deposits in the South Pennines that contain numerous macrofossils (but few spores) of Sequoia/Taxodium, and Sequoia is well-represented in continental Pliocene deposits. Taxodiaceae and other exotic flora occur sparingly in the early Pleistocene deposits of East Anglia and Holland, but they are not known in any British or Irish interglacial deposits (West, 1968).

The Pinacae have a similar fossil record in N.W. Europe, and in some Tertiary deposits Abies is an abundant macrofossil associate of Sequoia/Taxodium. This is the case in the Pliocene deposits of the South Pennines referred to above. Unlike

Sequoia, however, Abies became re-established in the British Isles during temperate stages of the Middle Pleistocene (Table 9.1). In England, Cromerian and Hoxnian interglacial deposits contain abundant Abies pollen at certain levels. Materials representive of the first of these interglacial stages are not known in Ireland, but deposits correlated in time with the second are present in several parts of the country. Abies pollen occur in comparative abundance in deposits of this age at Gort, County Galway (Jessen et al, 1959). Gort is situated 20 miles to the south of Tynagh (Fig. 9.3).

Abies apparently did not become re-established in the British Isles during subsequent interglacial periods, and, like Sequoia, is now extinct throughout western Europe.

To summarise, the fossil record suggests that much of the residuum is Tertiary in age, but not whether it formed in the early, middle or late Tertiary. An early Pleistocene age for the main residual mass cannot be ruled out on palaeontological grounds. The local cavity-fill to which Abies appears to be restricted may be Tertiary, early Pleistocene or mid-Pleistocene in age.

B. Denudation history of the Tynagh area

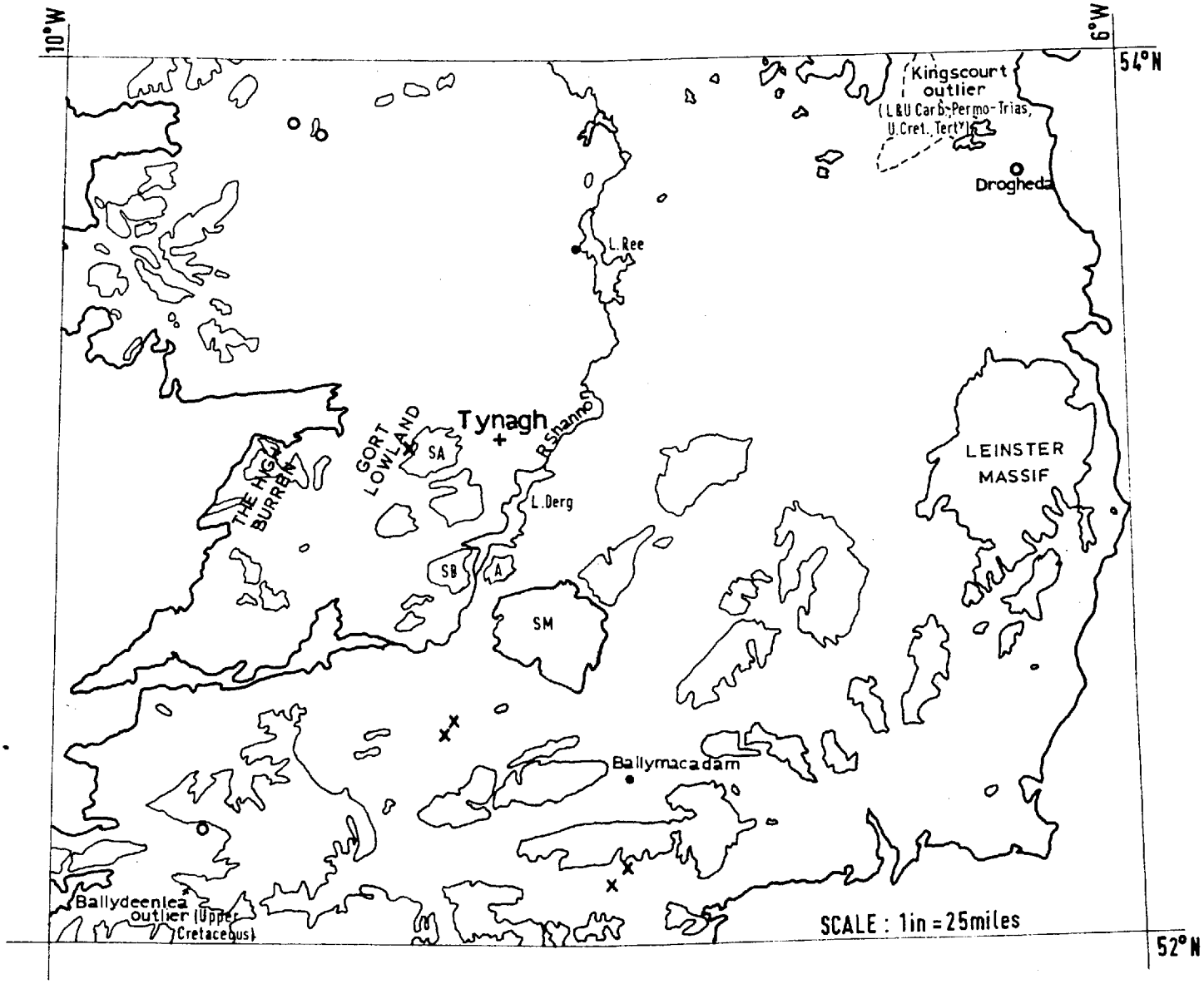
At the time of the Permo-Carboniferous (Armorican) earth movements, the Waulsortian Bank Formation at Tynagh was probably overlain by 3,500-4,500 ft. of Carboniferous rocks, including 2,000-2,500 ft. of Visean limestones, and up to 2,000 ft. of Namurian and Ammanian sandstones, flagstones, shales and coal beds. These estimates are based on extrapolations from the areas nearest to Tynagh in which an Upper Carboniferous succession has been well preserved (Fig. 2.1). It is pertinent to the

Table 9.1 Stages of the British Pleistocene

	Britain		Glacial stages in N.W. Europe	Approximate duration or mid-point (years B.P.)
	Stage	Climate		
Upper Pleistocene (including Holocene)	Flandrian	Temperate		10,000 - present
	Weichselian	Cold/Glacial	Weichselian	60,000 - 10,000
	Ipswichian	Temperate		80,000
	Gippingian	Cold/Glacial	Saalian	?
Middle Pleistocene	Hoxnian	Temperate		150,000
	Lowestoftian	Cold/Glacial	Elsterian	250,000
	Cromerian	Temperate		350,000
	Beestonian	Cold		425,000
	Pastonian	Temperate		?
Lower Pleistocene	Baventian	Cold		?
	Antian	Temperate		?
	Thurnian	Cold		?
	Ludhamian	Temperate		?

After West (1968)

Fig. 9.3



- CLAY DEPOSITS
- SILICA SAND DEPOSITS
- HOXNIAN INTERGLACIAL DEPOSITS

Enclosed areas lie above 500 I.O.D.

A ARRA MOUNTAINS (Summit height 1517 I.O.D.)
SA SLIEVE AUGHTY MOUNTAINS (1312)
SB SLIEVE BERNAGH MOUNTAINS (1748)
SM SILVERMINES MOUNTAINS (2279)

SOURCES - Bishopp and McCluskey (1948), Charlesworth (1963), Walsh (1966), West (1968), Williams (in press)
U.K. Geological Survey 1"=25miles map (4th edition, 1957)
Irish Ordnance Survey 1"=9miles map (1963)

C J.M. 1969

weathering history of the residual deposit that Carboniferous evaporites are not known in the Carboniferous rocks of either area (though thick beds of gypsum and anhydrite are present in the Permian rocks of the Kingscourt outlier). Minor occurrences of gypsum and anhydrite and pseudomorphic evidence of the former presence of sparse halite have recently been described in Visean rocks 60 miles to the north of Tynagh (West et al, 1968), but at stratigraphic levels well above that of the Waulsortian.

It has been suggested that the limestone lowland in which the residual deposit is entrenched was "roughed out" during a period of intense sub-aerial erosion that followed the Armorican uplift, and that it was invaded by the sea one or more times during the Mesozoic Era (Charlesworth, 1963). The evidence that supports this suggestion need not be reviewed here, for if Mesozoic rocks were ever present in the Tynagh area they were almost certainly removed by erosion before the deposit began to form. Most authorities prefer not to commit themselves about the extent of Mesozoic transgressions over Ireland, but some assert that they were restricted to the north-east and south-west parts of the country. Elsewhere, under the climatic conditions of the time, Lower Carboniferous limestones could have been protected from erosion throughout the Permian and Mesozoic by their Upper Carboniferous cover.

Where the age of the residual deposit is concerned, the crux of the matter is the rate of Tertiary denudation in central Ireland. Except for the Tynagh residuum, the only deposits in the region that have been dated as Tertiary on palaeontological evidence are small bodies of plant-bearing clay at Ballymacadam, County Tipperary (Fig. 9.3). These outcrop below till in a land surface of Waulsortian limestone

lying at about 250 I.O.D. - 50 ft. above the mean surface elevation of the Tynagh residual deposit - and are alleged to be up to 90 ft. deep. Their composition and structure have never been investigated in detail. Small pockets and pipe-like bodies of clay and fine silica sand outcrop in Carboniferous Limestone erosion surfaces at 200-250 I.O.D. in several other parts of the Central Plain (Fig. 9.3), but none of them appears to have yielded palaeontological evidence of its age. They are generally assigned to the Tertiary or early Pleistocene.

According to a report of 1857 the Ballymacadam clays contain chunks of (unidentified) timber up to 5 ft. across, and Watts (1957) found in them a pollen assemblage that he tentatively concluded to be of late Eocene age. So few plant species were represented in the clays, however, that it was not possible to assign them with confidence to any particular part of the Tertiary.

If the Ballymacadam deposits are as old as Watts suggests, and have not subsided far below their original level of deposition, it follows that parts of central Ireland had been eroded to approximately their present levels by the late Eocene, i.e. about 40 million years ago. This possibility is allowed by several writers who consider the central lowland to be essentially a post-Eocene feature.

Establishment of the Central Plain by Miocene karstic denudation, followed in post-Miocene times by slow fluvial erosion of the resulting lowlands and their lateral extension by subaerial solution planation has been cogently argued by Williams (1964, in press). Williams showed that the Gort lowland (Fig. 9.3) probably formed following the removal of Namurian rocks from the area in middle or late Tertiary times, and could have done so in less than five million years. The relative youth of cave

systems in the limestone highland immediately to the west (Ollier and Tratman, 1956) supports this view. No demonstrably pre-Pleistocene deposits are known in any of the caves of the region.

A post-Miocene sub-aerial origin for the central lowland has been suggested by George (1968), who sees the Ballymacadam sediments as synclinal remnants of lacustrine deposits on a wave-planed surface that was deformed and elevated by mid-Tertiary earth movements. Dewey and McKerrow (1953) have shown that the drainage system of N.W. Galway was probably superimposed from a Carboniferous Limestone cover following Miocene or Pliocene uplift of the area.

A minority view is that planation resulted largely from marine erosion and/or repeated rejuvenation of the drainage. No post-Mesozoic marine deposits are known in southern Ireland above the 8m. interglacial raised beaches, but alleged remnants of base-levelled planes have been described at numerous elevations up to about 2,500 ft. above present sea level (Kinahan, 1878; Sweeting, 1955). Tentative correlations have been proposed between some of them and planar erosion surfaces in S.E. England, including surfaces as 400 O.D. and 200 O.D. that are thought to be late Pliocene and Pleistocene in age respectively. As Williams (in press) points out, however, geomorphological evidence of Tertiary base-levelling to these and higher elevations is open to several interpretations, such as differential weathering of sandstone and limestone, and exhumation of Carboniferous and perhaps Mesozoic unconformities.

No review of the possible erosion history of central Ireland would be complete without a reference to the River Shannon, which flows gently southwards through the Central Plain nine miles to the east of Tynagh. The Shannon is evidently part of a superimposed

drainage system, for instead of being deflected by the resistant Devonian and Silurian rocks of the Slieve Bernagh and Arra Mountains inlier, it maintains its southward course through the core of the inlier (Fig. 9.3). Whether the surface from which it was superimposed resulted from Armorican uplift or from marine or sub-aerial planation at some later date has never been resolved, but since it presumably lay at least 1,750 ft. above present sea level this long-standing dilemma need not be further discussed here.

C. Summary and conclusions

It is not possible to deduce the age of the deposit precisely either from palaeontological evidence or from its situation. The presence in the residuum of Sequoia or a closely related wood type suggests that the deposit began to form during the Tertiary Era. Residuum containing a second type of fossil wood, Abies, may also be Tertiary in age, but its field relationships and analogy with deposits not far from Tynagh containing the same wood type indicate a mid-Pleistocene (Hoxnian) interglacial age. This being so, the deposit's oxide envelope may be to a large extent a Pleistocene feature.

There is no general agreement about the denudation history of the Central Plain, but on balance current theories support the writer's opinion that residuum formation began in the latter part of the Tertiary. It is hard to believe that a sulphide-rich residuum formed fairly close to surface could have survived under the climatic conditions of N.W. Europe in the early and middle Tertiary, which alternated between semi-arid, semi-tropical, humid sub-tropical and warm temperate (Schwarzbach, 1963).

It is unlikely, but not beyond the bounds of possibility, that the deposit is less than three million years old. During the early part of the period of about two million years referred to by some writers as the pre-glacial Pleistocene, climatic conditions in N.W. Europe were probably similar at times to those that prevailed during the preceeding five million years, and it is not known for certain that the marked climatic cooling that took place in non-polar regions $2\frac{1}{2}$ to 3 million years ago (MacDougall and Strip, 1968) caused the extinction in Ireland of flora characteristic of the Tertiary.

There is a remote possibility that the Sequoia is a derived fossil, in other words older than its present matrix. It could, conceivably, have been introduced into the Tynagh residuum as a result of weathering of a nearby residual deposit, perhaps of the Ballymacadam type. Its concentration in bodies of Calp mud indicates otherwise, however, and the extent to which some fragments have been replaced by zinc sulphide argues strongly for original fossilisation within the Tynagh residuum.

9.4 SURVIVAL OF THE RESIDUAL DEPOSIT

Some, perhaps most, of the sulphide-rich residuum has apparently been in existence for at least two and possibly more than seven million years. During that time residual sulphides have been pervasively oxidised, and some of their alteration products have accumulated in large amounts. Nevertheless, the deposit still contained of the order of six million cubic feet of sulphide when it was discovered, and very little of it was of supergene origin. This section discusses the probable ways in which residual sulphides were protected from more thorough oxidation, and the residual deposit as a whole from physical erosion.

A. Preservation of residual sulphides

The chief factor militating against more thorough oxidation of residual sulphides was the persistence of a near-surface water table within the area of the deposit. Geomorphological and other indications that water tables in the central lowland have never stood for long deeper than a few tens of feet below the present erosion level have been referred to in previous chapters, but it is worth repeating here that the depressed base levels of glacial stages of the Pleistocene were ephemeral - the glacial stages themselves probably only lasted between 50,000 and 100,000 years (Shotton, 1967; West, 1968) - and would have had little influence on drainage in the interior of the country.

There may have been relative depression of the central lowland in Pliocene times (Farrington, 1929; Corbel, 1952), and some writers (Cole and Hallisy, 1924; Williams, 1964) admit the possibility of a Pliocene marine incursion into the area. (Several 19th century geologists, notably Kinahan (1878), saw in the topography of the drift evidence of Pleistocene marine incursions, but this view is not held nowadays.)

If the Tynagh residuum was pre-Pliocene in age, its submergence under a Pliocene sea and subsequent slow removal of Pliocene deposits would certainly help to explain the preservation of the residual sulphides, but there is little reason to believe that this happened. It has already been mentioned that no marine sediments of post-Mesozoic age are known in central Ireland.

The climatic deterioration that marked the onset of the Pleistocene was probably a contributory factor to the preservation of residual sulphides. Rainfall tended to become perennial

rather than seasonal, ensuring continuous water-logging of the residuum, and decreasing atmospheric temperatures slowed down the rates of near-surface reactions. During periods of glaciation, chemical activity was reduced to a minimal level, and at times it may have been virtually halted within the residual deposit by freezing of the latter's pore waters (see below).

Another factor that inhibited oxidation was the poor permeability of the materials with which residual sulphides became mixed during the formation of the deposit. None of the residuum is truly impermeable, but mining experience shows that mixtures of protore fragments and Calp mud or clay are relatively slow to drain, whereas oxides formed by weathering of protore and non-argillaceous micrites and crinoidal limestones are good aquifers. The compactness of much of the fragmental protore also helped to prevent more thorough oxidation of residual sulphides.

The activity of sulphate-reducing bacteria may have been an important factor in the preservation of residual sulphides. These bacteria live by oxidising hydrogen to water using sulphate as their source of oxygen, and their metabolic reactions have as a side-effect the generation of the strong reducing agent hydrogen disulphide. Oxidation of organic matter, not necessarily higher plants, is the most probable source of energy for these reactions. All the sulphate-reducing bacteria are obligate anaerobes, i.e. incapable of survival in the presence of free oxygen, but their symbiotic association with organisms that use oxygen in their metabolism allows them to survive in slightly oxygenated materials. According to Baas Becking et al (1960), even large scale shifts from predominantly reducing to predominantly oxidising conditions would not eliminate them. The limits of the aqueous environment inhabited by sulphate-reducing bacteria is given by Baas Becking

as pH 4.15 to 9.92, Eh +115mV to -440mV. Maximum growth rates are promoted in the dominant genus Desulphovibrio by a temperature of about 30°C, but the sulphate-reducers as a group can withstand temperature extremes of 0°C and 70°C. Their trace element requirements are uncertain, but some species may require traces of such elements as iron, copper, zinc, cobalt, molybdenum and boron for optimum growth. Even in strong concentrations, heavy metal ions are not toxic to them, for they are protected by their sulphide envelope.

The dark residuum does not now represent a zone of bacterial sulphate reduction (which can be easily recognised by its smell), but it may have done so in the past. The Calp mud in particular contains an abundant supply of organic matter, and sulphate ion has been in continuous supply. The wide distribution of supergene galena and the extent to which fossil wood has been replaced by supergene sulphides suggests that sulphate-reducing bacteria were formerly very active throughout the deposit. The factors that subsequently caused pervasive oxidation of the residuum would have diminished their activity, and during glaciation they may have been eliminated almost entirely. There can be little doubt that they became re-established during interglacial stages of the Pleistocene, including the one now in progress. The replacement of the fossil wood Abies may be evidence of this, and bacterial sulphate reduction was probably involved in the recent formation of small amounts of supergene pyrite.

B. Physical erosion

The structure of the residual deposit and the constitution of the Weichsel till in its vicinity confirm that physical denudation of the residuum has taken place. However, the age

and origin of the deposit proposed in previous pages have as a corollary that the average rate of denudation has been fairly small - perhaps less than 100 ft. in more than five million years.

The deposit clearly owes its physical survival chiefly to its situation - entrenched in a sub-horizontal erosion surface at low elevation. Drainage of the Tynagh area is now largely subterranean, and has probably been so for most of the time that the deposit has existed. There is little evidence that high-velocity surface streams have flowed through the deposit's outcrop area at any time, though they may have done so during glacial stages of the Pleistocene.

It has been mentioned that the Weichsel ice probably scoured only a few feet of residuum from the top of the deposit, and that the Weichsel glaciation was preceeded by two others of unknown effect. Between successive glaciations the deposit was presumably protected from physical erosion, temporarily at least, by a cover of till. During glaciation it is thought to have been protected partly by its hard rock margins and partly by freezing of pore fluids before the arrival of the ice sheets. Slender evidence of the latter was the presence of a few steep, discontinuous fissures filled with glacial debris in residuum immediately below the Weichsel till. Although they did not have the attitude or cross-sectional shape of fossil ice-wedges, the filled fissures may have formed under periglacial conditions. Similarly, some of the minor faulting and other structures produced by post-depositional disturbance of, particularly, Calp mud may have originated by periodic freezing and thawing in the periglacial zone.

9.5 COMPARISON WITH OTHER RESIDUAL DEPOSITS

Many deposits that have some features of mineralogy, metal distribution or structure in common with Tynagh residuum have been referred to in previous chapters. It has been mentioned, for instance, that supergene galena is not uncommon in the weathered zone of base metal deposits containing primary galena, that silver-enriched gossans and large bodies of zinc oxidate minerals formed by supergene metasomatism of limestone occur in several parts of the world, and that structures in the Tynagh residuum are similar to those attributed in other deposits to simultaneous decomposition of rocks and subsidence of their residuum. Considerations of space make it necessary to limit the field of detailed comparison, so in this section the Tynagh residual deposit will only be compared with others in which base metal sulphides have been concentrated by weathering processes, and with other pre-glacial residual deposits in the British Isles. It will not be compared with deposits of unconsolidated and partially consolidated sulphides that occur in areas of active vulcanicity and/or appear to have been formed by processes related to vulcanicity (e.g. the "black mud" (kuroko) ores of Japan), or with bodies of unconsolidated material resulting from intense tectonism of pre-existing sulphide mineralisation.

A. Sulphide-rich residual deposits

Concentration of sulphides by chemical processes of weathering is, of course, common. Many copper deposits have owed their profitability largely to chemical concentration of supergene sulphides, and there are numerous references in geological literature to deposits in which weathering processes have concentrated lead, zinc, iron and silver in supergene

sulphide form. Supergene pyrite/marcasite bodies comparable in size to the Tynagh residual deposit have been formed by replacement of the fills of caves and other solution cavities in the limestones of Missouri, and some of the sulphidised fills have been worked for their content of supergene galena and sphalerite (Tarr, 1937; Grawe, 1945; Bretz, 1950).

Concentrations of pre-existing sulphides in unconsolidated materials formed by weathering are rare. Meteoric solutions normally dissolve sulphides more rapidly than associated minerals, and the small amounts of unaltered sulphide that they may liberate from its rock matrix generally tend to be dispersed rather than concentrated by physical processes. Detrital pyrite is a common minor constituent of cave deposits, but such deposits generally contain more iron as hydrated oxide than as sulphide. Small amounts of primary galena, generally as fragments protected from thorough oxidation by a crust of anglesite or cerussite, are sometimes concentrated in cavities in mineralised limestones - some typical instances are mentioned in the subsequent section - and physical concentration of residual sulphides is implied in a description of filled sink holes in the Yunnan province of China by Searls (1952). In such cases, however, sulphides are almost invariably subordinate in quantity to base metal oxidation products. Barite, being relatively insoluble is inherently more amenable to concentration by weathering processes than primary sulphides. Deposits of residual barite have been exploited in many parts of the world, e.g. at Sweetwater, Tennessee (Laurence, 1939).

Cases of concentration of little-altered primary sulphides by dissolution of associated calcite or dolomite have been reported from several mining districts. As in the South Pennines orefield, they usually concern lead-zinc mineralisation in calcareous rocks,

and concentration generally appears to have taken place well below the water table. Many large water-filled caverns were penetrated by workings at the Mill Close Mine, Derbyshire, and the floors of some were littered with angular blocks of galena, limestone and calcite accompanied by sand and clay (Cullingford, 1953; Varvill, 1959). Blocks were often coated by "fine black mud and hydrous iron oxides" (Cullingford, 1953). Such cavities sometimes yielded a natural concentrate with a lead content of 40-50% (Varvill, 1959). How large a tonnage of this material was mined is not recorded. An interesting feature of some of the caverns is that they were lined with large crystals of galena and calcite, yet galena veins in their walls are described by Cullingford as having been "eaten away".

It might be argued from occurrences of this kind that the apparent rarity of residual sulphide concentrates is due to the fact that they typically accumulate in caverns well below the water table, and are normally oxidised by emergence into the zone of aeration during the normal cycle of erosion. This argument is hard to reconcile with any of the accepted theories of cave formation, and the observations of geologists and speleologists do not support it. Their oxide coatings apart, the Mill Close residual deposits were probably not formed by meteoric waters alone but, as Ford and King (1965) have suggested for essentially identical deposits at the nearby Golconda Mine, by groundwaters modified by intermingling with metal-bearing hydrothermal solutions.

The Tynagh residuum seems to be a unique example of large-scale concentration of resistate sulphides by weathering processes.

B. Pre-glacial residual deposits in the British Isles

The Tynagh residual deposit is one of a number of bodies of unconsolidated material formed by weathering of Irish Carboniferous rocks in pre-glacial times (Fig. 9.3). Some bodies of rubble and mud that occur in parts of Ireland where no hypogene mineralisation is known are mentioned in other chapters and do not warrant fuller description here. More pertinent subjects of comparison are three bodies of metalliferous residuum formed by weathering of mineralised Lower Carboniferous limestones. Of these the only one that has been previously described is the so-called Calamine deposit near Silvermines, County Tipperary (Rhoden, 1958). This deposit was worked during the periods 1858-74 and 1950-53, but only its spoil heaps and shallow surface excavations are now accessible. Low grade materials of comparable type have recently been discovered by drilling at Keel, County Longford, and near Loughrea, County Galway.

The Calamine deposit comprises a zone of supergene concentration of oxidate minerals of zinc (hemimorphite and smithsonite) and iron (goethite and siderite) extending from a glacial erosion surface at 400-600 I.O.D. to depths of up to 200 ft. Like the Tynagh deposit it occurs on the faulted margin of a pre-Carboniferous inlier. The zone of supergene enrichment extends some 3,000 ft. from east to west in the immediate hanging wall of the Silvermines Fault and is about 2,500 ft. wide. In 1935 it was reported to contain half a million tons of high-grade ore with an average zinc content of 21%. Estimates of the tonnage of zinc-enriched material of lower grade vary between one and four million.

Rhoden (1958) considers that the Calamine deposit was formed in pre-glacial times by in situ chemical erosion of

superjacent dolomite containing hypogene sulphide mineralisation with an average tenor of 6% Zn as sphalerite and 1% Pb as galena. This is the average grade of the widespread mineralisation in massive dolomite now bounding the deposit. He divides the zinc oxide ores into an upper zone in which hemimorphite and goethite predominate over smithsonite and supergene siderite, and a lower zone in which the proportions are reversed. The suggested cause of the zoning is progressive alteration of smithsonite to hemimorphite by silica-bearing waters percolating from surface. Minor constituents of the zinc-enriched materials include anglesite, cerussite, barite, galena and pyrite; the last three are presumed to be relics of primary mineralisation. On the basis of one analysis of high-grade zinc oxide ore, Rhoden concludes that, relative to the parent protore, the supergene materials are not enriched in lead, but in high-grade sections may be slightly enriched in silver.

The Calamine ores are analogous in origin to the metasomatic zinc oxide ores at the margin of the Tynagh deposit. The comparative abundance of hemimorphite at Silvermines is probably due to weathering of sandy dolomite above the water table. Silification of limestones and alteration of smithsonite to hemimorphite is encouraged by a warm, humid climate, so the deposit may be of approximately the same age as the Tynagh residuum or somewhat older. It contains no palaeontological evidence of its age.

There is an intriguing possibility that the Calamine deposit was at one time overlain by galena-rich clays weathered superficially to a gossan. Boate's "Natural History of Ireland" (1645) records that two types of material were being mined in this locality in the 17th Century - a "reddish, hard, glistering ....

very barren sort, and another "like a marl, something blewish and more soft than the red...producing most silver". According to Boate, "the ore yielded one with another (sic) three pounds weight of silver out of each tun, but a great quantity of lead... also some quicksilver, but not any alom, vitriol, or antimony..."

As Rhoden suggests, the first type of material may have been a gossanised equivalent of the second, which he believes contained residual galena and unspecified silver minerals as minor associates of cerussite and anglesite. If so, experience at Tynagh suggests that Boate may have been in error about the distribution of silver, which was actually concentrated in the reddish material. Alternatively the latter may have been "calamine", or a limonitic residuum of silicified limestone. In any case, the "marl" was probably a clayey residuum containing primary and secondary sulphides. The reference to quicksilver suggests that the former may have included mercurian tennantite, which is one of the main hosts of silver at the Gortdrum deposit 40 miles to the south.

Another early reference to mineralisation in the Silvermines area may also be pertinent. In 1821 Weaver described the Gortnadyne deposit (surface elevation about 300 I.O.D.) in the following terms:

"Let us figure ourselves in an open space formed in the line of apposition of the limestone upon clay shale and probably formed by the parting of the former from the latter rock upon declevity. This space is several fathoms wide at the surface, but it contracts in descending, and finally closes at the depth of about 25 fathoms. It was filled with clay, sandy clay, sand, decomposed slate, and scattered blocks of limestone, lydian stone, and sandstone; the whole mass being cemented or pene-

trated by metallic depositions consisting of iron ochre in various stages of induration, iron pyrites, white lead ore, galena, malachite, copper pyrites and blende, with calcareous spar and heavy spar".

This suggests that the Gortnadyne ore may have been partly residual in origin, but since the workings are now inaccessible this cannot be proved. Rhoden describes the primary ore as a breccia of sandstone fragments recemented by quartz, carbonates, sulphides and barite.

Little information is available about the body of metalliferous residuum associated with the Keel sphalerite deposit. According to Patterson (pers. comm.) it too occurs within 300 ft. of the surface in a mineralised fault zone on the margin of a pre-Carboniferous inlier. The sandy residuum, which is apparently an in situ disaggregation product of a thick bed of Lower Carboniferous arenaceous dolomite, is localised in a zone some 2,000 ft. long that extends at least 300 ft. down the low-angle dip of the containing rocks from a high-angle fault. The parent material is thought to have been unmineralised, but the residuum widely contains about 1% zinc and lesser amounts of lead. All that can be said about the origin of this residual body at present is that it was probably formed near surface by the action of slow-moving groundwaters carrying metals leached from nearly primary mineralisation.

It has already been mentioned that many small bodies of unconsolidated material are known to occur, or are inferable from geophysical evidence, below the glacial cover of the Central Plain. One situated about six miles to the west of Tynagh has been investigated by diamond drilling. Two drill holes passed through an unusual thickness (up to 160 ft.) of glacial drift

into some 30 ft. of Calp mud and sandy material containing up to about 20% by volume of sulphide, almost entirely pyrite and marcasite. The Calp mud was underlain by cavernous dolomite, probably dolomitised Waulsortian bank limestone, containing disseminated pyrite and zones of ocherous material. There is a clear genetic relationship between this residual body and the one at Tynagh.

Turning briefly to other parts of the British Isles, residual deposits in limestone cavities are numerous and widespread. They are most common in Carboniferous limestone, and usually consist of clay, sand and unmineralised rock fragments, often coloured by hydrated oxides of iron and manganese, and sometimes containing small amounts of pyrite and accumulations of lignite and other organic materials. Some preglacial residua in unmineralised limestones are described by Dixon (1921), Thomas (1954), Yorke (1954) and Boulter and Chaloner (in press).

Limestone cavities occur in close association with base metal sulphide mineralisation in the Mendips, the South Pennines and in North Wales. In all these districts the mineralisation occurs predominantly in narrow tabular bodies rather than as masses, disseminations and stockworks in large irregular zones as is the case in the main Irish deposits. Cavities are often found immediately adjacent to or transecting sulphide veins, and they have been penetrated at depths of up to 400 ft. below the present water table (Cullingford, 1953). Some contain only water; others contain, in addition to some or all of the materials listed above, small amounts of smithsonite, cerussite and galena. The Mill Close residuum described previously is exceptional in containing lead largely in primary sulphide form. No other residual deposits in Britain have been worked specifi-

cally for their sulphide concent. Accumulated fragments of cerussite and galena in unknown proportions are reported in a small cave transecting a galena vein in Carboniferous limestones at Monyash near Buxton, Derbyshire (Waltham, pers. comm.), and lumps of cerussite are not uncommon in the fill of cavities adjacent to galena veins in North Wales (Strahan, 1890). Detrital smithsonite, cerussite and galena have been found in small amounts in similar cavities in the Mendips (Gough, 1930), and Balch (1926) records that some "ore of copper" was found among debris on the floor of a cave (Swildon's Hole) in the same district. Residual barite has been worked on a small scale in the Mendips, and substantial amounts of ocherous hematite - precipitated from waters percolating through a former or existing Triassic cover - have been extracted from solution cavities and fissures in Carboniferous Limestone (Cantrill et al, 1919). Finally, it is worth mentioning that tree trunks up to 1½ ft. in girth were found to depths of 1,300 ft. below surface in the cavernous Carboniferous Limestone of the Halkyn mining district, N. Wales. Strahan describes one wood fragment as having cracks and cavities "filled with yellow sulphur" (probably pyrite).

SUMMARY OF CONCLUSIONS

1. The Tynagh residual deposit originated by weathering of a large volume of Lower Carboniferous limestone, much of it richly mineralised by base metal sulphides and barite. The main sulphides present were galena, sphalerite, pyrite and, more locally, tennantite. The epigenetic minerals, which occurred chiefly as massive replacements, fracture fillings and disseminations, were strongly localised in Waulsortian micrites, biomicrites and crinoidal limestones in a zone up to 300 ft. wide in the immediate hanging wall of the North Tynagh Fault. A synclinal fold in the hangingwall limestones appears to have been an important structural control of mineralisation. The origin and age of the primary mineralisation have not been firmly established, but there are grounds for believing that the heavy metals were introduced in heated chloride-bearing solutions that migrated upwards into a zone of dilation caused by movement on the North Tynagh Fault in late Carboniferous or early Permian times. The maximum temperature of the sulphide-depositing solutions may have been about 350°C. The cationic and anionic constituents of the sulphides and barite may have been derived from different sources.

2. Weathering of the mineralised limestones was initiated in or not far below an erosion surface about 100 ft. above that of today. The contemporary water table was close to surface (where it has remained ever since), and the contemporary climate seasonally or perennially humid. One of the main effects of weathering was thorough-going subterranean decalcification of mineralised and carbonaceous limestones, yielding a residuum consisting essentially of sulphides, barite, quartz and clay minerals.

This took place largely below the water table, where reducing conditions discouraged oxidation of sulphides, but it was promoted by vadose oxidation of sulphides at higher levels, and consequent acidification of percolating waters. Phreatic weathering solutions were guided by tectonic and sedimentary structures in the ore zone and its surrounds.

3. In geomorphological terms, the deposit is a combination of solution-subsidence structures and roofless caverns with sedimentary infillings. An early and a late stage of phreatic cavern formation can be distinguished, but sedimentation and subsidence have been going on almost continuously since the deposit began to form. Solutional entrenchment of sediments has considerably modified their structure and the shape of the containing cavities, and there remains only vestigial evidence of the early phase of cavern formation.

4. The sedimentary materials that constitute the bulk of the deposit and form its core are largely weathering products of rocks that formerly occupied the same space and the space vertically above it. They have been augmented by fine-grained sediments and timber fragments from unknown but probably local sources, by sandstone pebbles from an adjacent Devonian inlier, and by small amounts of subsided glacial till. A marked unconformity separates most parts of the deposit from its complete cover of Pleistocene glacial till.

5. Sedimentation took place under still water, partly by catastrophic collapse of solution-undermined materials, partly by vertical settling of dissaggregated materials, and partly by water-lubricated slumping into depressions

in the deposit's constantly-changing surface. Its structure has been little affected by glaciations of the region, probably because the residuum was consolidated by freezing of its pore waters before the ice sheets arrived. Sedimentation in its upper levels may have been particularly encouraged by periglacial conditions.

6. The residual body has an extensive resistate mineralogy, and contains, in physically and chemically modified forms, distinct patterns of heavy metal zoning inherited from the weathered primary mineralisation. Neither reflects any major difference of mineralogy or metal zonation between the weathered part of the ore zone and that which remains below the residual deposit.

7. Residual primary sulphides in the central part of the deposit owe their survival chiefly to constant immersion in slow-moving water that, in the main, and for much of the time, had little or no oxidation potential. The activity of sulphate-reducing bacteria may have helped to depress the Eh of pore fluids in certain types of material. Reducing conditions were widespread during the early history of the deposit, when at least seven metals were reprecipitated from weathering solutions in sulphide form. Parts of the deposit have been enriched in silver, cadmium and probably copper in this way. In time, due partly to denudation of the area and consequent lowering of the local water table towards its present position, and partly to superimposition on the deposit of calcareous tills, conditions became generally unfavourable to supergene formation of sulphides of lead, zinc and iron except in materials undergoing bacterial decomposition.

8. For the same reasons, oxidation of sulphides tended to become more widespread with time, and increasing quantities of metal were carried in solution towards the deposit's periphery. Their main directions of migration were downwards and northwards. Some were cumulatively reprecipitated by reactions between migrant solutions and the deposit's limestone wallrocks, leading to the formation of a peripheral zone of supergene carbonate enrichment that has tended to expand both towards and away from the deposit's centre. Selective precipitation of metals within this zone has superimposed secondary patterns of metal zonation on those inherited from primary mineralisation.

9. Zones of relatively rapid groundwater flow developed in the deposit's oxide envelope as it formed. Streaming of highly oxidising, carbonate-deficient waters through these zones caused certain base metals, especially lead, to be strongly leached from them, and resulted in the formation of a gossan assemblage of minerals. Silver was concentrated in these zones, chiefly as native metal. A large gossan body at the centre of the deposit may have formed partly above the water table, but elsewhere gossanisation appears to have been a phreatic weathering effect. A consequence of gossanisation was local enrichment of nearby residuum in sulphides of silver and perhaps copper.

10. The deposit is thought to be Miocene or Pliocene in age, but an earlier Tertiary or a Plio-Pleistocene age cannot be ruled out on present evidence. Some late-formed residuum contains fossil wood indicative of a Hoxnian interglacial age.

11. The deposit is a uniquely large example of mechanical concentration of sulphides by weathering. It is, however, closely related in origin, and probably in age, to several other deposits of metalliferous residuum in central Ireland. Others of its kind may be found in Ireland where high-grade primary mineralisation in pure, fractured limestones has been subjected to prolonged weathering in or near a pre-glacial erosion surface at low elevation.

PRACTICAL APPLICATIONS AND IMPLICATIONS OF RESEARCH RESULTS

1. Much that has been learnt about the geology of the residual deposit in the course of this study has been put to practical use. In particular, the interpretation of the deposit's structure presented in this thesis was adopted as a basis for complete re-calculation of the residual ore reserve in 1966. Mineralogical studies have helped to rationalise concentrator performance, and since concentrating efficiency depends on careful blending of types of residuum with a limited range of physical and chemical properties, the research results have also had an important application to grade control.
2. Where future mining of the residuum is concerned, materials in the lower part of the deposit do not differ in any important physical or mineralogical respect from those that have been mined and treated already. The high clay content of some residuum in the lower parts of the deposit may constitute a mining problem, and its high pyrite content a treatment problem. The main hosts of lead, zinc and copper will continue to be sulphides and carbonates to the bottom of the deposit. There is no reason to believe that in its lower levels significant amounts of these metals or of silver will occur in minerals that are not amenable to current concentrating techniques.
3. Ground control may be difficult in protore below the central part of the deposit, where local collapse breccias may occur in places. Particularly in this area, a proportion of total lead and zinc in protore will be locally present as carbonate.

Except in the immediate vicinity of the residual body, primary copper minerals in protore will be usually altered to sulphides rather than to carbonates of copper. Weathering effects are to be expected locally at all depths in the Main Orebody.

4. Economically significant variations may occur in the composition of tennantite-tetrahedrite. It is possible, for instance, that in places it may be richer in silver and/or mercury than material analysed during this study.

5. It is unlikely that major compositional variations will occur in other economic constituents of protore, though the strontium content of barite and the cadmium content of sphalerite will almost certainly vary from place to place. The possibility that the amount of silver intimately associated with galena is to some extent dependent on reactions between lead-bearing solutions and pre-existing tennantite-tetrahedrite is worth keeping in mind as a possible guide to undiscovered zones of copper mineralisation that may be present in the Tynagh area.

6. Three of the four large base metal deposits so far discovered in the Lower Carboniferous rocks of Ireland have residual deposits associated with them. The absence of such a deposit at Gortdrum is probably due mainly to the low pyrite content of the mineralisation there. The chances of finding another large body of base metal-enriched residuum are less than they are of finding another large protore body. In the writer's opinion, the latter is most likely to be found in Tournaisean or lower Visean rocks cut by a major fault trending approximately ENE-WSW, but not necessarily on the margin of a pre-Carboniferous inlier. Further thoughts on this subject have been published elsewhere (Morrissey et al, 1969). For it to yield a metal-rich residuum the primary mineralisation would

have to be moderately pyritic and close to surface, and the surrounding rocks calcareous or dolomitic rather than argillaceous or siliceous. For an economic deposit of resistate sulphides to form, other conditions specified in section 8.2 would have to be met.

7. The existence of a deposit of metal-rich residuum below a glacial drift cover is not necessarily indicated by any peculiarity of the topography, surface drainage pattern, or vegetation type. A sub-drift deposit of this kind is most likely to be found by geochemical techniques, and one that has a cover of unmineralised rock by resistivity, and perhaps induced polarisation and gravimetric methods.

REFERENCES

Adams, C.S., and Swinnerton, A.C., 1937, Solubility of limestone: Trans. Am. Geophys. Union, v.18, p.504-508.

Allen, E.T., Crenshaw, J.L., and Merwin, H.E., 1914, Effect of temperature and acidity in the formation of marcasite (FeS_2) and wurtzite (ZnS): Am. J.Sci., v.38, p.393-431.

Anderson, A.L., 1930, The incipient oxidation of galena: Econ.Geol., v.25, p.528-542.

Andrews, H.N., 1947, Ancient plants and the world they lived in: Constable & Co. Ltd., London.

American Society for Testing Materials powder data file.

Baas Becking, L.G.M., Kaplan, I.R., and Moore, D., 1960, Limits of the natural environment in terms of pH and oxidation-reduction potentials: J. Geol., v.68, p.243-284.

Balch, H.E., 1926, Caves of the Mendips: Folk Press Ltd., London.

Bastin, E.S., Graton, L.G., Lindgren, W., Newhouse, W.H., Schwartz, G.M., and Short, M.N., 1931, Criteria of age relations of minerals, with especial reference to polished sections of ores. Econ. Geol., v.26, p.331-354.

Baskin, Y., 1956, A study of authigenic feldspars: J. Geol., v.64, p.132-155.

Bateman, A.M., 1950, Economic mineral deposits: John Wiley & Sons Inc., London.

Beales, F.W., and Jackson, S.A., 1966, Precipitation of lead-zinc ores in carbonate reservoirs as illustrated by Pine Point ore field, Canada: Trans. Inst. Min. Metall., v.75, p.B278-285.

Berry, L.G., and Thompson, R.M., 1962, X-ray powder data for ore minerals: Mem. Geol. Soc. Am. 85.

Bishopp, D.W., and McCluskey, J.A.G., 1948, Sources of industrial silica in Ireland: Geol. Surv. Ireland. Emergency Period Pamphlet No.3.

Blanchard, R., 1968, Interpretation of leached outcrops: Nevada Bureau of Mines, Bull. 66.

Blundell, D.J., Davey, F.J., and Graves, L.J., 1968, Sedimentary basins in the south Irish Sea: Nature, v.219, p.55-56.

Boate, G., 1645, The natural history of Ireland. Republished in 1755 with Molineux, T., and others by G. & A. Ewing, Dublin.

Borchert, H., 1960, Genesis of marine sedimentary iron ores: Trans. Inst. Min. Metall., v.69, p.261-279.

Boulter, M., and Chaloner, W.G., Late Tertiary fossil plants in Derbyshire: Review of Palaeobotany and Palynology (in press).

Boyle, R.W., 1965, Geology, geochemistry and origin of the lead-zinc-silver deposits of the Keno Hill-Galena Hill area, Yukon Territory: Bull. Geol. Surv. Canada 111.

Boyle, R.W., 1968, The geochemistry of silver and its deposits: Bull. Geol. Surv. Canada 160.

Boyle, R.W., and Jambor, J.L., 1966, Mineralogy, geochemistry and origin of the Magnet Cove barite-sulphide deposit, Walton, Nova Scotia: Trans. Can. Inst. Min. Metall., v.69, p.394-413.

Bragg, W.L., 1937, Atomic structure of minerals: Cornell Univ. Press, Ithaca, N.Y.

Brett, R., 1964, Experimental data for the system Cu-Fe-S and their bearing on exsolution textures in ores: Econ. Geol., v.64, p.1241-1269.

Bretz, J.H., 1938, Caves in the Galena Formation: J. Geol., v. 46, p.828-841.

Bretz, J.H., 1940, Solution cavities in the Joliet Limestone of north-eastern Illinois: J. Geol., v.48, p.337-384.

Bretz, J.H., 1942, Vadose and phreatic patterns of limestone caverns: J. Geol., v.50, p.675-811.

Bretz, J.H., 1950, Origin of the filled sink-structures and circle deposits of Missouri: Geol. Soc. Am. Bull., v.61. p.789-833.

Brown, J.S., 1936, Supergene sphalerite, galena and willemite at Balmat, New York: Econ. Geol., v.31, p.331-354.

Browne, P.R.L., 1969, Sulphide mineralisation in a Broadlands geothermal drill hole, Taupo volcanic zone, New Zealand: Econ. Geol., v.64, p.156-159.

Cantrill, T.C., Sherlock, R.L., and Dewey, H., 1919, Special reports on the mineral resources of Great Britain, Vol. 9, Iron ores: Mem. Geol. Surv. Gt. Britain.

Chaloner, W.G., and Boulter, M., 1966, Tertiary plants from the South Pennines: Report on a meeting of the Palynological Association at Imperial College, London, December 1966.

Chandler, M.E.J., 1957, Oligocene flora of the Bovey Tracey lake basin, Devonshire: Bull. Brit. Mus. Nat. Hist. Geol., v.3, no.3.

Charlesworth, J.K.C., 1963, Historical Geology of Ireland: Oliver & Boyd Ltd., Edinburgh.

Clark, A.H., Cooke, R.U., Mortimer, C., and Sillitoe, R.H., 1967, Relationships between supergene mineral alteration and geomorphology, southern Atacama Desert, Chile : Trans. Inst. Min. Metall., v.76, p.B89-96.

Cloke, P.L., 1961, The transportation and deposition of chalcophile metals by sulfide and polysulfide complexes in hydrothermal solution: Papers of the Michigan Acad. of Science, Arts and Letters, v.46, p.5-18.

Cole, G.A.J., 1912, The interbasaltic rocks of north-east Ireland: Mem. Geol. Surv. Gt. Britain.

Cole, G.A.J., 1922, Memoir and map of localities of minerals of economic importance and metalliferous mines in Ireland: Geol. Surv. Ireland.

Cole, G.A.J., and Hallissy, T., 1924, Handbook of the geology of Ireland: Murby & Co. Ltd., London.

Corbel, J., 1952, Une region karstique d'Ireland: le Burren: Rev. Geog. Lyon., v.27, p.21-33.

Cullingford, C.H.D. (Editor), 1953, British caving: Routledge & Kegan Paul Ltd., London, 2nd edition.

Curtis, C.D., and Spears, D.A , 1968, The formation of sedimentary iron minerals: Econ. Geol., v.63, p.257-270.

Dana, E.S., 1932, A textbook of mineralogy: Chapman & Hall Ltd., London.

Dana, J.D., and Dana, E.S , The system of mineralogy of, edited by Palache, C., Berman, H., and Frondel, C., 1944 (vol.1), 1951 (vol.2.): Chapman & Hall Ltd., London.

Davis, S.N., and DeWiest, R.J.M., 1966, Hydrology: John Wiley & Sons. Inc., London.

Davis, W.M., 1930, Origin of limestone caverns: Bull. Geol. Soc. Am., v.41, p.475-628.

Deans, T., 1948, The Kupferschiefer and the associated lead-zinc mineralisation in the Permian of Silesia, Germany and England: Int. Geol. Congress, Gt. Britain, Report of the 18th Session, pt. 7, p.340-351.

Deer, W.A., Howie, R.A , and Zussman, J., 1962, Rock-forming minerals, Vol. 5, Non-silicates: Longmans, Green & Co. Ltd., London.

Derry, D.R., Clark, G.R., and Gillat, N., 1965, The Northgate base metal deposit at Tynagh, County Galway, Ireland: Econ. Geol., v.60, p.1218-1237.

Derry, D.R., 1966, The Northgate base metal deposit at Tynagh, Ireland - a reply: Econ. Geol., v.61, p.1450-1451.

DeSitter, L.U., 1956, Structural geology: McGraw-Hill, New York.

Dewey, J.F., and McKerrow, W.S , 1963, An outline of the geomorphology of Murrisk and north-west Galway: Geol. Mag. v.100, p.260-275.

Dixon, E.E.L., 1921, The Geology of the South Wales coalfield, Pt. 13, The country around Pembroke and Tenby: Mem. Geol. Surv. Gt. Britain.

Donovon, P.R., 1965, Geochemical dispersion in relation to base metal deposits in glacial terrain in west-central Ireland: Ph.D. thesis of the University of London.

Douglass, R.M., Murphy, M.J. and Pabst, A., 1954, Geocronite: Am. Mineral, v.39, p.908-928.

Eadington, P., and Prosser, A.P., 1969, Oxidation of lead sulphide in aqueous suspensions: Trans. Inst. Min. Metall., v.78, p.C74-82.

Edwards, A.B., 1954, Textures in ore minerals and their significance: Aust. Inst. Min. Metall., Melbourne.

El Shazly, E.M., Webb, J.S., and Williams, D.W., 1957, Trace elements in sphalerite, galena and associated minerals from the British Isles: Trans. Inst. Min. Metall., v.66, p.241-271.

Ellis, A.J., 1969, Present-day hydrothermal systems and mineral deposition: Ninth Commonwealth Min. Metall. Congress, Mining and Petroleum Geology Section preprint 7.

Eyles, V.A., 1952, Composition and origin of Antrim laterites and bauxites: Mem. Geol. Surv. Gt. Britain.

Farrington, A., 1929, Preglacial topography of the Liffey Basin: Proc. Roy. Irish Acad., Ser. B., v.38, p.148-170.

Fetzer, G.W., 1946, Humic acids and true organic acids as solvents of minerals: Econ. Geol., v.41, p.47-56.

Fitzgerald, D.H.B., and Oram, R.A.T.J., 1969, Grade control at Tynagh mine, Ireland, using data processing techniques: Ninth Commonwealth Min. Metall. Congress, Mining and Petroleum Technology Section preprint 31.

Fleischer, M., 1955, Minor elements in some sulphide minerals: Econ. Geol. 50th Anniv. Vol., p.970-1024.

Ford, T.D., and King, R.J., 1965, Layered epigenetic galena-barite deposits in the Golconda mine, Derbyshire, England: Econ. Geol., v.60, p.1686-1701.

Frenzel, G., 1959, Idait und blaubleibender Covellin: Neues Jahrbk. Mineral. Abhandlg, v.93, p.87-133.

Frenzel, G., 1961, Der Cu-Uberschuss des blaubleibender Covellins: Neues Mineral., Monatsch. 9, p.199-204.

Frenzel, G., and Ottemann, J., 1967, Eine Sulfidparagenese mit kup kupferhaltigem Zonarpyrit von Nukudamu, Fiji: Mineral Deposita, v.1, p.307-316.

Friedman, G.M., and Sanders, J.E., 1967, Origin and occurrence of dolostones, in Carbonate rocks (ed. Chilangar, G.V., Bissell, H.J., and Fairbridge, R.W.): Elsevier, Amsterdam.

Fryklund, V.C., and Fletcher, J.D., 1956, Geochemistry of sphalerite from the Star Mine, Coeur d'Alene district, Idaho: Econ. Geol., v.51, p.223-247.

Gages, A., 1860, On the formation of orpiment in a mass of sulphate of barytes found interstratified in the Carboniferous Limestone near Silvermines, County of Tipperary: J. Geol. Soc. Dublin., v.8,p.243-244.

Garrels, R.M., 1941, The Mississippi Valley type lead-zinc deposits and the problem of mineral zoning: Econ. Geol., v.36,p.729-744.

Garrels, R.M., 1954, Mineral species as a function of pH and oxidation-reduction potentials, with special reference to the zone of oxidation and secondary enrichment of sulphide ore deposits: Geochim. et Cosmochim. Acta, v.5, p.153-168.

Garrels, R.M., and Christ, C.L., 1965, Solutions, minerals and equilibria: Harper & Row Ltd., London.

Garrels, R.M., and Dreyer, R.M., 1952, Mechanism of limestone replacement at low temperatures and pressures: Bull. Geol. Soc. Am., v.63, p.325-380.

Garrels, R.M., and Naeser, C.R., 1959, Equilibrium distribution of dissolved sulfur species for water at 25°C and 1 atm. total pressure: Geochim. et Cosmochim. Acta, v.15, p.113-130.

Garrels, R.M., Thompson, M.E., and Siever, R., 1960, Stability of some carbonates at 25°C and 1 atm total pressure: Am. J. Sci., v.258, p.402-418.

Garrels, R.M., Thompson, M.E., and Siever, R., 1961, Control of carbonate solubility by carbonate complexes: Am. J. Sci., v.259, p.24-45.

Garretty, M.D., and Blanchard, R., 1942, Post-mine leaching of galena and marmatite at Broken Hill: Proc. Aust. Inst. Min. Metall., v.127 (N.S.), p.149-170.

George, T.N., 1968, Landform and structure in Ulster: Scottish J. Geol., v.3, p.413-448.

Gill, W.D., 1962, The Variscan fold belt in Ireland, in Some aspects of the Variscan fold belt (ed. Coe, K.): Manchester Univ. Press, Manchester.

Goldschmidt, V.M., 1954, Geochemistry (ed. Muir, A): Oxford Univ. Press, London.

Gottschalk, V.H., and Buehler, H.A., 1912, Oxidation of sulfides: Econ. Geol., v.7, p.15-34.

Gough, D., 1962, Geology of the Greenside lead mine, Cumberland: Ph.D. thesis of the University of London.

Gough, J.W., 1930, The mines of Mendip: Oxford Univ. Press, London.

Granger, H.C., and Warren, C.G., 1969, Unstable sulfur compounds and the origin of roll-type uranium deposits: Econ. Geol., v.64, p.160-171.

Grawe, O.R., 1945, Pyrites deposits of Missouri: Missouri Geol. Surv. and Water Resources, Ser. 2, v.30.

Gray, I.M., 1961, Reflection characteristics of opaque minerals: Ph.D. thesis of the University of London.

Grondijs, H.F., and Schouten, C., 1937, A study of the Mount Isa ores: Econ. Geol., v.32, p.407-450.

Hall, W.E., and Heyl, A.V., 1968, Distribution of minor elements in ore and host rock, Illinois-Kentucky fluorite district and Upper Mississippi Valley zinc-lead district: Econ. Geol., v.63, p.655-670.

Hallimond, A.F., Dunham, K.C., Hemingway, J.E., Taylor, J.H., Davies, W., Dixie, R.J.M., and Bannister, F.A., 1951, The constitution and origin of sedimentary iron ores: a symposium: Proc. Yorks. Geol. Soc., v.68, p.61-101.

Halloff, P.G., Schultz, R.W., and Bell, R.A., 1962, Induced polarisation and geological investigations of the Ballyvergin copper deposit, County Clare, Ireland: Trans. Am. Inst. Min. Eng., v.223, p.312-318.

Hanor, J.S., 1968, Frequency distribution of compounds in the barite-celestite series: Am. Mineral., v.53, p.1215-1222.

Handbook of chemistry and physics, 1964, (Ed. Weast, R.C., Selby, S.M., and Hodgman, C.D.): The Chemical Rubber Co., Cleveland, Ohio. 45th edition.

Hey, M.H., 1962, An index of mineral species and varieties: Brit. Mus., London. 2nd edition.

Hills, E.S., 1963, Elements of structural geology: John Wiley & Sons. Inc., New York.

Hutta, J.J., and Wright, H.D., 1964, The incorporation of uranium and silver by hydrothermally synthesised galena: Econ. Geol., v.59, p.1003-1024.

James, H.L., 1954, Sedimentary facies of iron formations: Econ. Geol., v.49, p.235-293.

Jessen, K., Andersen, S.T., and Farrington, A., 1959, The interglacial deposit near Gort, County Galway, Ireland: Proc. Roy. Irish Acad., Ser. B., v.60, p.1-77.

Jolly, J.L., and Heyl, A.V., 1964, Mineral paragenesis and zoning in the Central Kentucky mineral district: Econ. Geol., v.59, p.596-624.

Kalliokoski, J., 1966, Diagenetic pyritization in three sedimentary rocks: Econ. Geol., v.61, p.872-885.

Kanehira, K., and Bachinski, D., 1967, Framboidal pyrite and concentric textures in ores of the Tilt Cove Mine, north-eastern Newfoundland: Canadian Mineral., v.9, p.124-128.

Keller, W.D., 1957, The principles of chemical weathering: Lucas Bros., Columbia, Missouri.

Kelley, W.C., Takahashi, T., Behre, C.H., Durek, J.J., Sloertz, G.E., and Felber, B., 1958, Progress in leached outcrop studies (abstract): Econ. Geol., v.53, p.921.

Kinahan, G.H., 1865, Explanation to accompany sheets 115 and 116 of the maps of the Geological Survey of Ireland: Mem. Geol. Surv. Ireland.

Kinahan, G.H., 1878, Manual of the geology of Ireland: Kegan Paul & Co., London.

Kutina, J., and Sedlackova, J., 1961., The role of replacement in the origin of some cockade textures: Econ. Geol., v.56, p.149-176.

Laurence, R.A., 1939, Origin of the Sweetwater, Tennessee, barite deposits: Econ. Geol., v.34, p.190-200.

Lees, A, 1961, The Waulsortian "reefs" of Ireland: a carbonate mudbank complex of Lower Carboniferous age:J. Geol., v.69, p.101-109.

Lees, A., 1964, The structure and origin of the Waulsortian (Lower Carboniferous) "reefs" of west-central Eire: Phil. Trans. Roy. Soc. Lond., Ser. B, v.247, p.483-531.

Leggo, P.J., Compston, W., and Leake, B.E., 1966, The geochronology of the Connemara granites and its bearing on the antiquity of the Dalradian Series: Q.J.G.S. Lond., v.122, p.91-118.

Lindgren, W, 1933, Mineral deposits: McGraw-Hill, New York, 4th edition.

Listova, L.P., 1966, Experimental data on the solubility of lead sulphide under oxidising conditions: Geochemistry International, v.3, p.25-34.

Locke, A., 1926, Leached outcrops as guides to copper ore: Bailliere, Tindall & Cox, London.

Loughlin, G.F., 1914, The oxidised zinc ores of the Tintic district, Utah: Econ. Geol., v.9,p.1-24.

Loughlin, G.F., 1918, The oxidised zinc ores of Leadville, Colorado: U.S.G.S. Bull.681.

Love, L.G. and Amstutz, G.C., 1966, Review of microscopic pyrite from the Devonian Chattanooga Shale and Rammelsberg Banderz: Fortsch. Mineral., v.43, p.273-309.

Love, L.G., and Murray, J.W., 1963, Biogenic pyrite in recent sediments of Christchurch Harbour, England: Am.J. Sci., v.261, p.433-438.

Love, L.G., and Zimmerman, D.O., 1961, Bedded pyrite and microorganisms from the Mount Isa Shale: Econ. Geol., v.56, p.873-896.

MacDougall, I., and Strip, J.J., 1968, Isotopic dating evidence for the age of climatic deterioration and the Pliocene-Pleistocene boundary: Nature, v.219, p.51-53.

Manning, P.G., 1967, Adsorption spectra of Fe(III) in octahedral sites in sphalerite: Canadian Mineral., v.9, p.57-64.

Millman, A.P., 1960, The descloizite-mottramite series of vanadates from Minas de Lueca, Angola: Am. Mineral., v.45, p.763-773.

Millman, A.P., and Gray, I.M., 1962, Reflection characteristics of ore minerals: Econ. Geol., v.57, p.325-349.

Morris, H.T., and Lovering, T.S., 1952, Supergene and hydrothermal dispersion of heavy metals in wallrocks near orebodies, Tintic district, Utah: Econ. Geol., v.47, p.685-716.

Morrissey, C.J., 1965, The Tynagh lead-zinc deposit, County Galway, Ireland: Undergraduate dissertation, Royal School of Mines, London.

Morrissey, C.J., Patterson, J.M., Steed, G.M., and Wheatley, C.J., 1969, Contributed remarks to discussion of Russell (1968): Trans. Inst. Min. Metall., v.78, p.B48-51.

Murphy, T., 1962, Some unusual low Bouguer anomolies of small extent in central Ireland and their connection with geological structure: Geophys. Prospecting, v.10, p.258-270.

Nesterova, Yu.S., 1958, The chemical composition of galena: Geochemistry (Geokhimiya), v.1, p.835-845.

Newhouse, W.H., 1933, Mercury in native silver: Am. Mineral., v.18, p.295-299.

Nishihara, G.S., 1914 , The rate of reduction of acidity of descending waters by certain ore and gangue minerals, and its bearing on secondary sulphide enrichment: Econ. Geol., v.9, p.743-757.

Nissen, A.E., and Hoyt, S.L., 1915, Silver minerals in galena: Econ. Geol., v.10, p.172-179.

O'Brien, M.V., 1969, Contributed remarks to discussion of Russell (1968): Trans. Inst. Min. Metall., v.78, p.B51-52.

Oelsner, E., 1966, Atlas of the most important ore mineral parageneses under the microscope (trans. Hazzard, B.J.): Pergamon Press, Oxford.

Ohle, E.L., 1959, Some considerations in determining the origin of ore deposits of the Mississippi Valley type. Econ. Geol., v.54, p..769-787.

Ollier, C.D., and Tratman, E.K., 1956, The geomorphology of the caves of north-west Clare: Proc. Spel. Soc. Bristol Univ.,1955-56.

Olson, H.J., 1966, Oxidation of a sulphide body, Glove Mine, Santa Cruz County, Arizona: Econ. Geol., v.61, p.731-743.

Park, C.F., and MacDiarmid, R.A., 1964, Ore deposits: W.H. Freeman & Co. Ltd., London.

Pauling, L., and Neuman, E.W., 1934, The crystal structure of binnite: Zeitschr. Kristall., v.88, p.54-62.

Pettijohn, F.J., 1957, Sedimentary rocks: Harper & Bros, New York. 2nd edition.

Pockley, R.P.C., 1961, Lead isotope and age studies of uranium and lead minerals from the British Isles and France: Ph.D. thesis of the University of Oxford.

Ramdohr, P., 1955, Die Erzmineralien und Ihre Verwachsungen: Academie-Verlag, Berlin.

Rhoden, H.N., 1958, The geology and mineralisation of the Silvermines area, north Tipperary, Eire: Ph.D. thesis of the University of London.

Rickard, D.T., 1968, The geological and microbiological formation of iron sulphides: Ph.D. thesis of the University of London.

Rickard, D.T., 1969, The chemistry of iron sulphide formation at low temperatures: Acta Univ. Stockholm, Contrib. in Geol., v.20, p.67-95.

Rickard, D.T., 1970, The origin of framboids: Logos, v.3. (In press)

Roedder, E., 1968, The non-colloidal origin of "colloform" textures in sphalerite ores: Econ. Geol., v.63, p.451-471.

Roland, G.W., 1968, The system Pb-As-S: composition and stability of jordanite: Mineral. Deposita, v.3,p.249-260.

Roseboom, E.H., 1966, An investigation of the system Cu-S and some natural copper sulphides between 25°C and 700°C: Econ. Geol., v.61, p.641-672.

Roseboom, E.H., and Kellerud, G., 1958, The solidus in the system Cu-Fe-S between 400°C and 800°C: Carnegie Inst. Washington Ann. Rep. Dir. Geophysics. Lab., v.58, p.222.

Ross, C.S., and Hendricks, S.B., 1945, Minerals of the montmorillonite group: U.S.G.S. Prof. Paper 205-B.

Ross, C.S., and Kerr, P.F., 1936, Halloysite and allophane: U.S.G.S. Prof. Paper 185-G.

Roy, D.A., and Mumpton, F.A., 1956, Stability of some minerals in the system $ZnO-SiO_2-H_2O$: Econ. Geol., v.51, p.432-443.

Russell, E.J., 1950, Soil conditions and plant growth: Longmans, Green & Co. Ltd., London, 8th edition.

Russell, M.J., 1968, Structural controls of base metal mineralisation in Ireland in relation to continental drift: Trans. Inst. Min. Metall., v.77, p.B117-128.

Sato, M., 1960, Oxidation of sulphide orebodies: Econ. Geol., v.55, p.928-961, 1202-1231.

Sato, R., 1959, Structure of precipitated cadmium sulphide as studied by single-crystal electron diffraction pattern: Nature, v.184, p.2005-2006.

Sawkins, F.J., 1968, The significance of Na/K and Cl/SO_4 ratios in fluid inclusions and subsurface waters with respect to the genesis of Mississippi Valley-type ore deposits: Econ. Geol., v.63, p.935-942.

Schaller, W.T., and Fairchild, J.G., 1938, Cadmium in smithsonite from New Mexico: Am. Mineral., v.23, p.894-897.

Schmalz, R.F., 1959, A note on the system Fe_2O_3-H_2O: J. Geophysics Research, v.64, p.575-579.

Schultz, R.W., 1966a, Lower Carboniferous cherty ironstones at Tynagh, Ireland: Econ. Geol., v.61, p.311-342.

Schultz, R.W., 1966b, The Northgate base metal deposit at Tynagh, County Galway, Ireland - A discussion: Econ. Geol., v.61, p.1443-1449.

Schultz, R.W., 1968, The geology of the primary sulphide-barite deposits at Tynagh, Ireland: Ph.D. thesis of the University of Dublin.

Schultz, R.W., and Sevastopulo, G.D., 1965, Lower Carboniferous volcanic rocks near Tulla, County Clare, Ireland: Sci. Proc. Roy. Dublin Soc., Ser. A, v.2, p.153-162.

Schwartz, G.M., 1953, Relations of chalcocite-stromeyerite-argentite: Econ. Geol., v.30, p.128-146.

Schwartzbach, M., 1963, Climates of the past: an introduction to palaeoclimatology (trans. and ed. Muir, R.O.): D. Van Nostrand & Co. Ltd., London.

Searls, F., 1952, Karst ores in the Yunnan: Econ. Geol., v.47, p.339-346.

Shotton, F.W., 1967, Problems and contributions of methods of absolute dating within the Pleistocene period: Q.J.G.S. Lond., v. 122, p.357-383.

Smith, G., 1922, Notes on the mineralogy of the Broken Hill district: Mem. Geol. Surv. N.S.W. 8, Appendix IV.

Smith, W.E., 1960, The siliceous constituents of chert: Geol. en Mijnbouw, v.39, p.1-8.

Smith, R.L., Simons, F.S., and Vlisidis, A.C., 1953, Hidalgoite, a new mineral: Am. Mineral., v.38, p.1218-1224.

Solomon, M., 1967, Fossil gossans (?) at Mount Lyell, Tasmania: Econ. Geol., v.62, p.757-772.

Springer, G., Electron probe analyses of tetrahedrite: Min. Mag. (in press).

Stanton, R.L., 1957, Studies of polished surfaces of pyrite and some implications: Canadian Mineral., v.6, p.87-119.

Stanton, R.L., 1964, Mineral interfaces in stratiform ores: Trans. Inst. Min. Metall., v.74, p.45-79.

Strahan, A., 1890, The geology of the neighbourhood of Flint, Mold and Ruthin: Mem. Geol. Surv. Gt. Britain.

Stringfield, V.T., and LeGrand, H.E., 1969, Hydrology of carbonate rock terranes - a review: J. Hydrol., v.8, p.349-417.

Swinnerton, A.C., 1932, Origin of limestone caverns: Bull. Geol. Soc. Am., v.43, p.662-693.

Sweeting, M.M., 1955, The landforms of north-west County Clare, Ireland: Inst. Brit. Geographers, Publication 21.

Takahashi, T., 1960, Supergene alteration of lead and zinc deposits in limestone: Econ. Geol., v.55, p.1083-1114.

Tarr, W.A., 1937, Origin of the marcasite sink-hole deposits of central Missouri: Am. Mineral., v.22, p.830-841.

Taylor, J.H., 1938, The formation of supergene galena at Broken Hill, Northern Rhodesia: Min. Mag., v.31, p.908-913.

Taylor, C.M., and Radtke, A.S., 1969, Micromineralogy of silver-bearing sphalerite from Flat River, Missouri: Econ. Geol., v.64, p.306-318.

Thomas, T.M., 1954, Solution subsidence outliers of the Millstone Grit on the Carboniferous Limestone of the North Crop of the South Wales Coalfield: Geol. Mag., v.91, p.220-226.

Thompson, I.S., 1967, The discovery of the Gortdrum deposit, County Tipperary, Ireland: Bull. Can. Inst. Min. Metall., v.60, p.85-92.

Thomson, D.S.R., 1960, The Yauricocha sulphide deposits, Central Peru: Ph.D. thesis of the University of London.

Thrailkill, J., 1968, Chemical and hydrologic factors in the excavation of limestone caverns: Bull. Geol. Soc. Am., v. 79, p.19-46.

Traill, R.J., and Boyle, R.W., 1955, Hawleyite, isometric cadmium sulphide: Am. Mineral., v.40, p.555-559.

Trudinger, P.A., and Bubela, B., 1967, Micro-organisms and the natural environment: Mineral. Deposita, v.2, p.147-157.

Uytenbogaardt, W., 1951, Tables for microscopic identification of ore minerals: Oxford Univ. Press, London.

Varvill, W.W., 1959, The future of lead-zinc and fluorspar mining in Derbyshire, in The future of non-ferrous mining in Great Britain and Ireland, p.175-203: Inst. Min. Metall., London.

Verhoogen, J., 1938, Thermodynamical calculations of the solubility of some important sulphides up to 400°C: Econ. Geol., v.33, p.34-51.

Walsh, P.T., 1966, Cretaceous outliers in south-west Ireland and their implications for Cretaceous palaeogeography: Q.J.G.S., v. 122, p.63-84.

Wang, Y.T., 1915, The formation of the oxidised ores of zinc from sulphide: Trans. Am. Inst. Min. Eng., v. 52, p.657-710

Warren, H.V., 1935, Distribution of silver in base metal ores: Trans. Am. Min. Eng., v.115, p.81-88.

Watts, W.A., 1957, A Tertiary deposit in County Tipperary: Sci. Proc. Roy. Dublin Soc., v.27, p.309-311.

Watts, W.A., 1962, Early Tertiary pollen deposits in Ireland: Nature, v.193, p.600.

Weaver, T., 1821, Memoir of the geological relations of the east of Ireland: Trans. Geol. Soc. Lond., 1st Series, v.5., p.117-305.

Weir, J.A., 1962, Geology of the Lower Palaeozoic inliers of Slieve Bernagh and the Cratloe Hills, County Clare: Sci. Proc. Roy. Dublin Soc., v.1, p.233-263.

Wells, R.C., 1910, The fractional precipitation of sulphides: Econ. Geol., v.5, p.1-14.

Weyl, P.K., 1958, The solution kinetics of calcite: J. Geol., v. 66, p.163-176.

Weyl, P.K., 1959, The change in solubility of calcium carbonate with temperature and carbon dioxide content: Geochim. et Cosmochim. Acta, v.17, p.214-225.

West, R.G., 1968, Pleistocene geology and biology: Longmans, Green & Co. Ltd., London.

West, I.M., Brandon, A., and Smith. M., 1968, A tidal flat evaporitic facies in the Visean of Ireland: J. Sed. Pet., v.38, p.1079-1093.

White, D.E., 1968, Environments of generation of some base metal ore deposits: Econ. Geol., v.63, p.301-335.

Williams, P.W., 1964, Aspects of the limestone physiography of parts of counties Clare and Galway, western Ireland: Ph.D. thesis of the University of Cambridge.

Williams, P.W., Limestone morphology in Ireland, in Geographical essays in honour of Estyn Evans (provisional title) (Ed. Stephens, N., and Glasscock, R.): Routledge & Kegan Paul Ltd., London. (In press).

Wurzburger, U.S., 1967, The occurrence of sulfides in the Timna Massif and secondary copper minerals in the Timna Copper Deposit, Negev (Southern Israel): M.Sc. thesis of the University of London.

Yorke, C., 1954, The pocket deposits of Derbyshire: Privately published.

Young, B.B., and Millman, A.P., 1964, Microhardness and deformation characteristics of ore minerals: Trans. Inst. Min. Metall., v.73, p.437-446.

Yund, R.A., and Kellerud, G., 1966, Thermal stability of some assemblages in the Cu-Fe-S system: J.Pet., v.7, p.454-488.

Zies, E.G., Allen, E.T., and Merwin, H.E., 1916, Some reactions involved in secondary copper enrichment: Econ. Geol., v.11, p.407-503.

Zuffardi, P., and Salvadori, I., 1964, Supergene sulphides and sulphates in the supergene zones of some sulphide ore deposits, in Developments in sedimentology, Vol.2, Sedimentology and ore genesis (ed. Amstutz, G.C.), p.91-99: Elsevier, Amsterdam.

APPENDIX 1

SOURCES OF ILLUSTRATED MATERIAL

Plate	
3.1	Old Tynagh Mine area; borehole 203; elevation approximately 5100 above Mine Datum.
3.2	Rock: 80W 350N, 5097.
4.1	Rock: 89W 242N, 4956.
4.2	Rock: 84W 50N, 5051.
4.3	Residuum: 5200W bench, Collapse Breccia
4.4	Residuum: 80W 150N, 5100, Llb grey grits
4.5, 6	As 4.3
4.7	Rock: 80W 150N, 5068
4.8	Residuum: 92W 150N, 5200, Collapse Breccia
4.9	Rock: 94W 350N, 4804
4.10	Rock: open pit wall, 5180E bench
4.11	Rock: 5180E bench, 20930N 32370E
4.12	As 4.9
4.13a	Residuum: 5200W bench, 20800N 31365E, Collapse Breccia
4.13b	Rock: 89W 242N, 4927
4.14	As 4.4
4.15	Residuum: 5180E bench, 20750N 32600E, Sulphide Rubble
4.16	As 4.15
5.1	Residuum: 5160E bench, Sulphide Rubble
5.2	Residuum: 93W 150N, 5100.
5.3	Residuum: 5200W bench, Collapse Breccia

7.1 Residuum: 5160E bench, Sulphide Rubble

7.2 Residuum: 5180W bench, 20750N 31325E, Calp mud ("sink fill")

7.3 As 5.1

7.4 Residuum: 5180E bench, Waulsortian bank oxides

7.5 As 7.4

7.6,7 As 5.3

7.8 Residuum: 5180W bench, Waulsortian bank oxides

7.9 Residuum: 5180E bench, 20700N 32500E, Sulphide Rubble

7.10,11 As 7.4

7.12 Residuum: 5200W bench, 20650N 31800E, Collapse Breccia

7.13 Residuum: 5160E bench

7.14 As 7.4

7.15 Residuum: 86W 50S, 5125, L3 grey grits

7.16 Rock: 5180E bench, 21070N 32280E

7.17a Rock: 5180W bench, 20890N 31650E

7.17b Rock: 78+75W 150N, 5133

7.17c Rock: 86W 250N, 5138

7.17d Residuum: 5180W bench, 20810N 31470E, Collapse Breccia

8.1 Residuum: 5200W bench, Collapse Breccia

8.2 Residuum: 5180W bench, Collapse Breccia

8.3 As 8.2

8.4 As 4.4

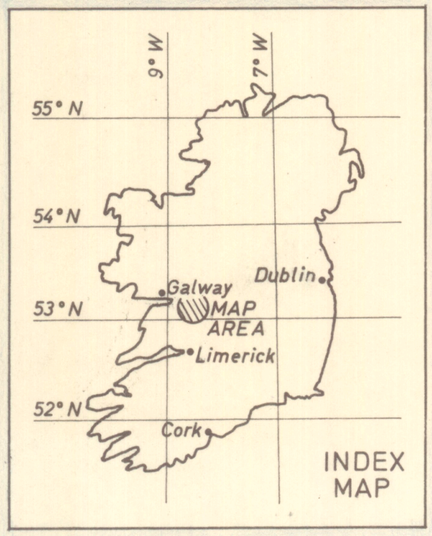
8.5 Residuum: 82W 50S, 5125

8.6 Residuum: 5180E bench, Sulphide Rubble

8.7 Copper-lead oxide concentrate

8.8a	Residuum: 5180E bench, in situ Calp mud
8.8b	Residuum: 5200W bench, 20850N 31300E, Collapse Breccia
8.9	Rock: open pit wall, 5180E bench
8.10	As 7.4
8.11	As 7.12
8.12	Residuum: 82W 50S, 5150, Sulphide Rubble
8.13	Residuum: 91W 50N, 5150, Collapse Breccia
8.14,15	As 7.12
8.16	As 4.2
8.17	Residuum: 85W 50S, 5100, Sulphide Rubble
8.18,19	Residuum: 5200 bench, 92W, exploration trench in Calp mud
8.20	Residuum: 5200W bench, 20900N 31500E, Waulsortian bank oxides
8.21,22	Residuum: 91W 150N, 5100, Collapse Breccia

Geology of part of Counties Galway and Clare, Ireland



INDEX MAP

0 2 4 6
STATUTE MILES

08° 30' W.

53° 00' N.

LOUGHREA
Lough Rea
.435
.312
.377
.216
KILLIMOR
Old Tynagh Mine
Pb
TYNAGH
River Shannon
PORTUMNA
N
Caherglassaun
Pb,Cu
GORT
1207
SLIEVE AUGHTY MOUNTAINS
Cu
Lough Cutra
Lough Graney
1312
.1243
.109
Pb
Lough Derg
Cu,Pb
Ballyvergin
Pb,Cu
Maghera Cross
Pb,Cu

LOWER CARBONIFEROUS
- Upper Limestone
- Middle Limestone (Calp)
- Waulsortian Bank Limestone
- Lower Limestone
- Lower Limestone Shale

- UPPER DEVONIAN
- SILURIAN
- ORDOVICIAN

Contact — defined — approximate - - - assumed
Fault — defined — approximate - - - assumed
Fold axis — anticline — syncline

MINERALISATION
- ABANDONED MINE
- O SHOWING
- TYNAGH RESIDUAL DEPOSIT

■ ■ Towns and villages
. Spot height
1312 FEET ABOVE IRISH ORDNANCE DATUM

Based on Geological Survey of Ireland One-inch sheets 115, 116, 124, 125, 133, 134, on Schultz (1968), and on unpublished company maps

C.J.M. 1969

Fig. 5.1

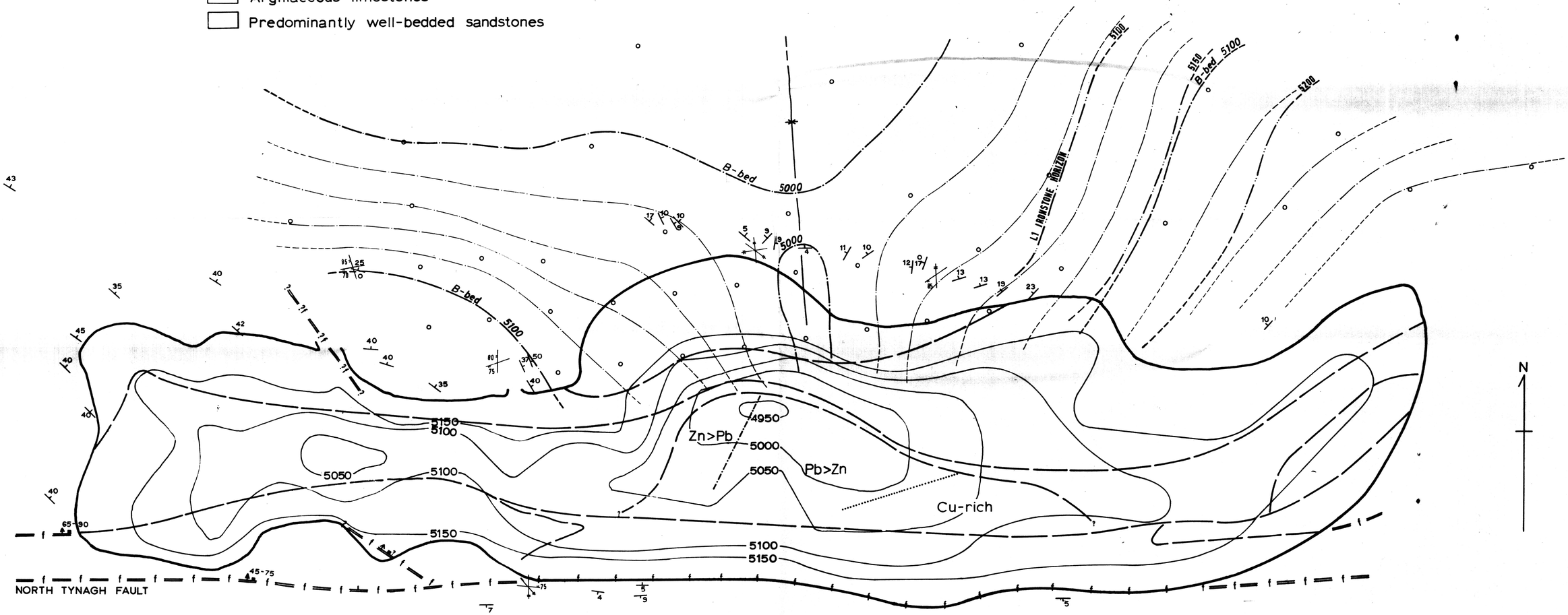
Tynagh residual deposit - WALLROCK LITHOLOGY AND STRUCTURE

Wallrock lithology:

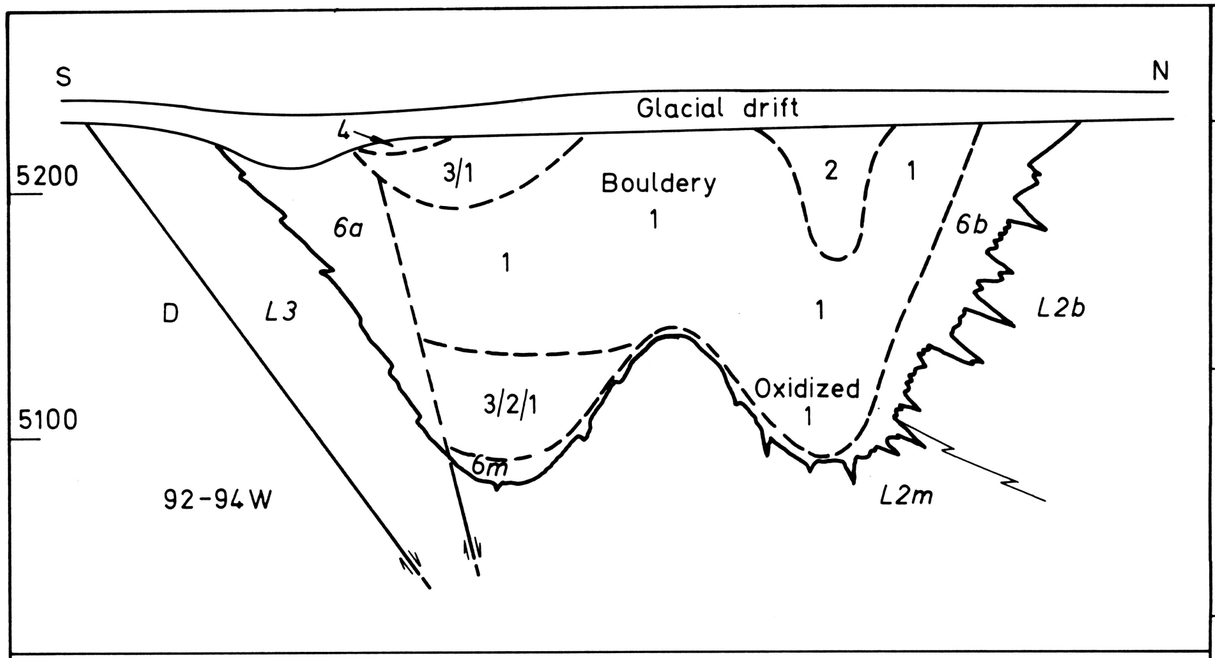
- Predominantly well-bedded carbonaceous limestones (Calp)
- Predominantly well-bedded crinoid limestones and biomicrites
- Predominantly massive micritic limestones
- Well-mineralised micritic limestones
- Argillaceous limestones
- Predominantly well-bedded sandstones

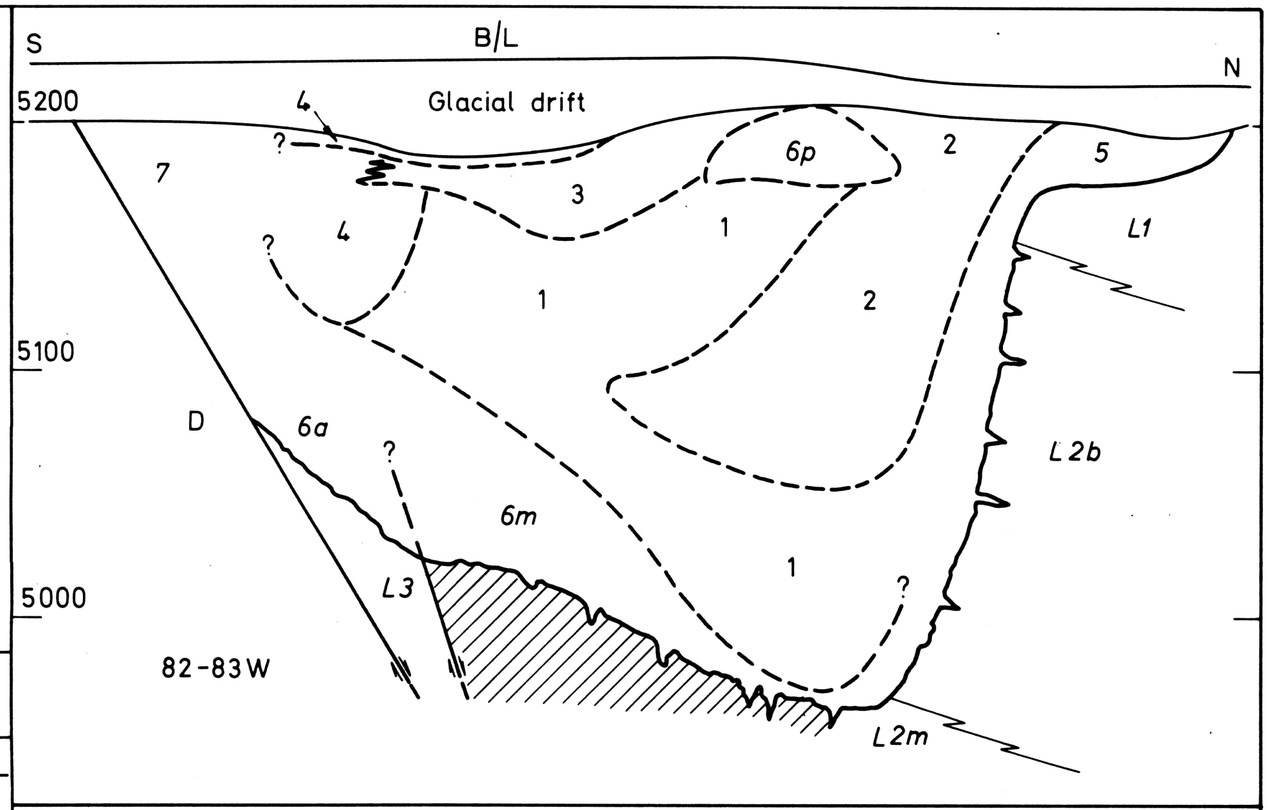
Dip and strike of bedding in outcrop
Main joint sets
Faults
Main fold axis
Structure contour control point
ALL ELEVATIONS ABOVE MINE DATUM (-5000 I.O.D.)

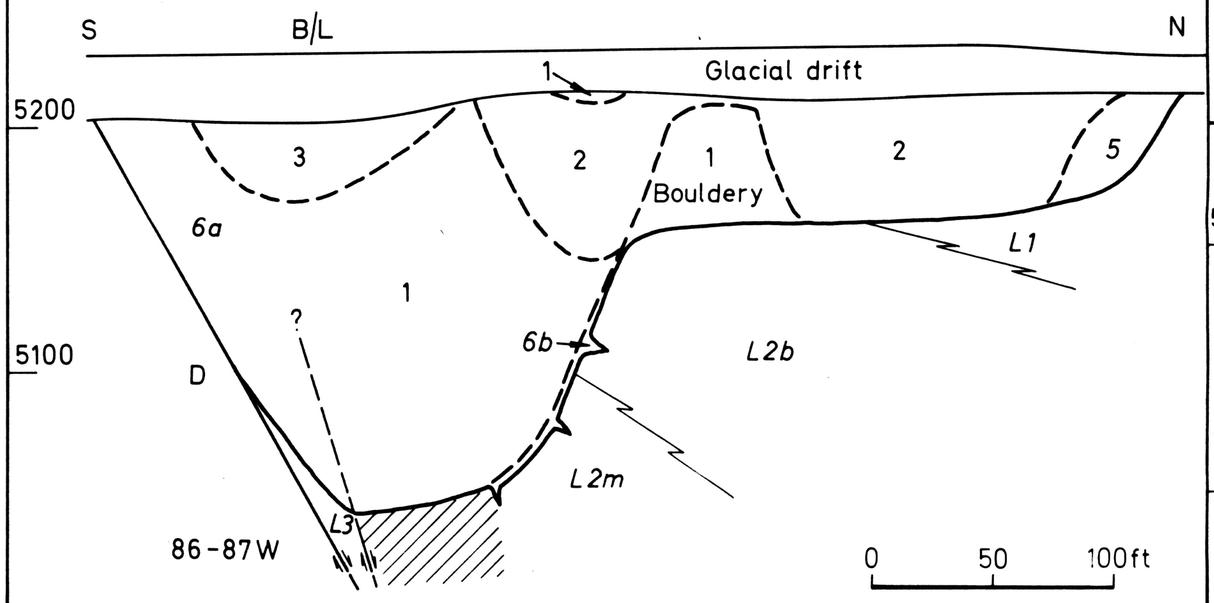
0 100 200 300 400 500
Scale in feet

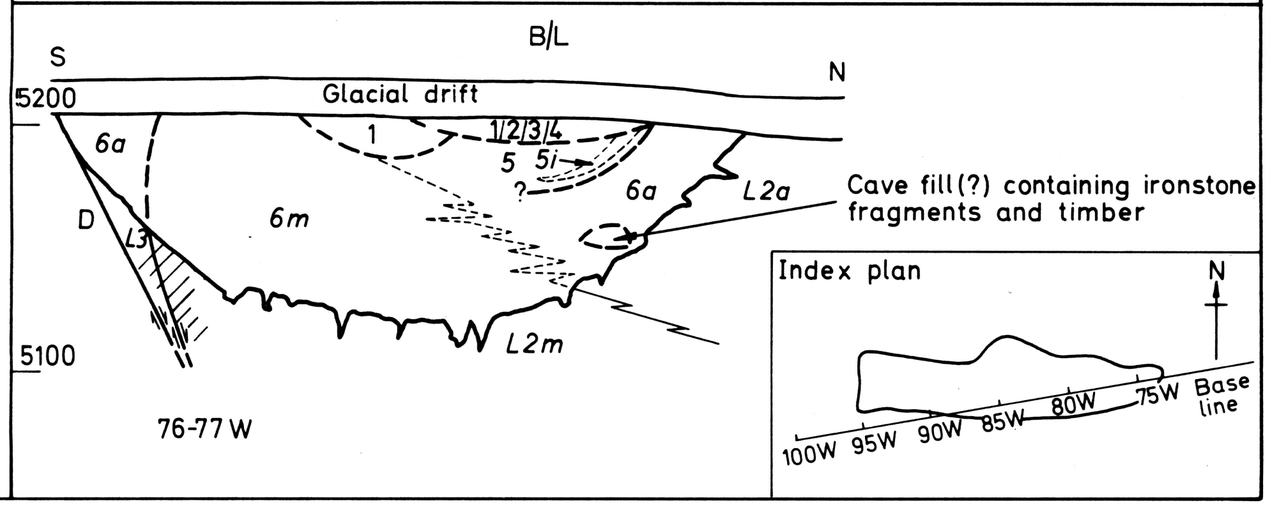


PARTLY BASED ON COMPANY DATA AND SCHULTZ (1968)
C.J.M. 1969









Transported residuum

1 Protore fragments mixed with Calp mud
2 Predominantly Calp mud
3 Oxide rubble and mud
4 Dark clayey mud and grit

Untransported residuum

5 Calp mud (*5i* ironstone residuum)
6a Oxidized residuum of argillaceous limestones
6b Oxidized residuum of bioclastic limestones
6m Oxidized residuum of micritic limestones
6p Gossan of massive protore
7 Residuum of shaley limestones

Rock

L1 Calp
L2a Argillaceous off-bank limestones
L2b Bioclastic bank-cover limestones
L2m Micritic bank limestone
L3 Lower Muddy Limestone
D Devonian sandstone
Primary mineralization

Waulsortian Bank Formation

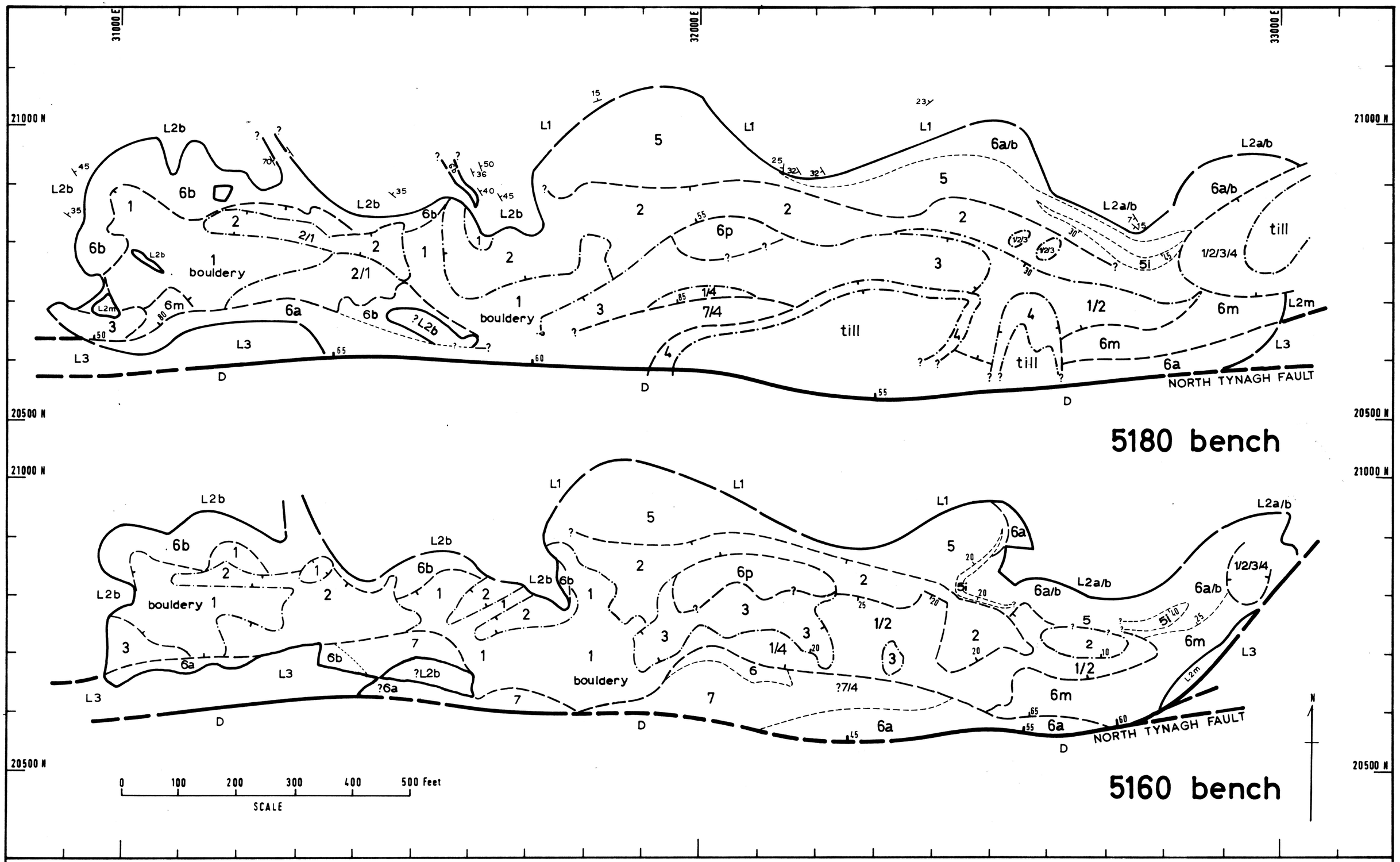
Rock–residuum contact
Contact between structural units of the residual deposit
Fault in rock
Facies contact

Fig. 6.2

TYNAGH RESIDUAL DEPOSIT

Diagrammatic cross-sections

Elevations above mine datum (-5 000 I.O.D.)



Transported residuum

1 PROTORE FRAGMENTS MIXED WITH CALP MUD
2 PREDOMINANTLY CALP MUD
3 OXIDE RUBBLE AND MUD
4 DARK CLAYEY MUD AND GRIT

Untransported residuum

5 CALP MUD (5i ironstone residuum)
6a OXIDISED RESIDUUM OF ARGILLACEOUS LIMESTONES
6b OXIDISED RESIDUUM OF BIOCLASTIC LIMESTONES
6m OXIDISED RESIDUUM OF MICRITIC LIMESTONES
6p GOSSAN OF MASSIVE PROTORE
7 RESIDUUM OF SHALEY LIMESTONES

Rock

L1 CALP
L2a Argillaceous limestones } with thin shales
L2b Bioclastic limestones } with thin shales
L2m Micritic bank limestone } with thin shales
WAULSORTIAN BANK FORMATION
L3 LOWER MUDDY LIMESTONE
D DEVONIAN SANDSTONE

Rock/residuum contact
Contact between two types of untransported residuum
Contact between transported and untransported residuum
Contact between two types of transported residuum
Fault bounded on one or both sides by rock
} VALUE AND/OR DIRECTION OF DIP INDICATED

Fig. 6.3

TYNAGH RESIDUAL DEPOSIT

GEOLOGICAL PLAN OF THE 5180 AND 5160 BENCHES

C.J.M. 1969

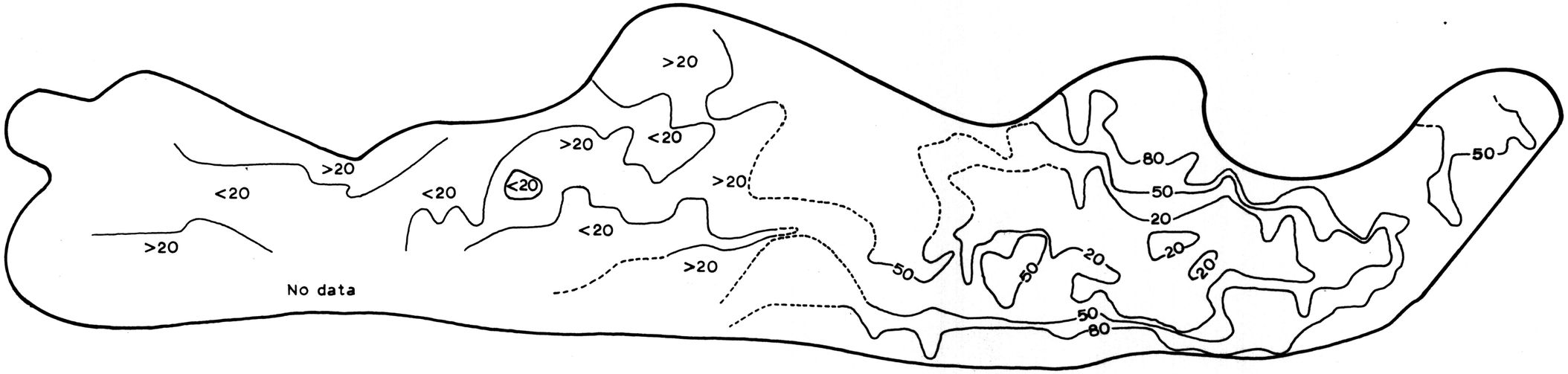
31000 E.

32000 E.

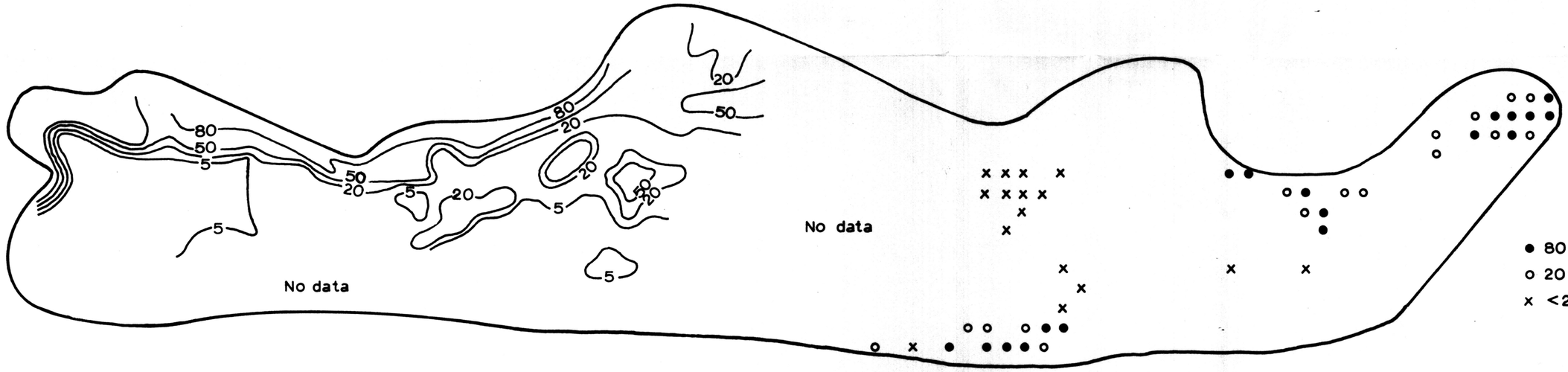
33000 E.

21000 N.

20500 N.



LEAD



ZINC

0 100 200 300 400 500 Feet

SCALE

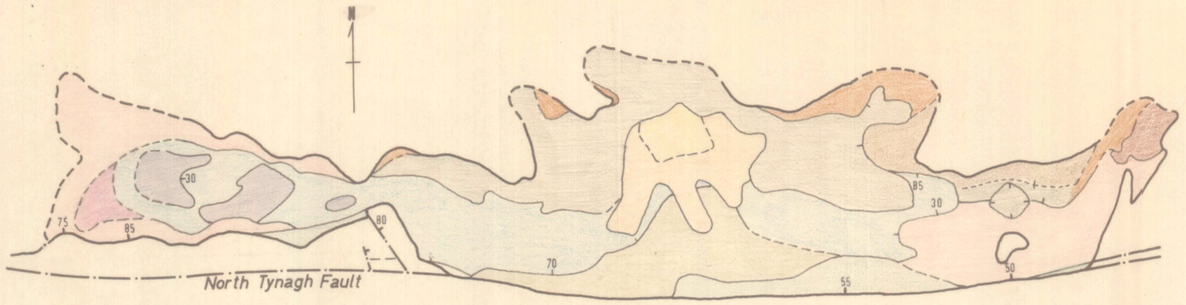
N

Fig. 8.2

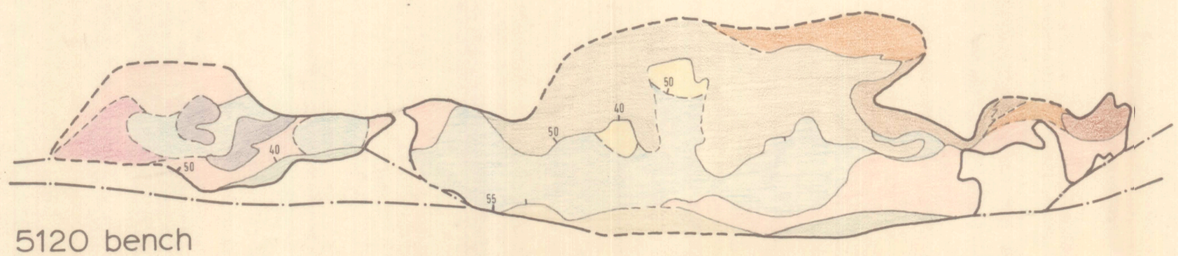
TYNAGH RESIDUAL DEPOSIT - 5160 BENCH

Percentages of total lead and zinc in non-sulphide minerals

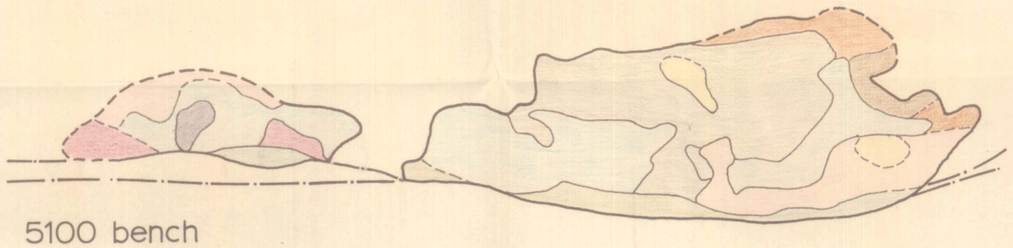
BASED ON MINE ASSAY DATA



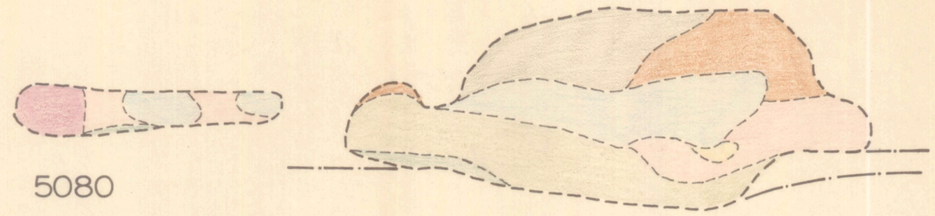
5140 bench



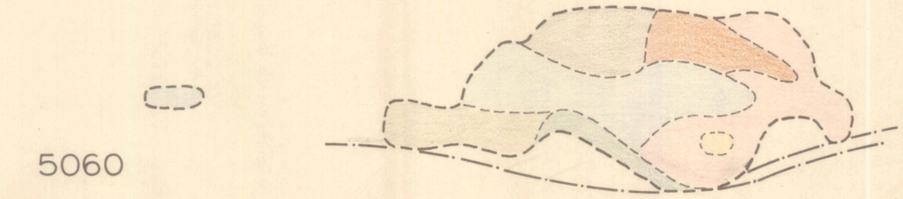
5120 bench



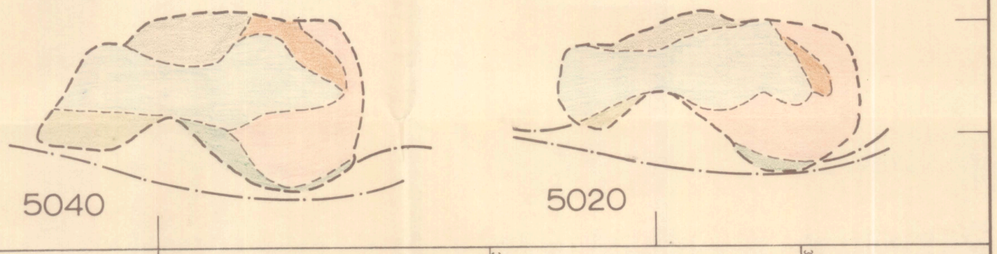
5100 bench



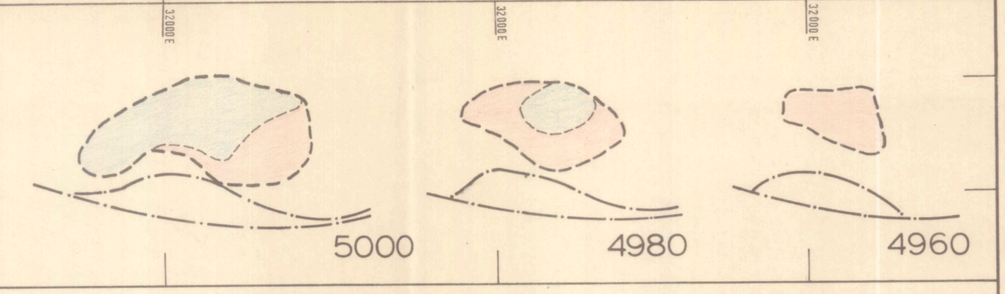
5080



5060



5040 5020



5000 4980 4960

RESIDUUM TYPE

- Sulphide-rich rubble and grit
- Calp mud
- "Sink fill"
- Transported gossan
- Polymict sediments including transported gossan
- Polymict sediments including ironstone fragments
- "Draped" Calp
- Oxidised supra-bank limestone
- Oxidised bank limestone
- Gossanised protore
- Oxidised Lower Muddy Limestone
- L3 grey gritty muds

Mapped Inferred

- ROCK-RESIDUUM CONTACT
- CONTACT IN RESIDUUM
- FAULT

0 100 200 300 400 500 Feet
Scale

Tynagh residual deposit

STRUCTURE

Fig. 6.4

PARTLY BASED ON BENCH MAPS BY D.WHITEHEAD (Mine Geologist) AND OTHER COMPANY DATA

C.J.M. 1969