Avoca mine, County Wicklow: a review of geological and isotopic studies

F.M. Williams, W.A. Sheppard & P. McArdle

Avoca mine, County Wicklow: a review of geological and isotopic studies.

F. M. Williams,[1] W. A. Sheppard[2] and P. McArdle[3]

1. Dept. of Geology,
   University College Dublin,
   Belfield,
   Dublin 4.

2. Rio Tinto Finance and Exploration Ltd.,
   3A, Avonbeg Industrial Estate,
   Longmile Road,
   Dublin 12.

3. Geological Survey of Ireland,
   Beggars Bush,
   Haddington Road,
   Dublin 4.

Abstract

The Avoca mine, a major Caledonian stratabound copper sulphide orebody, has had a long history of production. Total production to 1982 was approximately 16Mt of ore.

Volcanic rocks of the Duncannon Group, which host the mineralization at Avoca, represent the preserved remnant of a continental margin volcanic arc formed above a southeasterly dipping subduction zone. The mineralization occurs at the top of a major cycle of volcanism on the flank of a local volcanic centre. Subsequent to deposition, complex deformation with folding, shearing and faulting have resulted in the present-day disposition of the lithological units in a faulted synclinal core within the mine area.

The ores at Avoca comprise banded, vein and disseminated sulphide types. All of the ores may have a synsedimentary origin, but the interpretation of the vein and disseminated mineralization is complicated by the subsequent structural and metamorphic history of the deposit.

Sulphur isotopes suggest a sulphur source derived by mixing of magmatically equilibrated and reduced seawater sulphide. An ore-bearing fluid composed of a mixture of heated seawater and magmatic water is suggested by the oxygen isotopes. The carbon isotope results suggest stable redox conditions and a constant source of carbon. A magmatic source is consistent with the carbon isotope results.

Introduction

The Avoca mining district is centred on the Avoca Valley approximately 10km NW of Arklow, an important port on the SE coast of Ireland (Fig. 1). Mining records extend back to the mid-eighteenth century. Prior to the Second World War, it is estimated that a total of 5Mt of massive sulphides were extracted from small-scale workings. During the 1940s the State-owned mining company, Mianraí Teoranta, undertook extensive underground development on both sides of the Avoca Valley (East and West Avoca, Fig. 3) and proved substantial copper and pyrite reserves.

The mine was operated in the period 1958-1962 by St. Patrick's Copper Mines Ltd. and during 1969-1982 by Avoca Mines Ltd. A total of 16Mt grading about 0.6% copper has been produced to date and exported as chalcopyrite concentrates. These concentrates contained payable levels of silver and gold. In addition, substantial quantities of pyrite concentrates have been sold to a local fertilizer factory for the manufacture of sulphuric acid. Avoca Mines Ltd. is in receivership at present, and no mining or exploration is taking place in the immediate area of the mine.

Several references contain accounts of the history of mining and the development of genetic concepts at Avoca (e.g. Murphy, 1959; Wheatley, 1971; Platt, 1977).

Stratigraphy

The Avoca orebody lies in the Caledonides of SE Ireland. (Fig. 1). The Lower Palaeozoic rocks of this region were deposited in a major NE-trending depositional basin, the Leinster Basin (Phillips, 1978), and they have been divided as follows (Brück et al., 1979):

Kilcullen Group: Greywackes of Lower Ordovician-Wenlock age.

Duncannon Group: Llandeilo-Ashgill acid volcanic sequence.

Ribband Group: Middle Cambrian-Llandeilo succession of distal turbidites, mainly siltstones, with minor intermediate and basic volcanics.

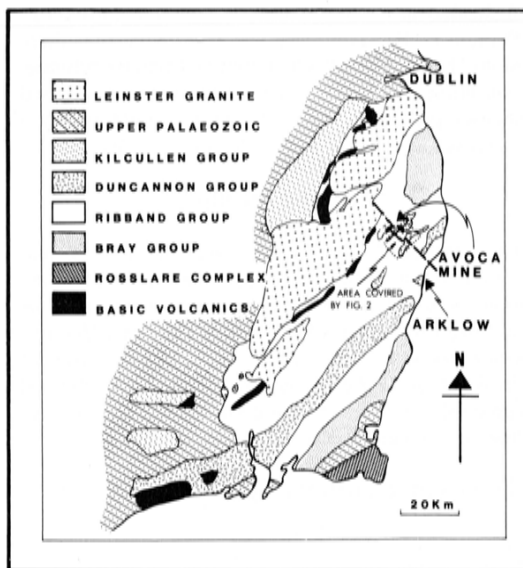Bray Group: Greywackes, slates and quartzites of Lower to Middle Cambrian age.

Figure 1. The geology of SE Ireland (after Brück et al., 1979). The area of Figure 2 is outlined.

	THIS STUDY	WHEATLY (1979)	BADHAM (1978)	PLATT (1978)	POINTON (1980)
200m	UNIT 5			MAGNESIAN TUFF	
	UNIT 4 — g, e/f, d, c, b, a	CHLORITE ZONE	CARBONACEOUS SHALE UNIT / DOLOMITIC TUFF UNIT	DOLOMITIZED TUFFS & SEDIMENTS	BALLYMURTAGH MEMBER
200m					
			BLACK ORE / YELLOW ORE	MASSIVE SULPHIDE	
1500m	UNIT 3		LOWER RHYOLITE UNIT / UPPER TUFF UNIT	CHLORITIZED & SERICITIZED RHYOLITIC TUFFS	CRONEBANE MEMBER
1500m	UNIT 2	UPPER VOLCANIC SERIES		RHYOLITE TUFFS & SHALE	
500m	UNIT 1				BALLYNAMONA MEMBER
		LOWER LAMINATED SERIES			AVONBEG FORMATION
	RIBBAND GROUP				KILMICHAEL FORMATION

Table 1. Lithological correlations of previous workers and of this paper.

The mineralization at Avoca (Fig. 3) is hosted in the Duncannon Group volcanic rocks which are interpreted as representing the preserved remnant of a continental margin volcanic arc formed above a southeasterly dipping subduction zone (Stillman and Williams, 1979).

The Duncannon Group at Avoca is represented by the Avoca Volcanic Formation (Pointon, 1979; 1980). This and the contiguous sediments of the Ribband Group have been divided into a series of members and formations by Pointon (1980). However, it is considered that these divisions (Table 1) do not adequately describe the lithological variations within the succession. The more detailed subdivision presented here for the Duncannon Group is a modified version of that used by Sheppard (1981).

Ribband Group

This is divided into the Avonbeg and Kilmichael Formations by Pointon (1980) who implies that unconformable relations with the overlying Duncannon Group may be present in places (See his Figure 4). We consider that any unconformity is a minor one as volcanic rocks are not confined totally to the Duncannon Group, and the red and green shales in the Ribband Group are, in this area, confined to the vicinity of Unit 1 volcanic rock.

Duncannon Group (Fig. 2 and Table 1)

Unit 1

Highly variable lithologies, mainly lithic and crystal lithic tuffs, intermediate flows, and black shales, which exceed 500m in thickness. Fossil evidence suggests a Caradocian age (Brenchley et al., 1977). They are spatially associated with shallow-water sediments of the Ribband Group at Rathdrum. Sericitic phyllites north of Ballycoog in the southwest are interpreted as distal equivalents.

Unit 2

The lower part (2a) consists of altered basic intrusions (10%-60% albite phenocrysts, 30% to 60% chlorite), meta-sedimentary phyllites and minor chloritic tuffs. The intrusions are regarded as near-surface bodies some of which were intruded into wet sediments and tuffs. They are very similar to aquagene tuffs (Carlisle, 1963). Their contacts with chloritic tuffs are frequently diffuse.

The upper part (2b) contains lithic chloritic siliceous tuffs and rhyolites in approximately equal proportions. The lithic tuffs contain rhyolitic and, locally, chloritic lapilli, as well as local shale bands near its base. The rhyolites display autobrecciation, flow banding and, in thin section, devitrification textures which elsewhere Cleverly (1977) described as typical rheo-ignimbrites. Individual rhyolites form linear topographic features which can be traced for 1.5km (Jones, 1983). The rhyolites are markedly potassic, containing a mean value of 7.62% K_2O (Sheppard, 1981), and those close to the mine are magnetic (Downes and Platt, 1978). The maximum thickness of Unit 2 is 1.5km.

Unit 3

This unit includes sericitic siliceous tuffs (quartz-eye tuffs of Platt, 1977) which are best developed to the north of the mine area (Fig. 2) and show marked thickness variations. The tuffs are typically lapilli tuffs or are finer grained. The lapilli are mainly quartz grains (frequently embayed), but
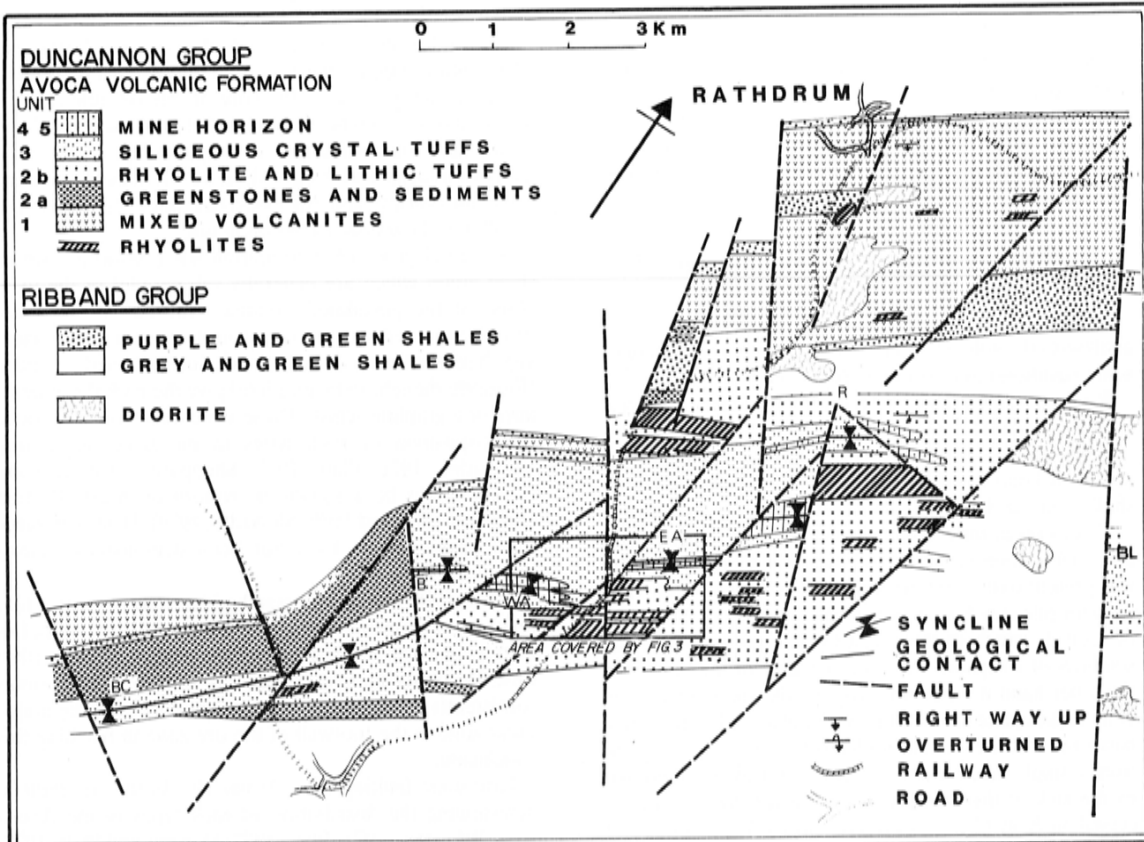
Figure 2.   The geology of the Avoca area.

albitized feldspar crystals and aggregates are present away from the mine area.

Towards the top of the Unit, and forming the mine footwall, are siliceous chloritic and sericitic lithic tuffs. The passage into chloritic tuffs is a gradual one which crosscuts the stratigraphy both vertically and laterally, suggesting chloritization. Chloritic tuffs host the disseminated ore at Avoca.

Unit 4

This Unit is 200m thick and contains a tuff sequence which has been studied in detail in the immediate mine area (Sheppard, 1981)(Figs. 2 and 3). The base of the sequence contains impersistent black chloritic schists (4a) which host laminated pyritic bands. An overlying agglomerate (4b; Fig. 4) is confined to the contact of the Cronebane rhyolite (see below). It is poorly sorted and matrix-supported, containing angular to sub-rounded rhyolite fragments set in a sericitic matrix. The fragments are typically 10cm in diameter but a number of blocks exceed 10m in maximum dimension. Some fragments have a pyritic matrix and are probably derived from the Cronebane rhyolite.

Lapilli tuffs (4c) overlie agglomerates in East Avoca (Fig. 3) and the basal chloritic schist in West Avoca (Fig. 4). The tuffs contain lapilli of siliceous tuff, rhyolite and occasional quartz and chloritic fragments. They generally are poorly sorted and a few bands are graded. There is a rapid variation into the overlying fine-grained sericitic tuffs (4d) which contain rare siliceous fragments. Black and green phyllites, (4e) and (4f), are well-developed in West Avoca. They contain, in place, phyllite fragments which can be recog-

nized by subtle colour variations. At the top of Unit 4, black carbonaceous shales (4g) occur in East and West Avoca (Figs. 3 and 4). Local sericitic tuff bands provide valuable way-up evidence. Poorly preserved graptolites are locally present (Badham, 1978). While carbonate is rare in East Avoca, in West Avoca some calcareous bands are found in Unit 4. Carbonate (mainly dolomite/ankerite) nodules and porphyroblasts are present in sub-units 4c-4f and there are also carbonate veins of various ages. In spite of the lateral impersistence of Unit 4 lithologies, the relative location of each lithology within the sequence never varies.

The Cronebane rhyolite (Fig. 5), in the hangingwall of the Cronebane Open Pit, can be traced along strike for over 1km. Its eastern limit is marked by a fault. It occurs at the contact between Units 3 and 4 on the southeastern limb of the Avoca syncline. Drilling data suggest that its thickness decreases at depth and that it does not extend to the west of its western exposure limit. The Cronebane rhyolite, unlike that of Unit 2, lacks topographic expression, possibly as a result of relatively intensive sericitization and weathering. Regular flow banding is often emphasized by the distribution of pyrite. The most striking features of the rhyolite are its zones of brecciation. Within the zone exposed at Cronebane, peripheral crackle breccia gives way to a central area where a simple refit of fragments is not possible. The matrix in this central part is for the most part felsitic, although locally sericitic, and contains varying amounts of pyrite. The felsitic matrix shows devitrification textures in this section, suggesting autobrecciation. Some rhyolite fragments have a selvage of pyrite and this indicates that brecciation continued after deposition of much of the pyrite.

Unit 5

This is the Magnesian Tuff of Platt (1977). It is interpreted as a basic or intermediate lava; sub-ophitic textures have been recognized 20m above the base of the Unit. The base of the Unit is fragmented, partly the result of tectonism, but possibly this is a product of extrusion onto wet sediment. It is over 200m thick (Fig. 2).

Volcano-sedimentary environment

In spite of the structural complexity (see below) an analysis of the volcano-sedimentary environment highlights some significant aspects of the Avoca geology.

Rocks of Unit 1 are considered the products of a local volcanic centre at Rathdrum (which was probably submarine) and pre-dated the main volcanic cycle at Avoca, represented by Units 2 and 3. The nature of the Ribband Group shales beneath Unit 1 suggests shallow-water conditions.

Variations in lithology thicknesses and in fragment size and composition in Unit 2 indicate that a volcanic centre was present east of the orebody during its deposition. The volcanic pile may have emerged above sea level. The rocks of Unit 3, which thicken westwards, may represent the products of a separate vent located west of the mine. On the other hand it is possible that the thickness increase in Unit 3 takes place towards the centre of a local depositional basin and that the rocks of both Units 2 and 3 were derived from a single volcanic centre. This latter idea is favoured by the lack of rhyolites and the unusually high content of crystal tuffs in Unit 3. Certainly such a large volume of crystal tuffs, unusual in SE Ireland, suggests an exceptional type of volcanism in the Avoca area.

The rocks of Unit 4 mark the waning stages of a volcanic cycle. Ashes were deposited from several volcanic centres, including one at Cronebane which shows a progressive decrease in tuff grain size with increasing distance from the centre and with time. Mass flow mechanisms were important but it seems that slumping on the large scale envisaged by Badham (1978) did not operate. Conditions gradually stabilized and deposition of black shales containing graptolites became dominant.

Volcanism subsequently restarted in Unit 5, where the intermediate flows mark the beginning of a new volcanic cycle.

Structure and metamorphism

The large scale distribution of rock types in SE Ireland is generally regarded as the result of strain in late Silurian - early Devonian times (e.g. Phillips, 1978). The regional structure has generally been considered in terms of large scale folds (Gardiner, 1970). One of these folds, the Wicklow Syncline, was considered by Gardiner to extend through the Avoca area; the volcanic host rocks of the mine area were considered to form the core of the structure. More recently the influence of NE-trending tectonic zones, such as shears or faults has been recognised as significant in determining the pattern of rock type distribution (e.g. Kennan et al., this vol.).

On a more local scale, the rock type distribution in the immediate mine area has also been considered (although perhaps not conclusively proven) to be controlled by the same large scale folding (Platt, 1977; Downes and Platt, 1978; Sheppard, 1980). The host rocks of the mineralization are preserved in the sheared core of an isoclinal upward-

facing syncline; it trends NE, its southeastern limb is overturned and it plunges to the SW at about 30° (Sheppard, 1980). Mine mapping has indicated that the youngest rocks of the sequence occur in the core of this syncline (Figs. 2 and 4) and revealed no indication that ore zones have been remobilized into fold hinges. A slaty cleavage is present in many lithologies and it dips SE at 55°. It is axial planar to the main syncline and has associated lineations which are parallel to the plunge of the main fold.

A second phase of deformation has produced a set of shear zones which are generally sub-parallel to the axial plane of the postulated isoclinal syncline. These zones produce marked structural discontinuities, the slaty cleavage being distinctly disturbed, and finely crushed sulphides (formerly thought to be graphite) give the rock the appearance of a graphite schist. These structures have influenced the disposition of rock types in the mineralized area (Wheatley, 1971; Platt, 1977; Sheppard, 1980) and are considered to be a significant control on mineralization (Badham, 1978 and 1979; McArdle, 1979). However, large scale displacements have not been demonstrated along these structures.

Jones (1983) used cleavage/bedding and parasitic fold relations in Cronebane to argue that the mine sequence lies on the same limb of a syncline whose axial plane lies further west. He argued that the sequence is overturned and youngs consistently to the north, and evidently ignored the major shear zone in the footwall of the ore zone in reaching this conclusion.

Late-stage faulting (Fig. 2) has also been important in determining the distribution of rock types in the Avoca area (Wheatley, 1971; Platt, 1977; Downes and Platt, 1978; Pointon, 1980; Sheppard, 1980). The dominant strike of faults is northerly, and Sheppard (1980) has recognized two sets of normal faults, one trending NW, the other NNE. The main fault, the Avoca Fault, is considered by Brück and O'Connor (1982) to be coincident with a linear which extends northwestwards into the Leinster Granite.

In summary the authors wish to emphasize that they consider the available evidence on balance favours isoclinal folding as the main control on the distribution of mineralization. However they recognize that the structural geology of the mine area is not well understood and that shearing has considerably complicated the pattern of rock type distribution. Additional tectonic research is clearly necessary.

No comprehensive review of metamorphism in the Caledonides in this part of SE Ireland has been published. The rocks have been subjected to a late-Silurian metamorphic event which, in general, causes slight crystallization but very locally rises to upper greenschist facies (Fettes, 1979). The rocks of the Avoca mine area are examples which have suffered greenschist facies metamorphism and display characteristic assemblages (see above). Prehnite and pumpellyite, characteristic of lower facies than greenschist, have been recognized by Pointon (1979), but they evidently represent a late stage event.

Intrusions

Diorite and dolerite intrusions occur in eastern Co. Wicklow (Fig. 2) within both Ribband Group and Duncannon Group lithologies (Reeves, 1976 and 1977). A whole-rock isochron for one intrusion gave a Rb/Sr age of 412±21 Ma (O'Connor and Reeves, 1979). A number of feldspar porphyry dykes occur in the immediate mine area. Some examples are deeply weathered. They cut across the slaty
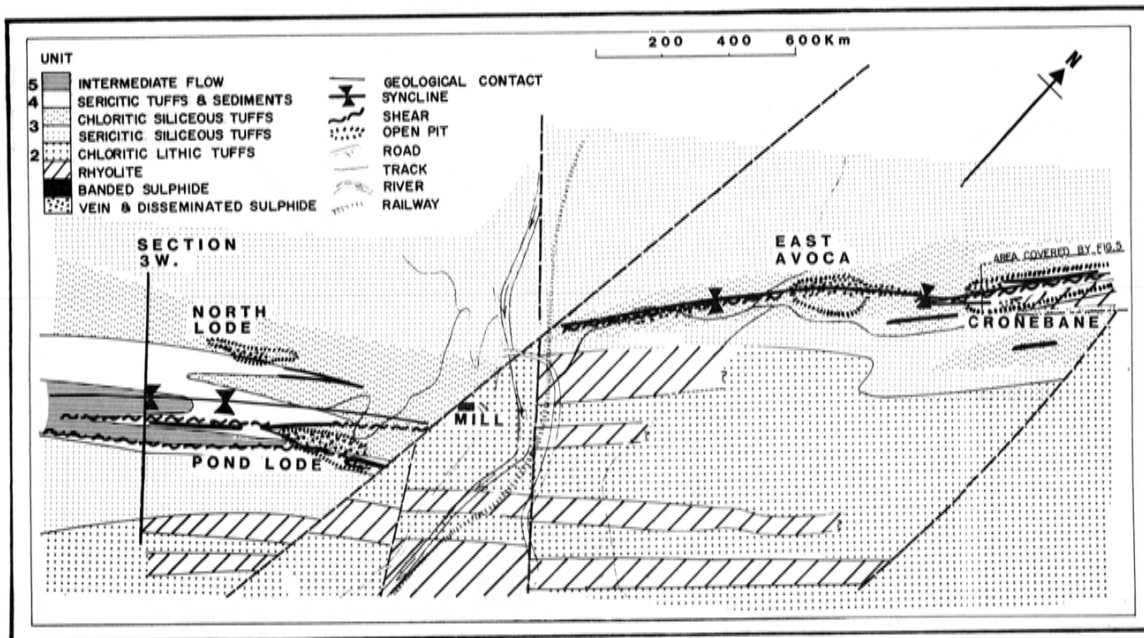
Figure 3.   Local geological setting of the main Avoca orebodies.

cleavage without signs of deformation and hence are regarded as later in age. The main example in the Cronebane open pit is largely parallel to the strike of the host rocks but cross-cuts it in the centre of the pit. It is weakly boudinaged in the plane of the slaty cleavage.

Some lamprophyric dykes occur in West Avoca (McArdle, 1974). The rocks are pale green or grey, massive and friable microdiorites and cut across the slaty cleavage without being deformed and therefore are considered to be later in age.

Mineralization

Sulphide minerals occur as tabular or lens-shaped orebodies which are disposed essentially parallel to the pervasive S1 slaty cleavage (Figs. 4 and 5). The orebodies in West Avoca and Tigroney plunge to the SW at 30-35°. This plunge is parallel to that of the major fold, the parasitic folds and the mineral lineation associated with D1. In Cronebane, a subhorizontal stretching lineation and the distribution of old workings suggests that the orebody plunge is more gentle.

The relation of the orebodies to each other is unclear. An *en echelon* relation was suggested by Murphy (1959). A folded relation complicated by shearing was suggested by Platt (1977), and supported by Pointon (1980) and Sheppard (1980 and 1981).

Two types of mineralization are prominent on a macroscopic scale. These are:

(i) Banded sulphides (massive sulphides of Platt, 1977), and

(ii) Disseminated and vein sulphides (stringer ore of Platt, 1977 and Sheppard, 1980).

Banded Sulphides

The banded sulphide ores are hosted in the black chloritic schists of Unit 4a. The ore bodies generally have sharp wallrock contacts and consist of pyritic sulphide bands alternating with bands of host rock. Banded sulphide zones occur in East and West Avoca; those in West Avoca are illustrated in Figure 4. *In situ* grades range between 0.80 and 1.20% copper and individual zones may contain in excess of 1Mt. Typically 40% sulphur is present.

The banded sulphides of the Pond Lode, the major source of massive sulphide in recent mining, alternate with chloritic schist and have an anastomosing relationship. Bands of laminated pyrite range up to 20cm thick with individual laminae varying from 1-30mm in thickness. Sphalerite and galena bands are confined to the hanging wall of the lode.

Massive pyrite laminae vary from 1 to 30mm in thickness and are interbanded with chloritic schist. The dark chloritic schist bands contain small (less than 0.5mm in length) elongate grains of pyrite disposed as slightly curved bands. The elongation of the pyrite grains is parallel to the lamination of the schist, and is interpreted as tectonic elongation due to slip along the schistosity. These bands of elongate pyrite occur on the margins of undeformed massive pyrite bands.

In the deeper levels of the West Avoca mine, banded mineralization occurs in association with the disseminated and vein-type mineralization of the South Lode. However, when banded mineralization occurs close to vein mineralization it is noticeable that the banded mineralization contains strongly boudinaged lenses of quartz.

Elsewhere (e.g. Keating Zone) bands carrying colloform pyrite and chalcopyrite alternate with sphalerite and galena-rich bands (1-10mm thick). Circular and elongate lenses of colloform pyrite, up to 10mm in diameter, are easily visible. There is very little quartz associated with the ore and there are no pressure shadows around pyrite grains. there is no evidence of remobilization of the ore.
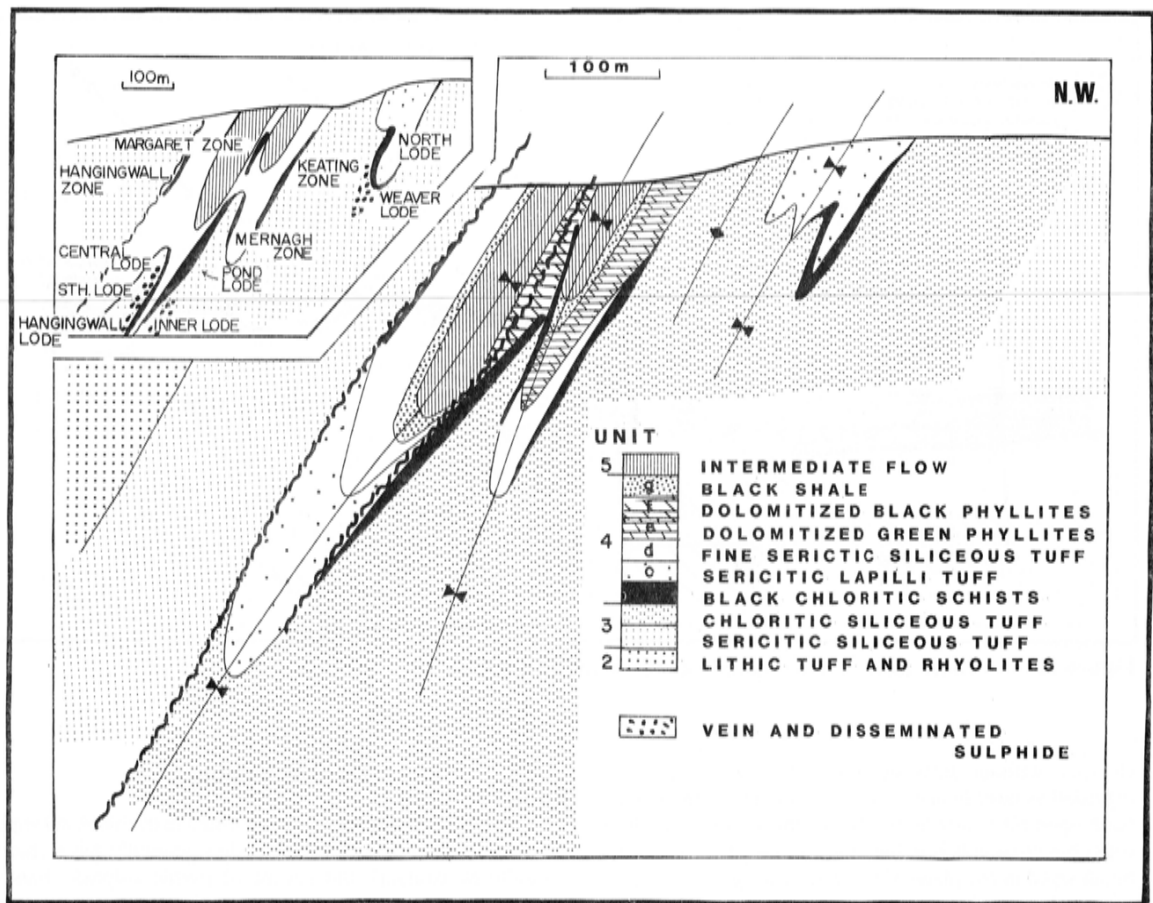
75

Figure 4. Geological cross-section (3W) of W Avoca. Location shown on Figure 7.

Vein and disseminated mineralization

The vein and disseminated ores at Avoca are hosted by the chloritic siliceous tuffs at the top of Unit 3 (Figs. 3 and 4) and are thus stratigraphically immediately below the banded sulphides (Platt, 1977; Pointon, 1980; Sheppard, 1981). The orebodies consisting of this ore type have diffuse contacts except where they occur in contact with banded sulphides. The South and Weaver Lodes of West Avoca and much of the footwall mineralization at East Avoca is of this type. Copper grades range from less than 0.5% to 0.8% and up to 20% sulphur may be present. Typical combined lead-zinc values for this ore are 0.04% for West Avoca and 0.44% for East Avoca.

In West Avoca quartz-rich vein ore is always remobilized and forms veins individually continuous for over 100m from cross-cut to cross-cut. The veins cut across the stratigraphy at a shallow angle (Platt, 1977). Veins range up to 85cm in thickness and are generally composed of chalcopyrite carrying pyrite and quartz. This ore is always accompanied by intense quartz veining. Many of the quartz veins are ptygmatically folded and some show stylolitic seams. The quartz within chalcopyrite veins often has the appearance of being composed of the separated fold closures of ptygmatic veins. The formation of the vein ore is considered to be syn-D1 in age (Sheppard, 1981) and folding of these veins is often seen. The quartz veining styles, lithology and the prevalance of banded pyrite may vary.

In the East Avoca area, the style of mineralization is slightly different with ore veins generally being less continuous. Irregular veins of massive chalcopyrite, up to 20cm thick, contain rounded and fractured pyrite grains, which range from 1mm to 10mm in diameter with an average diameter of 3mm. Sphalerite and galena also form irregular veins and 10mm bands distinguishable from pyrite-rich bands of similar thickness. The pyrite has recrystallized as large sub-idiomorphic grains up to 10mm in diameter. The associated folded quartz veins often show stylolitic seams and layers of silicate inclusions parallel to the vein walls.

Zonation and nature of sulphides

The percentage of sphalerite and galena present in the ore increases towards the stratigraphic tops of massive ore bodies in East and West Avoca (Lampard, 1960; Platt, 1977). Calcite veins and dolomite-ankerite lenses occur in association with laminated galena and sphalerite ore within Unit 4 tuffs and phyllites. They are exposed on the 1040 and 720 levels at West Avoca.

Macroscopically, the zonation of the orebodies and the lamination within the banded sulphides are likely to be the only primary features of ore deposition preserved. Zonation of the orebodies suggests a simple paragenetic sequence from pyrite-chalcopyrite-rich ore to pyrite-chalcopyrite-sphalerite-galena-rich ore.

Sulphide bands are conformable and internal banding is conformable with the margins of the orebodies. This suggests a primary origin for the banding in the massive ore.
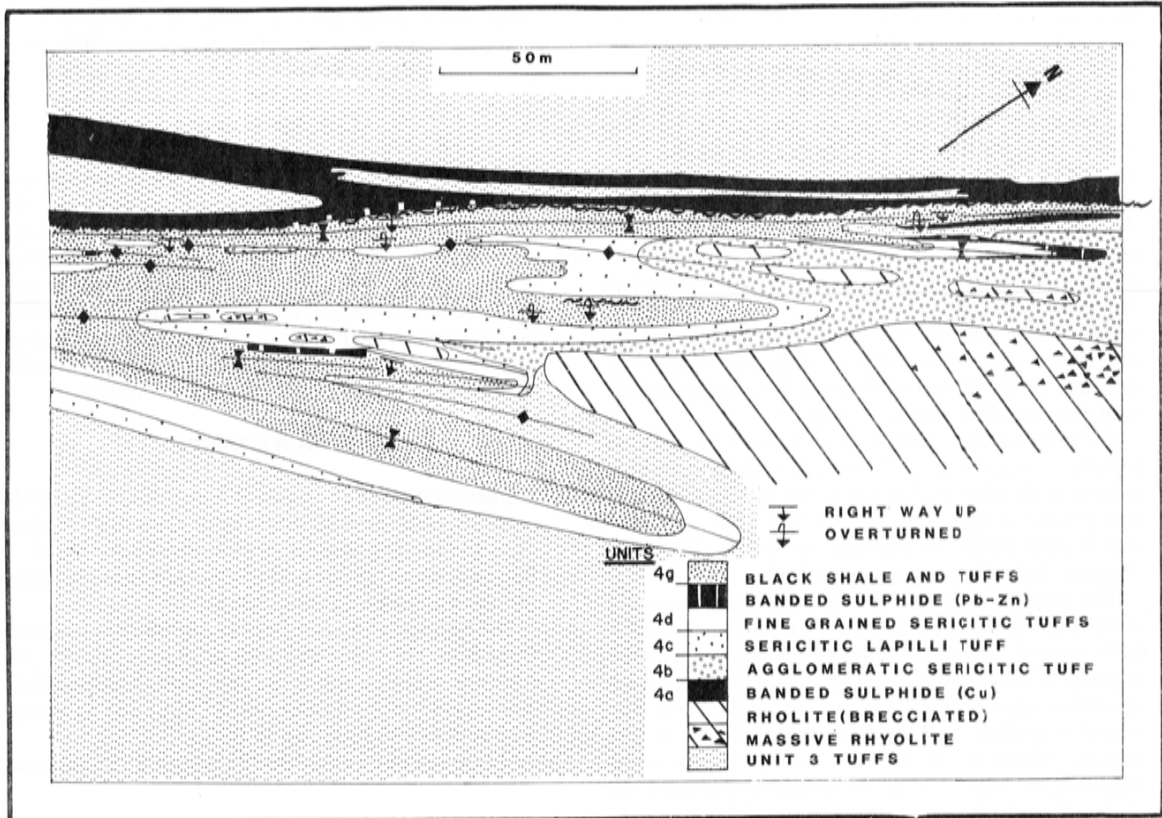
Figure 5.   Detailed geological map of the central area of Cronebane open pit.

The mineralization at Avoca is associated with strong wallrock alteration and occurs within and adjacent to an intrusive rhyolite, suggesting that the deposit is proximal. The stratabound nature of the ores and their zonation suggests an exhalative origin for them.

Comparison with other Kuroko-type deposits suggests that the mineralized rhyolite at Cronebane marks one site of the exhalative conduit through which the ore-bearing fluids rose (Platt, 1977; Badham, 1978; Pointon, 1980; Sheppard, 1981; Williams, 1984).

Stable isotope and fluid inclusion characteristics

Gangue and sulphide minerals from Avoca were analysed for stable isotopes of sulphur, carbon and oxygen. Samples
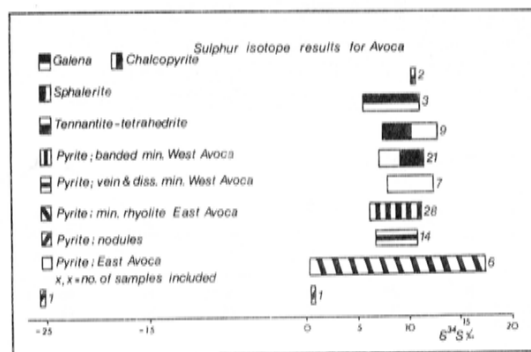

Figure 6.   Sulphur isotopes for Avoca.

were chosen to give good vertical and horizontal coverage of the mineralization. Details of the analytical techniques and method of interpretation are contained in Williams (1984). A total of 90 samples were analysed for their sulphur isotope contents and 13 for their stable isotope contents of carbon and oxygen.

Sulphur isotopes

The results for pyrite analyses indicate two sets of $\delta^{34}S$ values (Fig. 6). The main set, comprising those from massive, disseminated and vein mineralization, ranges from +6.8 to +12.3‰ except for two pyritic nodules which have values of +0.8 and −25.5‰ respectively. Both banded mineralization and disseminated and vein mineralization share a similar range of values. No systematic change in values occurs within either the banded mineralization or the vein and disseminated mineralization. Furthermore, samples from East and West Avoca have a similar range. The second set of values, those from the mineralized rhyolite at East Avoca, have a much wider range. they vary from +0.2 to +17.4‰ (Fig. 6.).

Sulphur isotope fractionation values for coexisting sulphides have a range of positive and negative values which contradict the predicted order of $\delta^{34}S$ enrichment (Bachinski, 1969). This implies disequilibrium, suggesting that equilibrium either was not established during sulphide deposition or else was destroyed by isotopic exchange with a fluid phase (e.g. during metamorphism). It may be significant that the least tectonized samples, from the Pond Lode, have a narrow range of pyrite-chalcopyrite fractionation values (-0.7 to +1.0‰) compared with the range in the

more tectonized samples elsewhere in the deposit (−2.7 to +41.0‰). It may suggest that a parallel increase in pyrite and chalcopyrite $\delta^{34}S$ values, although not marked, also reflects the more intensive deformation in these samples.

The mineralogy suggests that the ore-bearing fluid was weakly acidic and sulphate-poor. Its dominant sulphur species is likely to have been hydrogen sulphide. The range of $\delta^{34}S$ values in pyrite at Avoca is +9 ±3‰. Since the fractionation value between hydrogen sulphide and pyrite decreases from 1.15‰ at 100°C to 0.26‰ at 500°C (Ohmoto and Rye, 1979), the total $\delta^{34}S$ value of the ore-bearing fluid should be within 1‰ of the range shown by pyrite. A $\delta^{34}S$ value of about +9‰ might have originated in either of two ways, (i) by organic or inorganic reduction of seawater sulphate, or (ii) by mixing of reduced seawater sulphide with magmatically equilibrated sulphide.

The presence of sulphate in the seawater is by no means certain at Avoca because there are no sulphate minerals present in the mine or elsewhere in the region. If sulphate was present it might have had a $\delta^{34}S$ value similar to that of other Ordovician deposits, viz. +26‰ (Thode and Monster, 1965; Holster and Kaplan, 1966).

The range of values seen in the mineralized rhyolite is consistent with mixing magmatically equilibrated sulphur ($\delta^{34}S$ about 0 ‰) with bacteriogenically reduced seawater sulphate or with seawater sulphide. Assuming that oceanic conditions were reducing and that all sulphate was converted to sulphide, then the dominant species would be a reduced sulphur species with the same $\delta^{34}S$ value as the sulphate, viz. +26‰. The range of values preserved in the mineralized rhyolite could represent the different proportions of volcanic sulphur versus seawater-derived sulphur which Sangster (1971) suggested should be present if mixing of sulphur from two sources occurred. A proportion of approximately two thirds magmatic sulphur to one third seawater sulphur would produce a fluid with a $\delta^{34}S$ value of +9‰.

Preservation of unmixed $\delta^{34}S$ values in the rhyolite could have occurred through quenching of the system due to a sudden pressure drop within the fluid following brecciation of the rhyolite.

Oxygen isotopes

The $\delta^{18}O$ values of calcite from veins and lenses range from +11.2 to +20.9‰ with most values being in the range +11.2 to +12.0‰. The $\delta^{18}O$ values of dolomite/ankerite veins vary from +16.0 to +23.8‰. These carbonates are found associated with banded lead-zinc mineralization and are thought to have formed late in the history of ore deposition. The calcite veins could be expected to have formed at temperatures of up to about 250°C if the fluid inclusions found in quartz veins are representative of the late stages of ore deposition. Consideration of equilibrium fractionation factors suggests that the calcite crystallized between 100° and 160°C from heated seawater, or it crystallized at higher temperatures from a mixture of magmatic water and seawater.

The calcite and dolomite/ankerite nodules with values of about +20 to +23‰ could have formed from seawater at temperatures of about 50°C or less. Carbonate with intermediate $\delta^{18}O$ values of about +15‰ could have formed from seawater at temperatures of about 100°C or from a mixture of seawater and magmatic water at higher temperature.

The $\delta^{18}O$ values show that if the carbonates were deposited from seawater then the depositional temperature

varied from about 160°C to 50°C. If a component of magmatic water was involved then higher depositional temperatures are appropriate.

Carbon isotopes

The $\delta^{13}C$ values of both the calcite veins and dolomite lenses share a similarly narrow range, varying from −5.3 to −8.8‰ with a mean value of −6.6‰. This narrow range suggests that both redox conditions and the source of carbon remained stable with time. If −6‰ represents the total $\delta^{13}C$ value of the system, a magmatic source is implied for the carbon. The small range of values would imply that the magmatic carbon dominated the system and therefore that the ascending hydrothermal fluid was carbon-rich.

Fluid inclusions

Quartz samples were collected from veins parallel to the pervasive slaty cleavage and one of the veins contained chalcopyrite. The samples were examined by Dr. T. J. Shepherd (pers. comm.). Only two contained inclusions that were considered to be primary.

The homogenization temperatures of the fluid inclusions range from 155°C to 198°C with an average of 177°C. No evidence of boiling was seen. The average salinity of the fluid inclusions is 3.5 equiv. wt. % NaCl and they range from 3.15 to 3.85 equiv. wt. % NaCl.

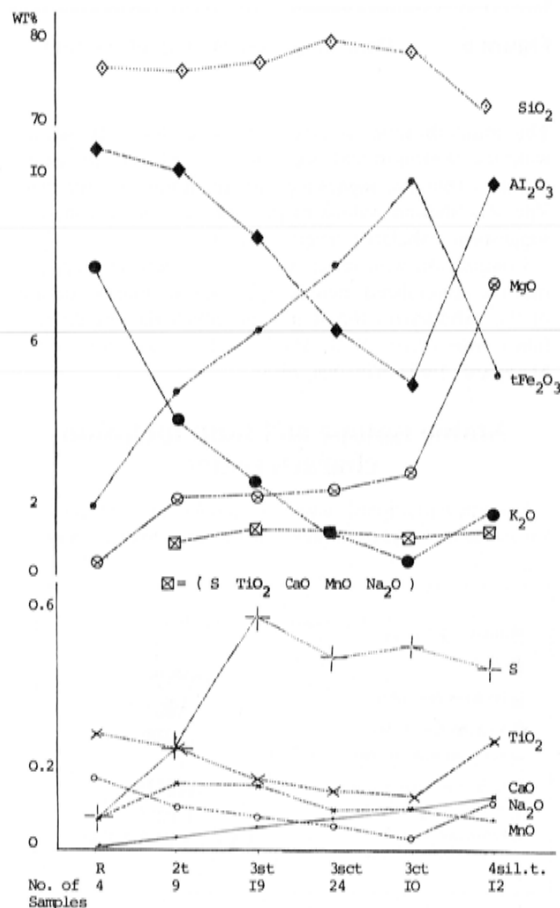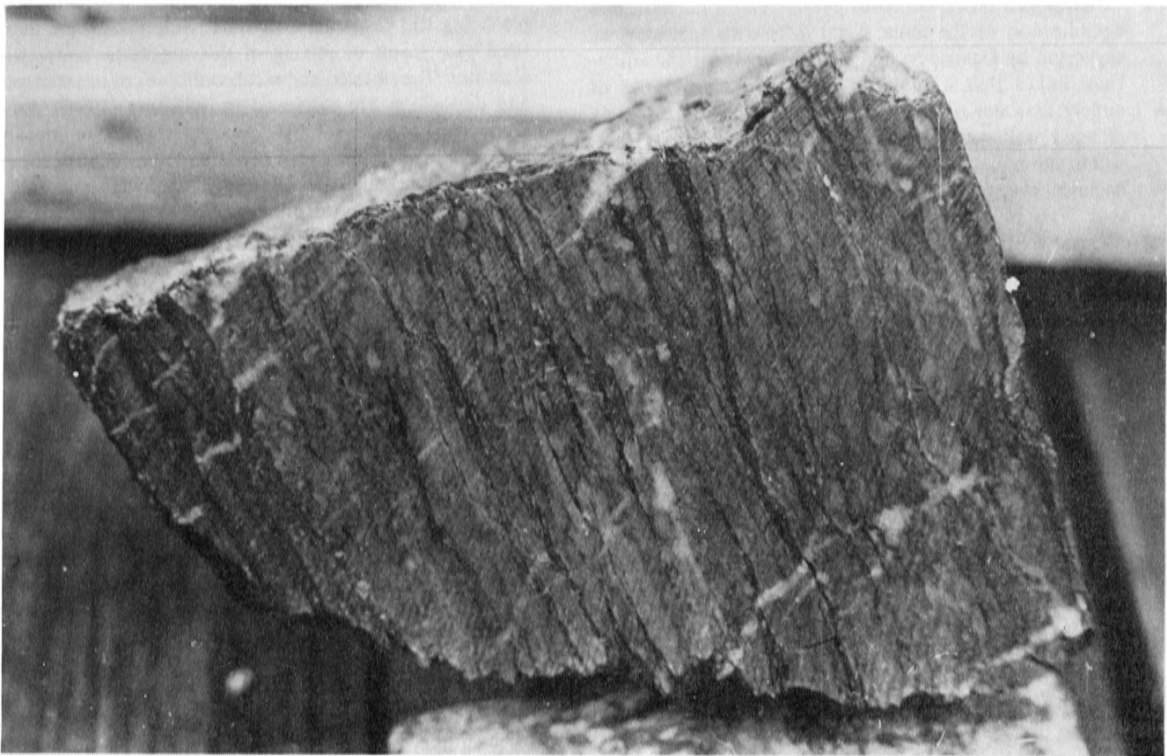These temperatures and salinities are within the range

Figure 7.   Wall rock geochemistry: mean values for various lithologies.

Figure 8.   (a) Brecciated rhyolite.

(b) Host rock for vein and disseminated mineralization.

cited by Roedder (1976) for other deposits with similar temperature ranges and salinities of up to 10 equiv. wt. % NaCl. The solutions are more saline than normal seawater and indicate a fluid composed, in part, of magmatic water.

While these results are consistent with an origin associated with syngenetic ore formation, the dating of the veins is open to question. If the veins formed during the subsequent deformation of the deposit, then the temperatures quoted above may represent metamorphic events.

Lithogeochemistry

Two lithogeochemical studies have been completed in the Avoca area, a wall-rock study (Sheppard, 1981) by atomic absorption spectrometry with data analysis using the non-parametric Mann-Witney U-test (Siegel, 1956). A more regional geochemical study by ICP with multivariate statistical analysis was carried out by G. Gonzalez (pers. comm.).

Wall rock geochemistry

The sericitic tuffs of Unit 3 are generally lower in K_2O, Na_2O, Fe_2O_3, Al_2O_3 and TiO_2 and higher in Mn, SiO_2 and S than Unit 2b tuffs (Fig. 7). Within Unit 3 tuffs, this trend continues as chlorite (chamosite) content increases. Chamosite with anomalous birefringence in thin section, only found close to ore, is richer in Mg, Mn, Fe and Zr and poorer in K than non-anomalous chlorite. No significant geochemical variation between East and West Avoca was found. However, mapping indicates that the Unit 3 wall rocks of East Avoca contain less chlorite and generally more conspicuous sphalerite and galena. Essentially the same elements show apparent enrichment with increased alteration within the footwall rocks as are enriched generally in Unit 3 relative to Unit 2. The host rock geochemical variation can be explained by the increased reaction and equilibration of the more distal tuffs with seawater, as suggested by Davenport and Nichol (1973) for the Birch-Uchi Lakes Belt. Circulating hydrothermal solutions of largely seawater origin at elevated temperature probably effected wall rock alteration. This study suggests that, within the mine wall rocks, these solutions produced geochemical changes greater than, but similar to, those which took place in comparable rocks further away from hydrothermal activity.

Regional geochemistry

Statistical analysis of the data, corrected for rock type, revealed that four associations of elements were developed in the Avoca area. Two of these associations occurred within the mine area, namely, an As-Cu with minor Pb-Mo-Fe halo and a Mn-Fe-Co-Mg halo with minor Zn-Mo. On the fringes of the mine area a Sn-S-Ag halo with minor Pb-Cd-W was found. Finally, a Be-Zn-Pb halo with minor Ag-Fe-Mn was discovered, largely confined to unit 2 tuffs and extending NE to Ballard, approximately 7km from the mine area.

Genesis of the ore

Early interpretations of ore genesis at Avoca during the 1950s indicated that the deposit was epigenetic, being deposited by hydrothermal solutions associated with contemporaneous Caledonian plutonism (O Brien, 1958; Murphy, 1959). Lampard (1960) recognized the syngenetic character of the banded sulphides, suggesting that later metamorphism achieved the metal redistribution necessary to produce the zones of disseminated sulphides.

The genetic significance of the volcanic host rocks was recognized by Wheatley (1971) who interpreted the banded sulphides as syngenetic deposits on the sea floor, while the disseminated mineralization formed epigenetically at a later stage.

Platt's (1977) interpretation of the mineralization as Kuroko style, with both massive and disseminated sulphides formed at the same time, is based on detailed stratigraphic and lithological comparisons with other deposits. Although Badham (1978) agrees with Platt (1977) on the importance of the rhyolite intrusion at the Cronebane Open Pit during the early stages of mineralization, he suggests that the later stages of mineralization originated from a centre not yet located at Avoca. Study of the regional setting by Pointon (1980) suggests a regional NW-trending structural control on the location of the volcanic centres associated with mineralization.

This review has summarized the results of recent geological and petrological studies. It has integrated these with geochemical and isotopic data in an attempt to produce a comprehensive picture of the evolution of the Avoca deposit. The rocks of the Avoca mine area appear to occupy the core of a major synclinal structure, the geometry of which has been disrupted by subsequent shearing. The complex distribution of lithologies is largely attributed to tectonism. Structural studies indicate that in West Avoca shearing has largely removed the Unit 4 rocks of the overturned southern limb of the syncline, while in East Avoca it is this overturned northern limb which is best preserved. The mineralization developed adjacent to a volcanic centre during the waning stages of regional volcanism. Isotopic evidence indicates that magmatic fluids emanated from feeder vents associated with the volcanism, a specific example being the Cronebane rhyolite. Sulphides were deposited as a result of mixing of this magmatic water with seawater. The physico-chemical conditions of ore transport and deposition are discussed in Williams (1984). As in many other massive sulphide deposits, there is an intensive alteration zone in the footwall of the Avoca deposit (Sheppard, 1981) although the vein and disseminated mineralization within this zone is not regarded as a primary feeder zone.

The geotectonic and geological setting of the Avoca deposit, together with the nature of its ores, indicate that it is an example of a polymetallic volcanogenic exhalative sulphide deposit. It bears comparison with many deposits of this type in various parts of the world, for example the Pre-Cambrian deposits of the Canadian Shield (Franklin et al., 1981), the Kuroko-type deposits of Japan (Ishihira, 1974) and the massive sulphide deposits of the Iberian Pyrite Belt (Williams et al., 1975). It is one of many such deposits within the Caledonian-Appalachian orogen (Stephens et al., 1984). In more detail the Unit 3 sericitic siliceous crystal tuffs of the mine footwall can be closely compared with the footwall rocks of the New Brunswick No. 12 deposit in Canada (Van Staal and Williams, 1984). The spatial relation of mineralization to a rhyolite body is repeated in certain Kuroko-type deposits in Japan (Sato, 1974). The vein and disseminated mineralization at Avoca may be compared with similar lithologies in other deposits, for example, the Funtana Raminosa deposit of Sardinia (Garbarino et al., 1980). It is difficult to identify a similar combination of features to that of Avoca in other deposits,

but this is perhaps characteristic of volcanogenic exhalative sulphide deposits.

Acknowledgements

References

BACHINSKI, D. 1969. Bond strength and sulphur isotope fractionation in coexisting sulphides. *Econ. Geol.* 64, 56-65.

BADHAM, J. P. N. 1978. Slumped sulphide deposits at Avoca, Ireland and their significance. *Trans. Instn Min. Metall. (Sect. B: Appl. Earth Sci.)* 87, B21-26.

BRENCHLEY, P. J., HARPER, J. C., MITCHELL, W. I. and ROMANO, M. 1977. A re-appraisal of some Ordovician successions in eastern Ireland. *Proc. R. Ir. Acad.* 77B, 65-85.

BRÜCK, P. M., COLTHURST, J. R. J., FEELY, M., GARDINER, P. R. R., PENNY, S. R., REEVES, T. J., SHANNON, P. M., SMITH, D. G. and VANGUESTAINE, M. 1979. Southeast Ireland: Lower Palaeozoic stratigraphy and depositional history. *In: The Caledonides of the British Isles — reviewed.* Geol. Soc. Lond. 533-544.

BRÜCK, P. M. and O'CONNOR, P. J. 1982. Relationship of hydrothermal phenomena within the Leinster Granite to crustal fractures delineated from Landsat imagery., *Photogrammetria* 37, 151-159.

CARLISLE, D. 1963. Pillow breccias and their aquagene tuffs. Quadin Island, British Columbia. *S. Geol.* 71, 48-71.

CLEVERLY, R. W. 1977. The structural and magmatic evolution of the Lebombo Monocline, Southern Africa, with particular reference to Swaziland. Unpub. Ph.D. thesis Oxford Univ.

DAVENPORT, P. H. and NICHOL, I. 1973. Bedrock geochemistry as a guide to areas of base metal potential in volcano-sedimentary belts of the Canadian Shield. *In: Jones, M. J. (ed.), Geochemical exploration 1972: Proc. Fourth Internat. Geochem. Exploration Symp.* Instn. Min. Metall., London 45-57.

DOWNES, K. M. J. and PLATT, J. W. 1978. the Avoca-Ballard mineralized belt, Co. Wicklow. *J. Earth Sci. R. Dubl. Soc.* 1, 121-133.

FETTES, D. J. 1979. A metamorphic map of the British and Irish Caledonides. *In: The Caledonides of the British Isles reviewed.* Geol. Soc. Lond. 307-321.

FRANKLIN, J. M., LYDON, J. W. and SANGSTER, D. F. 1981. Volcanic-associated massive sulphide deposits. *Econ. Geol. 75th Anniv. Vol.,* 485-627.

GARBARINO, C., MACCIONI, L., MINZONI, N., PADALINO, G., TOCCO, S. and VIOLO, M. 1980. The stratabound copper-lead-zinc mineralization of the Sardinian microplate (Italy). *In: Jankovic, (Ed.) European Copper Deposits,* 251-260.

GARDINER, P. R. R. 1970. Regional fold structures in the Lower Palaeozoics of southeast Ireland. *Geol. Surv. Ir. Bull.* 1, 47-51.

HOLSER, W. I. and KAPLAN, I. R. 1966. Isotope geochemistry of sedimentary sulphates. *Chem. Geol.,* 54, 84-92.

ISHIHARA, S. (Ed.) 1974. Geology of Kuroko deposits. *Min. Geol. Spec. Issue 6.* Soc. Min. Geol. Japan, Tokyo. 435p.

JONES, W. B. 1983. The geological association of sulphide mineralization at Avoca, County Wicklow — a new interpretation based on field evidence. *J. Earth Sci. R. Dubl. Soc.* 5, 145-52.

KENNAN, P. S., McARDLE, P., WILLIAMS, F. M. and DOYLE, E. 1986. A review of metal deposits associated with the Leinster granite, southeast Ireland, and a model for their genesis. *This volume.*

LAMPARD, W. J. 1960. Mineralization at West Avoca, Co. Wicklow, Ireland. Unpub. Ph.D. thesis, Univ. London.

MCARDLE, P. 1974. A Caledonian lamprophyre swarm in southeast Ireland. *Sci. Proc. R. Dubl. Soc.* 5A, 117-122.

MCARDLE, P. 1979. Contributed remarks to Badham (1978). *Trans. Inst. Min. Metall. (Sect. B: Appl. Earth Sci.)* 88, B69-B74.

MURPHY, G. 1959. The Avoca enterprise. 2: The geology of the mineralized area. *Mine and Qy. Eng.* 25, 330-38.

OBRIEN, M. V. 1958. The future of non-ferrous mining in Ireland. *In: The future of non-ferrous mining in Great Britain and Ireland. Inst. Min. Metall.,* London, 5-26.

O'CONNOR, P. J. and REEVES, T. J. 1979. Age and provenance of the Carrigmore Diorite, Co. Wicklow. *Geol. Surv. Ir. Bull.* 2, 307-314.

OHMOTO, H. and RYE, D. O. 1979. Isotopes of sulphur and carbon. *In: Geochemistry of Hydrothermal Ore Deposits.* Barnes, H. L., (Ed.), Wiley, 2nd Ed., 509-561.

PHILLIPS, W. E. A. 1978. The Caledonide Orogen in Ireland. *Geol. Surv. Canada* Paper 78-13, 97-103.

PLATT, J. W. 1977. Volcanogenic mineralization at Avoca, Co. Wicklow, Ireland and its regional implications. *Instn. Min. Metall. and Geol. Soc. Lond.* 163-170.

PLATT, J. W. 1978. Contributed remarks to Badham (1978). *Trans. Inst. Min. Metall. (Sect. B: Appl. earth sci.)* 87, B184-B188.

POINTON, C. R. 1979. Palaeozoic volcanogenic mineral deposits at Parys Mountain, Avoca and S. E. Canada. Unpub. Ph. D. thesis, Univ. of Aston.

POINTON, C. R. 1980. Some environmental features of volcanogenic mineralization at Avoca, Ireland and Parys

Mountain, Anglesey, Wales. *Norges geol. unders.*, 360, 259-268.

REEVES, T. J. 1976. Some diorites in eastern Co. Wicklow. *Geol. Surv. Ir. Bull.* 2, 15-26.

REEVES, T. J. 1977. The dolerites in part of eastern Co. Wicklow. *Geol. Surv. Ir. Bull.* 2, 159-165.

ROEDDER, E. 1976. Fluid inclusion evidence on the genesis of ores in sedimentary and volcanic rocks. *In: Handbook of Stratabound and Stratiform Ore Deposits.* Wolf, K. H., (Ed.), Elsevier, 2, 67-110.

SANGSTER, D. 1971. Sulphur isotopes, stratabound sulphide deposits and ancient seas. *Soc. Mining Geol. Japan, Spec. Issue* No. 3, 295-299.

SATO, T. 1974. Distribution and Geological setting of the Kuroko deposits. *In:* S. Ishihara (Ed.). *Geology of Kuroko deposits.* Min. Geol. Spec. Issue 6. Soc. Min. Geol. Japan, Tokyo, 1-9.

SHEPPARD, W. A. 1980. The ores and host rock geology of Avoca mines, Co. Wicklow, Ireland. *Norges geol. unders.* 360, 269-283.

SHEPPARD, W. A. 1981. The host rock geology and geochemistry of the Avoca mine, Co. Wicklow, Ireland. Unpub. Ph.D. thesis, Univ. Dublin.

SIEGEL, S. 1956. *Nonparametric statistics for the behavioural sciences.* New York, McGraw-Hill, 312pp.

STEPHENS, M. B., Swinden, H. S. and SLACK, J. F. 1984. Correlation of massive sulphide deposits in the Appalachian-Caledonian orogen on the basis of palaeotectonic setting. *Econ. Geol.* 79, 1442-1478.

STILLMAN, C. J. and WILLIAMS, C. J. 1979. Geochemistry and tectonic setting of some Upper Ordovician volcanic rocks in east and southeast Ireland. *Earth Planet, Sci. Lett.* 42, 288-310.

THODE, H. G. and MONSTER, J. 1965. Sulphur isotope geochemistry of petroleum, evaporite and ancient seas. *In:* Fluids in Subsurface environments. *Am. Assoc. Pet. Geol. Mem 4,* 367-377.

VAN STAAL, C. R. and WILLIAMS, P. F. 1984. Structure, origin and concentration of the Brunswick 12 and 6 orebodies. *Econ. Geol.* 79, 1669-1692.

WHEATLEY, C. J. V. 1971. Economic geology of the Avoca mineralized belt S. E. Ireland and Parys mountain, Anglesey. Unpub. Ph. D. thesis, Univ. Lond.

WILLIAMS, D., STANTON, R. L. and RAMBAUD, F. 1975. The Planes-San Antonio pyritic deposit of Rio Tinto, Spain: Its nature, environment and genesis. *Trans. Inst. Min. Metall. (Sect. B: Appl. Earth Sci.)* 84, 73-82.

WILLIAMS, F. M. 1984. Isotopic and mineralogical studies of the Avoca stratabound sulphide deposit and brecciated veins in the Leinster granite. Unpub. Ph.D. thesis, National Univ. Ireland.

Discussion

P. J. O'CONNOR (Geological Survey of Ireland) asked:
Could the authors comment on the age of the important NE shearing at Avoca mine in terms of the regional structural sequence?

REPLY:
The NE-trending shearing at Avoca forms a well-defined narrow zone which post-dates the main cleavage development. At least one other similar zone has been identified in the Caledonides of SE Ireland. This is the parallel East Carlow Deformation Zone (McArdle, P. and Kennedy, M. J., in press), whose development coincided approximately with the emplacement of the Leinster Granite in the early Devonian. The authors consider that the shearing at Avoca is of similar age.

Reference

MCARDLE, P and KENNEDY, M. J. In press. The East Carlow Deformation Zone and its regional implications. *Bull. Geol. Surv. Ir.*