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SOME NOVEL ASPECTS OF ECONOMIC MINERALOGY

by

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The main theme of this paper is the economic implications of mineralogical and other changes that effect heavy metal precipitates on or near the seafloor. In the first part, inspired by thoughts about the nature and origin of lithochemical aureoles around volcanogenic massive sulphide (VMS) deposits, it deals with the maturation and diagenesis of modern seafloor sulphide accumulations - processes that are ultimately capable of transforming them into orebodies. In the second it deals with aspects of sequential mineralisation in Palaeozoic sulphide deposits that appear to have formed at and near the seafloor, those in the Lower Carboniferous platform carbonates of Central Ireland. Both parts carry the message that the formation of sulphide ores in submarine settings is a very complicated process and not one that can be unravelled without extreme diligence in characterising and interpreting the mineralogy and textures of the resulting ores. Note that the word "sulphide" has often been used loosely in this paper, as shorthand for compounds with reduced sulphur that may not be simple sulphides and for that matter may not even be minerals in the accepted sense of the word.

Modern Submarine Sulphides

Submarine sulphide deposit deposits are now known at about 140 localities around the world, in a variety of geotectonic and sedimentological settings. These include the axes and flanks of oceanic ridges, incipient spreading centres within cratonic blocks, back arc basins and other subduction related settings. In chemistry and style they differ quite considerably from one place to another, even between different localities along the same oceanic ridge. There are also marked similarities between them, regardless of their setting, suggesting that submarine venting of metal bearing fluids tends to give rise to similarly variable precipitates in a range

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of environments. All this gives one some reassurance that they are relevant to orefields like the Iberian Pyrite Belt, where the deposits have quite a wide range of chemical characteristics and their environment of formation is difficult to classify.

Texturally and mineralogically, recent seafloor sulphide precipitates differ greatly from those in most onshore sulphide deposits of similar origin. This cannot be explained by metamorphism as it is true even of deposits that are quite young in geological terms and occur in unmetamorphosed terrains. It is not equally true of all deposits and it is not equally true of all parts of particular deposits.

Dealing briefly with texture, modern seafloor sulphides are characterised by:

High porosity
Heterogeneous grain size
Skeletal crystals and dendrites
Collomorphic and textureless material

Initial porosity is commonly 30% or more, implying that seafloor sulphides start out by being vastly more porous than those one finds in onshore mineral deposits. They also have a dull clinkery appearance that is relatively uncommon in the massive mineralisation of fossil analogues. This is partly due to the abundance of colloidal material, which can play a very important role as a temporary host of heavy metals. In the Red Sea Deep sediments, for instance, substantial amounts of copper and zinc have been reported as amorphous sulphides that defy characterisation (BROCKAMP et al., 1978). Mineralogically unclassifiable colloidal material has also been reported as the main host of heavy metals in some samples from the East Pacific Rise that are generally dominated by pyrite, chalcopyrite and sphalerite. At that locality it was noted that metastable colloform precipitates concentrated most of the zinc and were the main host of minor elements (MARCHIG et al., 1990).
The mineralogy of seafloor sulphide accumulations is shown in Table 1. Concentrating on the most common minerals, it is immediately clear that this is not the mineralogy of a typical VMS deposit, certainly not one in the Pyrite Belt. In fact nearly half of the commonest minerals are absent or very rare in most VMS deposits, including monosulphides of divalent iron, wurtzite, chalcopyrrhotite, cubanite and isocubanite, gypsum and anhydrite, amorphous silica and opal.

The reason why is becoming increasingly clear from studies of how submarine sulphides mature. Three different types of effect are involved, summed up in Table 2. Note especially the second effect of time, crystallisation of colloidal materials, which is tied up in many ways with hydrothermal diagenesis. Colloidal materials in seafloor precipitates tend to act as chemical dustbins, concentrating not only metals that form simple sulphides but also whatever there happens to be around in the way of trace elements like arsenic, antimony and mercury. As the colloids age, or get destabilised by changes in their surroundings, they tend to form crystals that have a relatively low ability to retain elements that sit uncomfortably in their structure. These elements presumably go back into solution and become available for incorporation in new mineral hosts.

Table 1: Mineralogy of Seafloor Precipitates

COMMON			
IRON SULPHIDES	Marcasite, pyrrhotite, pyrite		Fe(II) monosulphides
COPPER SULPHIDES	Chalcopyrite		Chalcopyrrhotite, cubanite/isocubanite
ZINC SULPHIDES	Sphalerite		Wurtzite
SULPHATES	Barite	Anhydrite, gypsum	
SILICA, SILICATES			Amorphous silica, nontronite, Mg smectites
OXIDES			Fe, Mn oxides/oxyhydroxides
RARE	Galena, Pb sulphosalts		Cerussite
	Tetrahedrite series, covellite, digenite		Atacamite
	Native silver		Native sulphur

Given favourable conditions of permeability, fluid flow and fluid chemistry, it is quite easy to visualise elements purged from colloids being precipitated as mineral halos around the main sulphide concentrations, say by reaction with biogenic sulphides in seafloor muds and mudstones.

1)	**Effect of time**
	Skeletal crystals develop idiomorphic forms Colloidal materials crystallise Grain sizes become more uniform
2)	**Effect of reaction with seawater**
	Sulphides resorbed by reduced seawater Sulphides oxidised
3)	**Effect of reaction with hydrothermal fluids (hydrothermal diagenesis)**
	Porosity reduced by mineral overgrowths Mineral transformations and new minerals formed Bulk geochemical changes

Table 2: Effects of Increasing Maturity

Be that as it may - and it is a subject on which there is certainly scope for economically relevant research - hydrothermal diagenesis has a major effect on the mineralogy and bulk chemistry of the sulphide pile. Original precipitates of iron and copper can undergo numerous reactions and mineral transformations such that most of the iron is ultimately incorporated into pyrite or pyrrhotite and most of the copper into chalcopyrite. Examples of these reactions and transformations are:

$$FeS + S^0 \rightarrow FeS_2$$
$$FeS + H_2S \rightarrow FeS_2 + H_2$$
marcasite → pyrite
chalcopyrrhotite → chalcopyrite + Fe sulphide
$$2FeS + Cu^{2+} \rightarrow CuFeS_2 + Fe^{2+}$$ via "cubanite"
$$FeS_2 + 2Cu^{+} \rightarrow CuFeS_2 + Cu^{2+}$$

Partly as a consequence of the mineralogical changes and of the progressive "curing" of colloidal precipitates, important changes can take place in the bulk chemistry of the sulphide pile. The following changes can be of fundamental importance to the economic geology of the resulting VMS deposit:

Increased copper content: This comes about through continued flushing of copper-bearing fluids through the sulphide pile, their reaction with existing iron sulphides and a gradual build up of chalcopyrite via such metastable intermediates as isocubanite (see COWPER & RICKARD, 1989). One of the consequences is the gradual cementing and sealing of the sulphide pile, reducing its porosity and permeability to the extent that the hydrothermal system can eventually become choked off. Economically the most important effect is to turn massive pyrite that is lean or sterile in base metals into copper-rich sulphide that may become ore. This effect is particularly marked in the lower parts of massive sulphide deposits and in the pyritic stockwork zones that commonly underlie them. A classic example is the Neves Corvo deposit in Portugal, which is probably the richest copper deposits of its size and type ever found.

Mobilisation of gold: The behaviour and mineralogy of gold in submarine hydrothermal systems is rather obscure. Initial precipitates tend to be geochemically enriched in gold but only up to a level of about 200 ppb, which is not the sort of figure that starts a gold rush. Figures of that order are the norm for the bulk of the massive sulphide in the ancient deposits that seem to have formed on or just below the seafloor. However some ancient deposits have much higher gold grades, not throughout but strongly concentrated in particular zones. Studies of gold distribution in Tasmanian VMS deposits show in some a gold-zinc association with gold concentrated along with barite towards the stratigraphic top of certain deposits (Figure 1). This effect may be primary but has also been attributed to a process of zone refining whereby cooling hydrothermal solutions leach gold together with lead and zinc from the lower parts of sulphide masses and reprecipitate them in the upper levels of the sulphide pile. Some evidence that this is actually what happens has been found in the eastern Pacific, where gold-rich samples have been recovered from the tops of sulphide mounds and the gold appears to be hosted by sulphosalts deposited from fairly low temperature solutions (HANNINGTON et al., 1986). A recent report from the Woodlark Basin in the southwest Pacific of gold rich samples dominated by barite and Fe-Mn-Si oxides may have different implications in this regard (SCOTT & BINNS, 1993).

Enhanced capture of trace elements: This effect is attributed to re-reaction of existing sulphides with trace elements in low temperature fluids that probably include fluids released by the aging of colloidal materials. The sort of reaction that takes place is between preexisting chalcopyrite and fluids containing arsenic, antimony, mercury, zinc and silver to form members of the tetrahedrite-tennantite series. A wide variety of sulphosalts can form in this way, and electron probe work has shown that common sulphides like pyrite can develop overgrowths and internal zones that are rich in elements such as arsenic, cobalt and selenium. Economically the effect has its upside and its downside. The upside can be the fixing in the sulphide pile of large amounts of silver that can potentially add considerable value to an eventual ore. The downside is the fixing of deleterious elements like arsenic, antimony and bismuth that can attract significant penalty charges when they end up in smelter feed.

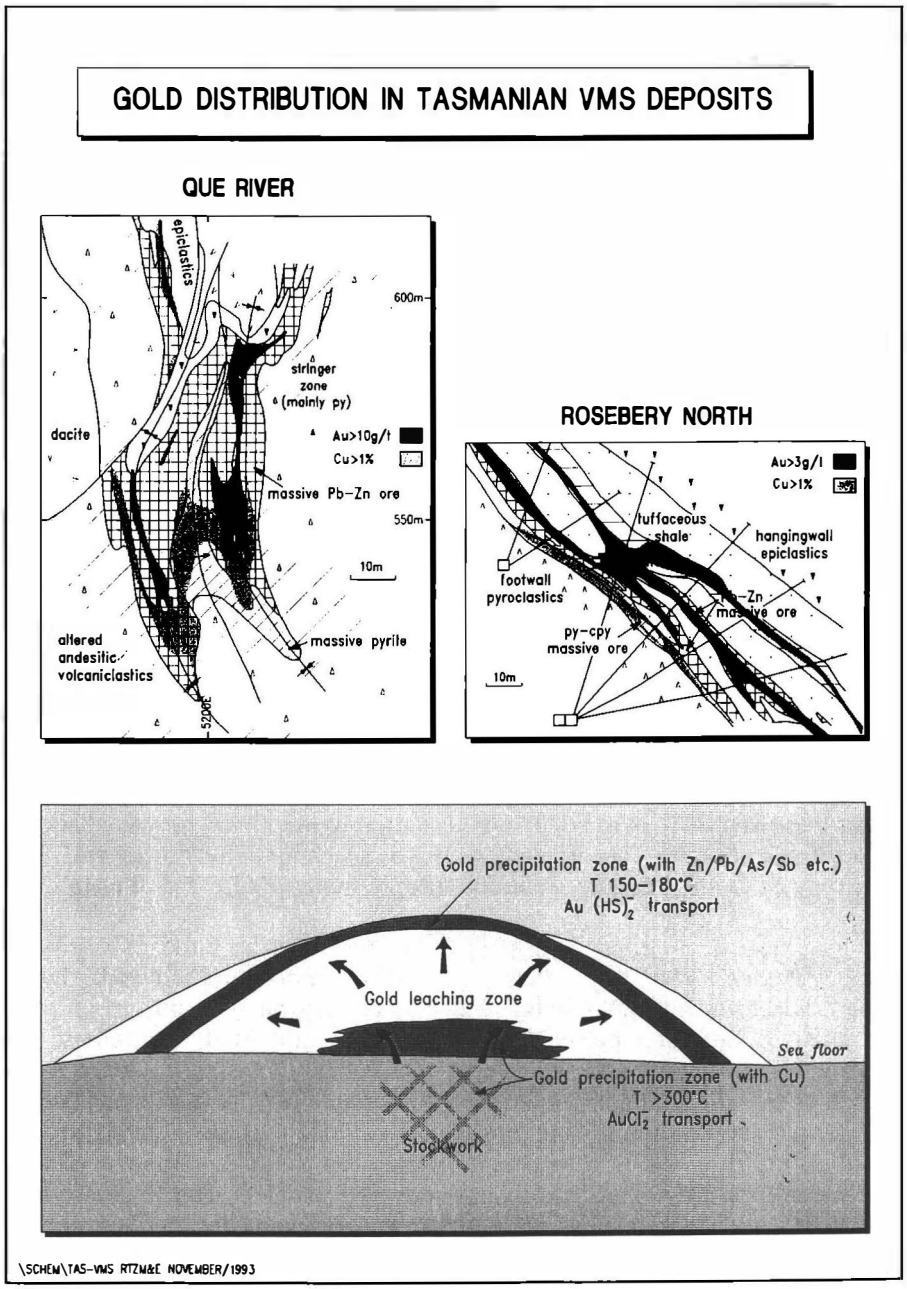

Fig. 1: Profiles through Tasmanian VMS Gold deposits.

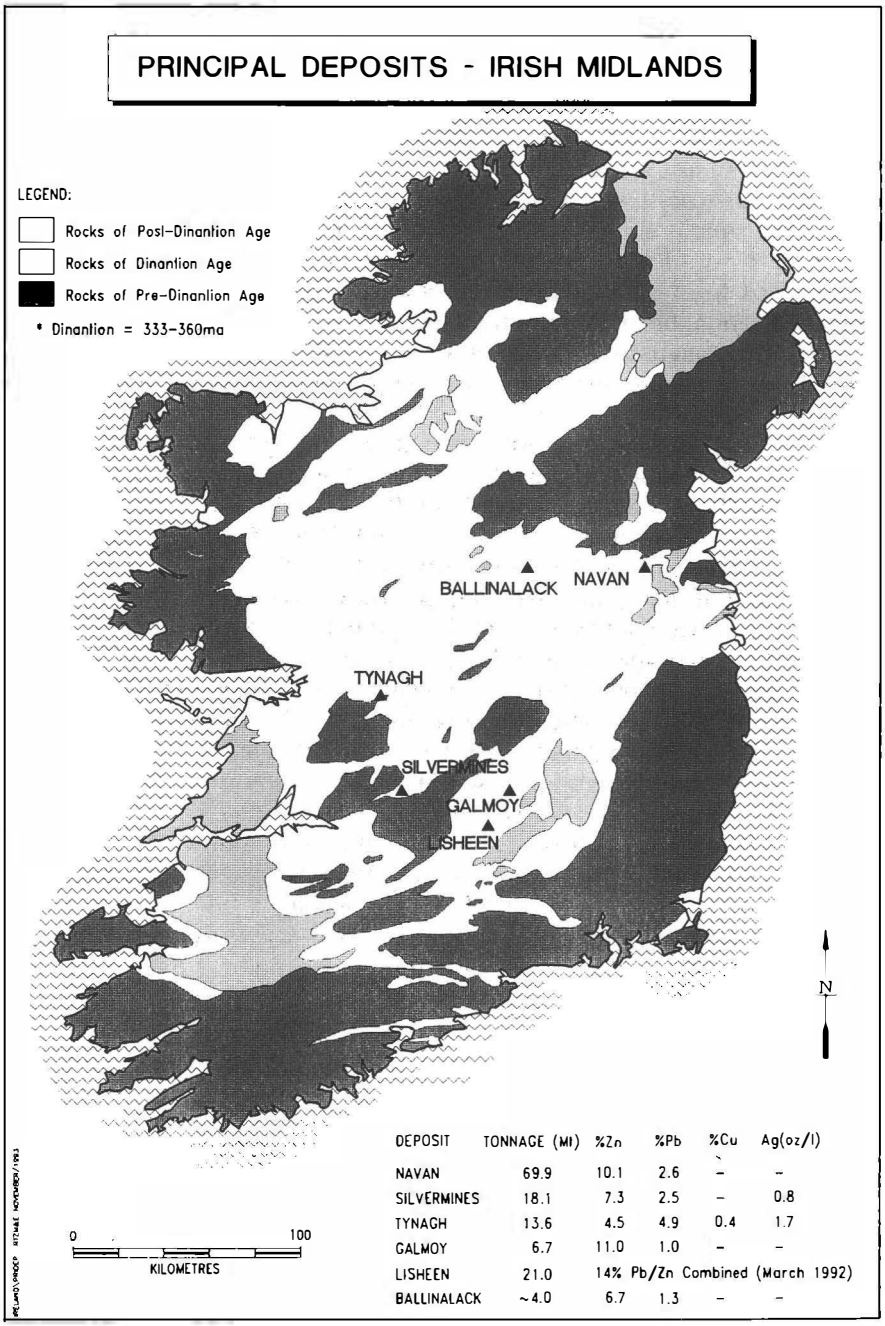

Fig. 2: Geologial sketch map of Ireland.

Central Irish Orefield

The complexity of the ore forming processes that take place in submarine settings, and the important role of precursor minerals in establishing the economic characteristics of resulting orebodies, have been elucidated by detailed mineralogical studies carried out by Dr Harry Kucha of the Institute of Geology and Mineral Deposits in Kraków, Poland. Concentrating on carbonate-hosted mineralisation, Dr Kucha has found time and again that normal study methods failed to reveal whole suites of minerals that are in many cases nameless and together tell a story of ore formation that is crucially different from the one that can be deduced from conventional microscopy. Some scientists do not accept Dr. Kucha's findings, believing that they relate to artifacts or simply to weathering effects, but since they challenge conventional wisdom and make sense of things that are otherwise mysterious that is not the position of the author.

In this paper they will be reviewed in relation the Tynagh deposit in County Galway, Ireland. This is one of a diverse family of deposits in platform carbonates of Lower Carboniferous age that underlie most of Central Ireland (Fig. 2). These deposits resemble each other in ways that are just as striking as the differences between them, many of which form patterns that seem to make some sort of regional sense. For instance lead isotope ratios seem to show that all the mineralisation is consanguineous and attributable to the same mineralising event, with differences in isotopic ratios reflecting regional changes in the nature of the Caledonian basement. Much of the mineralisation has epigenetic characteristics - replacive textures and some degree of discordance with the host strata as well as local isotopic evidence of deep-sourced sulphur - but even so the main orebodies (at Navan, Tynagh and Silvermines) contain many signs of synsedimentary and early diagenetic origin. This implies a major pulse of hot metal-bearing fluids in early Carboniferous times, some of the fluid venting and precipitating metals on the seafloor and a lot precipitating metals within weakly lithified sediments dominated by carbonates. It is an interesting sidelight on these deposits that among the sulphides in several of them have been found pyrite chimneys, very small compared with those on present day mid-oceanic ridges but evidence nonetheless that submarine hydrothermalism operates similarly in a range of different environments.

Tynagh Mineralisation History

Mineralisation at Tynagh is focused on part of a late Courceyan carbonate mudbank structure that has been preserved along with a mantle of sedimentary breccias and limestone turbidites on the downthrow side of a major fault zone. Tynagh is a polymetallic deposit, worked in its time as orebody of zinc, lead, copper and silver. It also represents a major accumulation of pyrite and barite. Metal seeps into the seafloor muds apparently began around the time that the carbonate mudbank was starting to build up, producing synsedimentary mineralisation of no economic importance that is now dominated mineralogically by pyrite and sphalerite. The main mineralising pulse, again dominated by zinc and

iron where heavy metals are concerned, took place when the reef structure was well developed and fairly rigid, though riddled through with cavities resulting from the consolidation of carbonate muds and the decay of organic remains within them. The trigger seems to have been movements on the adjacent fault zone as a high proportion of the mineralisation follows disorderly fractures that merge into a breccia zone along the main fault. Soon afterwards in geological terms there was another pulse of mineralisation, this time dominated by lead and copper, which has an even more epigenetic appearance but again was synsedimentary in a broad sense. The last manifestation of this phase of mineralisation was thoroughgoing dolomitisation of much of the remaining limestone, especially along the line of the main fault.

Sulphide Precursors

To bring the focus onto the main ore metal in deposits of this sort, the concentrations of zinc reported in certain generations of calcite and dolomite at Tynagh go up to several percent, and it is quite clear that carbonates played a key role as precursor minerals in the formation of sphalerite. Textural relationships between sphalerite and zinc-rich calcite indicate clearly that the sulphide is the successor to the carbonate, formed from solutions that brought a supplementary supply of zinc and were marked by strong swings in the valency state of the sulphur they contained.

The last point is strongly suggested by Kucha's identification of a range of metastable sulphur bearing compounds, interpreted as sulphide precursors, in carbonate hosted mineralisation from Ireland and a number of other countries. In a recent publication (KUCHA & VIAENE, 1993) he describes observations and measurements on colloform varieties of what seemed to be ordinary sulphides, mainly pyrite and sphalerite, from localities in Belgium and Upper Silesia. Table 3 lists the types of compound that were present and gives an indication of their chemical composition with respect to iron, zinc, lead and arsenic. Note the invariable presence of arsenic and how far the metal contents of these compounds fall short of what one would expect in simple sulphides.

Down the microscope the compounds tend to have a fibrous habit and occur in low reflectivity bands that look like poorly polished "crud". They are easy to dismiss as being unfit for detailed study, too inhomogeneous and suspect in origin, but the writer believes that Kucha's observations have given a glimpse of a large neglected family of natural compounds that has a definite bearing on the genesis and the commerciality of certain types of ore deposit.

Kucha has described a similar range of compounds from one of the Irish deposits, Ballinalack. His microprobe analyses of sphalerite formed at Ballinalack, by replacement and breakdown of thiosulphate precursors, underline the inhomogeneity of the end product, showing zinc contents that were always well short of the stoichiometric ideal and in five cases out of eleven were less than 50% with a minimum of only 21.5%. Obviously these are not analyses of

sphalerite but of mineral mixtures, which Kucha was able to confirm by X-ray analysis. He concluded that he was dealing with microscopic domains within which there were very fine grained mixtures of stable sulphides formed by replacement or decomposition of a thiosulphate precursor and collectively reflecting the original chemical composition of that precursor.

S ANION	S VALENCE	GENERAL FORMULA	RELATIVE WT%
SULPHOXYLANE	2+	MSO_2	Fe>>As>Pb>Zn 39.3 2.4
SUBSULPHITE	3+	MS_2O_4	Fe>>Pb>As 23.9 5.6
SULPHITE	4+	MSO_3	Zn>Fe>>As 29.9 4.07 Fe>>As>Pb>Zn 40.0 2.35
PYROSULPHITE	4+	MS_2O_5	Fe>>Pb>As>>Zn 22.7 0.3
THIOSULPHATE	2- and 6+	MS_2O_3	Fe>>Zn>Pb>>As 32.6 0.2 Fe>>Zn>Pb>As 30.1 0.3

Table 3: Sulfide precursors compounds.

Economic Implications

All this can have quite serious economic implications and helps to explain why some base metal mines have metallurgical problems or simply fail to recover several percent of the metal that is reported by assay.

Loosing a couple of percent of contained zinc may not sound like a serious problem but in a really large orebody, say 100 million tonnes at 10%, the loss could amount to about 200,000 tonnes of metal, which is equivalent to a couple of years' output by a fairly large zinc refinery and worth in refined form about a quarter of a billion dollars. There may be no solution to this particular problem: the compounds concerned have received very little study from this point of view and

are generally hard to characterise in mineralogical terms because they are very fine grained in nature and evidently highly variable in composition.

Compositionally sulphide precursors present another problem that can also be serious when it comes to commercialising orebodies that contain them. This relates to the analytical evidence that they commonly contain arsenic, presumably in substitution for sulphur, and may do so in amounts that exceed 5%. Indeed it may well be that arsenic and other trace elements such as bismuth, antimony, selenium and mercury help to stabilise compounds of this sort. Several are penalty elements under normal smelter contracts, implying that if their concentration in concentrates exceeds certain levels their presence makes inroads into the revenue of the mine concerned. In reality penalty elements are usually present in stable mineral form such as arsenopyrite, tetrahedrite-tennantite and other sulphosalts but metastable precursors may sometimes share part of the blame.

If there is a practical conclusion to be drawn from all this it is that detailed mineralogical studies of "suspect" orebodies are needed at an early stage in the mine planning process. Mineralogical studies ought also to be part of the exploration process, if not day-to-day then at least as soon as one has found some mineralisation in the ground that could eventually be part of an orebody. These would not generally be the sort of studies that are capable of unravelling the compositional and structural complexities of fine grained precursor minerals, which may only be present in trace amounts but are nevertheless a very rich vein of ore for the academic community to work.

Finally, the alert reader will not have missed the point that metal-rich carbonates that fail to get sulphidised may form geochemical anomalies in rocks and overburden that may not relate to ore mineralisation or may do so only peripherally. Figure 3 gives some measure of the efficiency of the processes that formed and concentrated zinc sulphide at Tynagh. Kucha calculates that only 45% of the zinc introduced during the main stage of mineralisation ended up by forming ore while 49% became dispersed through weakly mineralised calcitic reef where a substantial proportion, perhaps as much as 50%, was precipitated in the lattice of calcite. The remainder of the introduced zinc, about 5%, was even more widely dispersed and now reports as a component of geochemically anomalous off-reef and basinal sediments that extend to the north of the orebody. This effect is even more marked with the late stage of mineralisation, when over a third of the introduced zinc migrated into off-reef sediments and there contributed to a manganese-dominated hole that extends several kilometres away from the orebody.

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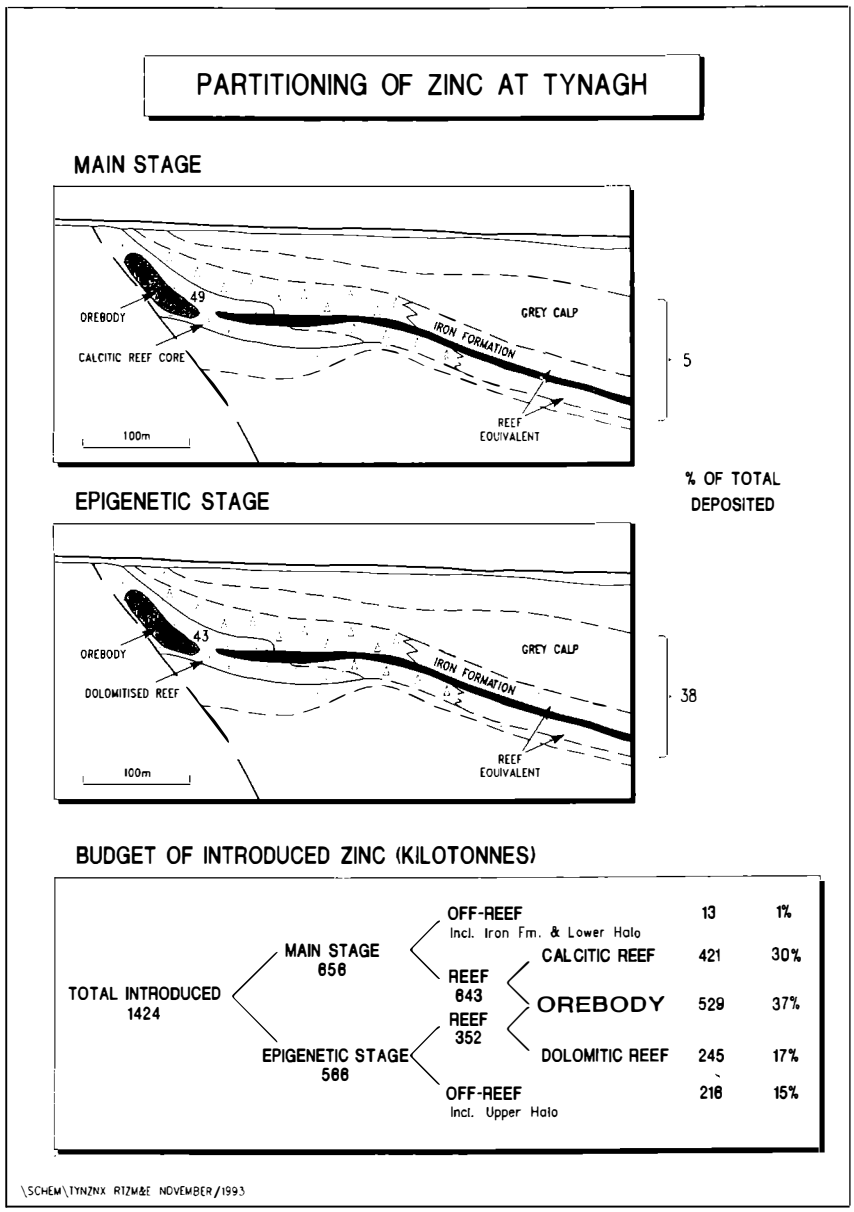

Fig. 3: Profiles, partitioning and budgeting of zinc at Tynagh deposit, Ireland.

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