

Magmatic sulfide ore deposits

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ABSTRACT

Magmatic sulfide ore deposits are products of natural smelting: concentration of elements from silicate magmas (slags) by immiscible sulfide liquid (matte). Deposits occupy a spectrum from accumulated pools of matte within small igneous intrusions or lava flows, forming orebodies mined primarily for Ni and Cu, to stratiform layers of weakly disseminated sulfides, mined for platinum group elements, within large mafic-ultramafic intrusions. One of the world's most valuable deposits, the Platreef in the Bushveld Complex in South Africa, has aspects of both of these end members. Natural matte compositions vary widely between and within deposits, controlled largely by the relative volumes of matte and slag that interact with one another.

KEYWORDS: nickel, sulfide, platinum, layered intrusions, large igneous provinces, magma, igneous petrology

INTRODUCTION

Magmatic sulfide deposits are nature's smelters. By the same process that has been used since prehistoric times to extract metals from ores, magmatic sulfide ores form by the interaction between immiscible sulfide-oxide liquids (mattes) with silicate magmas (slags). Scavenging of chalcophile elements – Ni, Cu, Au and the platinum group elements (PGE) - and accumulation of the matte component (Figure 1), has produced some of the world's most valuable economic metal concentrations (Naldrett 2004). These currently account for ~56% of the world's Ni production and over 96% of supply of Pt, Pd and the other PGE (Mudd and Jowitt 2014).

[Figure 1. Field appearance of magmatic sulfide ores...](#)

Magmatic sulfide deposit settings

On a deposit scale, magmatic sulfide accumulations are found in a variety of host igneous rock bodies. Broadly they fall into two major categories: sulfide-rich, exploited primarily for Ni and Cu; and sulfide-poor (typically less than 5% sulfide) where the dominant value is in the platinum-group elements (PGE) and Au.

Sulfide-rich Ni-Cu dominant deposits can be further categorized:

1. Sulfide-rich accumulations in small mafic or mafic-ultramafic intrusions, (Fig. 1A,B) usually identifiable as magma conduits (Lightfoot and Evans-Lamswood 2015). Important examples include Voisey's Bay (Canada), Jinchuan (China) and the Norilsk-Talnakh deposits, Siberia. With the notable exception of the Norilsk-Talnakh ores, the PGE are minor by-products.
2. Accumulations of sulfide in komatiites (e.g. the Kambalda and Perseverance deposits in Australia, Barnes 2006), or ferropicrites (e.g. the Pechenga deposits, Russia, Hanski *et al.* 2011). Deposits are hosted in lava flows (Fig. 2A) or shallow subvolcanic intrusions; exploited dominantly for Ni only.
3. Sulfide accumulation beneath an impact-generated crustal melt sheet: the unique example of the Sudbury Ni-Cu-PGE ores (Keays and Lightfoot 2004).

Sulfide-poor PGE-dominant deposits fall into two types:

1. Stratiform accumulations of a few percent of disseminated sulfide in cumulates within large layered mafic-ultramafic intrusions, including PGE-enriched "reefs" (Naldrett *et al.* 2008). Such deposits are typically exploited for PGEs with by-product Ni, Cu and Co. They generally occur as remarkably thin and persistent layers: the best-known example, the Merensky Reef of the Bushveld Complex (Figure 1C) is commonly only a few tens of cm thick but extends continuously for over 400 km.
2. Generally thicker, stratabound sulfide disseminations, commonly PGE-rich, in the marginal rocks of large layered intrusions such as the Platreef, Bushveld Complex (McDonald and Holwell 2011).

The form of ore-hosting magma bodies

Stratiform reef-style PGE deposits are exclusively hosted within large sill-like or boat-shaped layered mafic-ultramafic intrusions, usually several km thick. The magma bodies that host Ni-Cu dominant, sulfide-rich orebodies are more diverse in form (Figure 2). They all represent the products of magma flowing through restricted conduits or channels. These can be feeder tubes or channels within extensive komatiite lava flow fields (Leshner 1989; Barnes 2006) (Fig. 2A), or feeders to large igneous province magmatism in the form of sill-dike combinations (Fig. 2C) or tube-like “chonoliths” (Fig. 2D,E) (Barnes *et al.* 2015; Lightfoot and Evans-Lamswood 2015). Almost all examples show much higher proportions of sulfide and cumulus silicate minerals (typically olivine) within the flow or intrusion than could have been dissolved in a volume of magma equal to that of the host body, indicating that much larger volumes of magma flowed through the conduit leaving crystals and sulfide liquid behind. Commonly there is evidence of thermal or thermomechanical erosion, in the form of transgressive footwall troughs beneath komatiite flows (Fig. 2A), or in “chonoliths” (Fig. 2D,E) that truncate layering within the country rock and often contain partially digested wall rock fragments. Such host bodies are usually very small compared to the total volume of magmatism in the province: in the case of the ore-hosting intrusions of the Norilsk-Talnakh camp, about 1 millionth of the total volume of the Siberian Trap lavas.

Figure 2. Intrusion geometries...

THE NATURE OF MAGMATIC SULFIDE ORES

Mineralogy

Magmatic sulfide ores have a wide range of sulfide contents: from less than a tenth of a percent in some stratiform PGE ores, to pure sulfide in some Ni-Cu deposits (Figure 1).. Almost all unaltered magmatic sulfide ores, regardless of sulfide mode, have a characteristic assemblage of pyrrhotite-pentlandite-chalcopyrite-platinum-group minerals (PGM); an assemblage formed from the cooling and crystallization of a magmatic-derived sulfide matte. Natural mattes, consisting predominantly of Fe, Ni, Cu and S fractionate to form a sequence of phases on cooling. Below ~1100°C, (Ni,Fe)S monosulfide solid solution (mss) crystallizes leaving a Cu-rich sulfide liquid enriched in Pt, Pd and semi-metals (e.g. Te, Bi, As). At ~900°C, the Cu-rich liquid crystallizes to

intermediate solid solution (iss, approximately CuFeS_2), leaving a residual melt progressively enriched in Pt, Pd and semi-metals (Li *et al.* 1996). This fractionation process takes place on scales from that of individual $\sim\text{cm}$ sized globules (Figure 3) to entire orebodies, e.g. the supergiant Cu-PGE rich Oktyabrynsky orebody at Talnakh in Siberia (Torgashin 1994). On further cooling to below $\sim 700^\circ\text{C}$, mss breaks down to pyrrhotite and pentlandite, iss to chalcopyrite, and the low-T residual liquid crystallizes Pt and Pd tellurides, bismuthotellurides and arsenides. The common co-occurrence of magnetite arises from the ability of mattes to also dissolve substantial amounts of FeO (Naldrett, 2004).

Figure 3. Norilsk differentiated bleb

Sulfide Ore Textures and Evidence for Magmatic Origins

Textural relationships between sulfides and their host silicates are key evidence for their origin (Figure 4). One of the critical textures from a historical point of view is that interpreted by Hawley (1962) as a frozen emulsion of immiscible silicate and sulfide liquids, in one of the first papers to argue persuasively for the primary magmatic origin of the Sudbury ores (Figure 4A). Other diagnostic magmatic features are: (1) net- or matrix textures (Fig. 4B), where sulfides form a continuous 3D matrix enclosing cumulus silicates; (2) interspinifex ores in komatiites (Fig. 4C) where sulfide occupies the original spaces between dendritic olivine plates (Barnes *et al.* 2016); (3) sub-spherical globular ores, sometime associated with infilled vesicles (Fig. 4D,E); and (4) breccia textures where silicate fragments are disaggregating through melting within a sulfide liquid matrix (Fig. 1B).

Figure 4. Sulfide ore textures.

ORE FORMING PROCESSES

The great majority of magmatic sulfide deposits form from much the same sequence of processes: generation of a sulfide-silicate liquid emulsion; physical separation of a mixture of sulfide liquid droplets and cumulus silicate minerals from this emulsion; and deposition and coalescence of sulfide liquid in specific sites. In some cases, the final disposition of the ores is influenced by post-deposition migration of coalesced sulfide liquid pools, driven by the balance between surface tension and gravitational forces (Barnes et al, 2016).

Generation of sulfide liquids

This fundamental process can happen by a variety of mechanisms.

Partial melting of sulfide-bearing mantle.

Sulfide liquid can be generated at source where the degree of partial melting is low enough that the sulfide component of the source melts, but does not completely dissolve in the silicate partial melt. The S content of silicate magmas in equilibrium with matte (S content at sulfide liquid saturation, or SCSS) increases with decreasing pressure, such that sulfide-saturated magmas generated in the mantle are likely to be undersaturated on arrival in the upper crust (Edmonds and Mather, 2016, this issue).

Fractional crystallization of silicate magma.

Sulfur behaves as an incompatible element under sulfide-undersaturated conditions, so fractional crystallization causes S content to increase. Sulfide liquation occurs once the S content of the magma exceeds the SCSS, which itself decreases with decreasing temperature and Fe content. Within cumulate sequences, the first onset of sulfide liquid saturation can generate extremely PGE enriched mattes, as in the Platinova Reef of the Skaergaard intrusion (Holwell et al., 2016).

Mixing of two magmas both of which are at or close to sulfide liquid saturation.

This mechanism can give rise to a hybrid magma with transient sulfide supersaturation. This process has been invoked to explain the origin of PGE Reefs associated with major magma influxes in large chambers, such as the Merensky Reef of the Bushveld Complex (Campbell *et al.* 1983).

Incorporation of external crustal S, giving rise to sulfide "xenomelts".

Addition of external S is regarded as the dominant process in the formation of all komatiite-hosted ores (Leshner, 1989), and in the great majority of intrusion-hosted deposits (Ripley and Li 2013). Crustal rocks can have S isotope and S/Se ratio signatures that are usually very distinct from mantle S, such that these signatures can be used as tracers for orebody S sources. In some cases of deposits where S isotopic composition is mantle like (e.g. Jinchuan in China; Ripley et al., 2005) the crustal signal may have

obliterated by high R-factor equilibration with large volumes of magma. A variety of mechanisms exist for incorporation of external S, but direct melting of physically incorporated sulfidic country rock fragments (xenoliths) to form sulfide “xenomelts” is the fastest and most effective (Robertson *et al.* 2016).

COMPOSITION OF MAGMATIC SULFIDE ORES

Figure 5. Ore compositions

Variability in Ni and Cu content

The first order variability in Ni and Cu tenors (tenor = concentration of the metal in 100% sulfide) is related to the composition of the host rocks (Figure 5a). There is a decrease in the Ni:Cu ratio from values around 20:1 in komatiites through 4:1 in ores associated with komatiitic basalts, to between 0.5 and 5:1 in most deposits (both Ni-Cu sulfide-rich type, and reef-style low sulfide PGE type) associated with mafic magmas. Lower Ni:Cu ratios are found in ores where there has been extensive sulfide liquid fractionation, as at Norilsk-Talnakh and in the Sudbury footwall veins (Naldrett *et al.* 1997) but also in disseminated ores associated with advanced fractionation of tholeiitic mafic magmas. Values of Ni/Cu in ores correspond reasonably well with those in the parent magmas themselves (Barnes and Lightfoot, 2005), which for mafic host magmas range from high-Mg basalts through to fractionated tholeiites. Nickel becomes depleted in more evolved magmas due to olivine crystallization, whereas Cu becomes enriched due to incompatibility in the major crystallizing silicate phases. Hence, primitive high-T komatiites have very high Ni and low Cu compared with more fractionated mafic magmas that attain progressively lower Ni/Cu. This contrast is reflected in sulfide compositions (Fig. 5A). The most extreme Cu-rich example is the Platinova Reef (PN in Figure 5) of the Skaergaard Intrusion. Here, sulfide saturation occurred very late in the crystallization history, and the magma attained saturation in Cu-Fe sulfide liquid rather than the typical Fe-Ni-dominated sulfide (Holwell *et al.* 2016).

Variability in PGE content

Platinum group element (PGE) tenors (represented in Figure 5B by Pd) show a much wider range than those of Ni and Cu. PGE tenors range over nearly 6 orders of magnitude between the most depleted Ni-Cu deposits to the most enriched, Reef-style ores. The PGE tenors correlate broadly with Ni and Cu over the komatiite and komatiitic basalt

associated groups, but much less strongly in deposits associated with dominantly mafic intrusions.

PGE tenors are controlled by two major effects: parent magma compositions, and mass balance effects. The PGE contents of silicate melts in part reflect the variable degree of igneous compatibility of the different PGEs: Ir, Os and Ru are moderately compatible, and Pt and Pd are strongly incompatible. Superimposed on this effect is the very strong tendency of all the PGEs to become strongly depleted during fractional extraction of sulfide liquid, owing to their extreme chalcophile character (Mungall and Brenan 2014). The tendency of mafic magmas to lose PGEs to sulfides either through retention in the mantle during partial melting, or sulfide liquid extraction during ascent, accounts in part for the much wider range in PGE tenors in mafic relative to komatiitic settings; komatiite form by much higher degrees of partial melting and therefore have a much lower susceptibility to sulfide-related PGE extraction at depth (Barnes et al., 2015).

A further control on sulfide liquid compositions is the mass ratio, R , of silicate to sulfide liquid that react with one another (Campbell and Naldrett, 1979). This relationship is expressed as:

$$Y_i^{sul} = \frac{X_i^{sil} D_i^{sul} (1 + R)}{R + D_i^{sul}} \quad (1)$$

where Y_i^{sul} is the final concentration of element i in the sulfide liquid, X_i^{sil} the initial concentration in the silicate liquid, and D_i^{sul} is the partition coefficient between sulfide and silicate melt. Formation of magmatic sulfides is treated here as a batch equilibrium process: a batch of sulfide liquid forms and segregates from R times its mass of silicate melt. The effect of variations in R is shown on the model curves in Figure 5. Where R is very low compared with D_i^{sul} , the tenor of element i is relatively low and tenor depends almost entirely on R . If R is large relative to D_i^{sul} the opposite applies: both silicate and sulfide melt have high metal contents that increase almost linearly with D independently of R . The effect operates in natural systems through the wide range in the partition coefficients for the different chalcophile metals: typically around the low hundreds for Ni, ~ 1000 for Cu, and of the order of hundreds of thousands for the PGEs (Kiseeva et al., this volume). Hence the extremely chalcophile PGEs are much more susceptible to R factor effects than Ni and Cu, as can be seen in the model curves in Figure 5. Nickel and Cu tenors

approach maximum values where R is greater than about 1000, while the PGE tenors continue to increase with increasing R owing to their extreme D values. Extremely high silicate /sulfide ratios are necessary to produce the high PGE tenors of Reef-style deposits.

Sulfide liquid differentiation can produce additional variability in the proportion of Cu to Ni and of Pt and Pd to Ir, Ru and Os, and is progressively more important in orebodies containing initially higher Cu contents where the melting range of the sulfide component extends to much lower temperatures. This effect produces dispersion at metre to decimetre scale within orebodies (and at cm scale in individual droplets as seen in Fig. 3), but in some very large systems differentiation is accompanied by physical migration of residual Cu-rich liquid into veins and fractures. At Sudbury this process generates very high grade Cu-PGE orebodies hundreds of metres below the base of the host magma body (Naldrett et al., 1997).

THE PLATREEF: THE PGE RESOURCE OF THE FUTURE

The giant layered ultramafic-mafic Bushveld Complex, South Africa, hosts over three-quarters of the world's PGE resources in three main deposits: the UG2 chromitite, the Merensky Reef and the Platreef. The former two are archetypal stratiform reef deposits, with a few percent of PGE-rich sulfides associated with chromite, and thicknesses of a few centimetres to a few metres. The Platreef, in the northern part of the complex, is a much thicker orebody (~10-400 m) emplaced as a series of sills with stratabound disseminated sulfides present in a package of mostly pyroxenites that rest directly on Archaean-Proterozoic country rocks (Figure 6). The PGE tenors (Fig. 5B) overlap with those of the Merensky Reef. The Platreef has been interpreted as the lateral equivalent of the Merensky Reef and as the propagating marginal facies of the Bushveld Complex formed as magma was squeezed out at the edges of the expanding magma chamber (Naldrett *et al.* 2008). The Platreef is likely to be the main source of future supply of PGE in the coming decades, making it one of the most economically significant of all known magmatic sulfide ore deposits.

The Platreef displays much complexity due to its multi-stage origin (McDonald and Holwell 2011). Mass independent S isotopes and S/Se ratios give evidence that sulfide saturation was initially triggered by a bulk assimilation event, most likely of pyritic shales at depth (Penniston-Dorland *et al.* 2008). Contaminated magma with a cargo of dispersed

sulfide liquid droplets was then emplaced higher in the crust, at which point interaction with the diverse range of country rocks resulted in further addition of external S, lowering the PGE tenor of the sulfides and modifying isotopic and PGM compositions to different degrees depending on the country rock lithology (McDonald and Holwell 2011).

Recent exploration in the northern limb has identified a much more regularly layered sequence, with traceable stratiform mineralization down dip from the surface outcrop of the Platreef, with the addition of thick underlying ultramafic cumulates. This “Flatreef” sequence has many similarities to the Merensky Reef in the rest of the complex, and represents a transition from stratabound ‘contact-type’ or ‘marginal’ styles, to stratiform, reef-style mineralization.

Figure 6. Block model of the northern limb of the Bushveld complex.....

THE ELEPHANT IN THE SHIELD: SUDBURY

No review of magmatic sulfide ores could ignore the world’s largest known accumulation of magmatic ores, the extraordinary Sudbury impact structure in the southern part of the Canadian Shield, Ontario. In this case, ore formation followed wholesale melting of almost the entire thickness of the crust following a giant bolide impact (Mungall et al 2004). Sulfide liquid segregated from the resulting melt sheet on subsequent cooling. While many aspects of Sudbury ore genesis are unique, one aspect is highly significant to understanding processes in other deposits: the presence of extensively mobilized veins and dikes of sulfide rich rocks that extend for distances of kilometers below the original base of the melt sheet. These features attest to the extreme physical mobility of sulfide magmas, or possibly sulfide-rich melt emulsions charged with rock fragments, driven by gravity into fracture systems. This is an important clue to the origin of late stage injections of sulfide-rich breccia-textured ores, common in many intrusion hosted deposits (Barnes et al., 2016).

RESEARCH QUESTIONS

Research in magmatic sulfides has made substantial advances over the five decades from the pioneering work of Naldrett and others, particularly in understanding geochemical processes, but a number of fundamental questions remain about physical processes of ore formation.

1. Is the addition of external S through assimilation of crustal rocks essential, and by what mechanisms does this addition take place?
2. How is sulfide liquid transported in magmas, in what proportions and in what physical form? How far can sulfide liquids be transported from the original site of liquation to the point of deposition?
3. What is the physical process of deposition, and to what extent is it governed by mechanical sedimentation versus in-situ chemical deposition of sulfide liquid at the point of nucleation?

Magmatic sulfides continue to be fascinating topics of research, leading to advances in exploration models as well as new insights into magmatic and even climatic processes. Applications have been made to meteoritics, in studies of the origin of planetary cores, and into processes of metal and S transport with implications for the origin of porphyry deposits and climate-impacting giant eruptions (Mungall *et al.* 2015).

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