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3D textural evidence for the formation of ultra-high tenor precious metal bearing sulphide microdroplets in offset reefs: An extreme example from the Platinova Reef, Skaergaard Intrusion, Greenland

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ABSTRACT

The Platinova Reef in the Skaergaard Intrusion, east Greenland, is an example of a type of layered-intrusion-hosted, precious metal-enriched, stratiform, disseminated sulphide deposit referred to as "offset reefs". These typically show platinum-group element (PGE) enrichment immediately below a major increase in the abundance of Cu-rich sulphides, with a prominent peak in Au enrichment exactly at that transition between the PGE-rich and the Cu-sulphide-rich zones. The reasons for the relative sequence of offsets in metal peaks, and the occasionally very high metal tenors have been subject to great debate. Here we use an integrated approach of high-resolution X-ray computed tomography (HRXCT), SEM, synchrotron and desktop microbeam XRF mapping, and thin section petrography to comprehensively classify the textural relations of the precious metal-bearing sulphides of the Platinova Reef as an extreme end member example of an exceedingly high tenor offset deposit. Our results show that in the zones of PGE enrichment, precious metal minerals (PMMs) are intimately associated with Cu sulphide globules, mostly located at, or close to, silicate and oxide boundaries. The textures are identical in zones enriched in Pd and Au, and thus we do not see any evidence for different processes forming the different zones. The PMM:Cu sulphide ratio in each globule varies significantly but overall the size of the globules increases from the Pd-rich, through the Au-rich, and into the Cu zone, with a significant corresponding decrease in PM tenor. As such, this records a progression of exceedingly high tenor, microdroplets of sulphide, which progressively get larger up through the section, and decrease in tenor proportionally to their size. Cumulus droplets of Cu sulphide became enriched in metals, and were trapped *in situ* without significant transport from their point of nucleation. The transition to larger sulphides represents a change from sulphides nucleated and trapped *in situ*, to larger ones that liquated from magma devoid of crystals, and that were able to grow and sink. This feature is common in all offset reef deposits, and is marked by the major enrichment in Au. Although the metal ratios of PGE to Au in the Pd- and Au-rich offset zones differ, the identical textures and comparable mineralogy show the physical mechanisms of concentration are the same, indicating a similar physical method of concentration. The relative position of the Pd, Au and Cu peaks in the Platinova Reef is essentially the same as that in numerous other offset reefs, suggesting that common overarching processes are responsible for the enrichment in metals, and relative offsets in peak metal concentrations in all such deposits. The most important of these processes are their relative $D_{sul/sil}$ values and the diffusivities of the metals, which determine the order of offsets and the high tenors of the smallest sulphide droplets. The Platinova Reef therefore records the extreme enrichment via equilibrium and diffusive partitioning into sulphide liquid microdroplets very close to their point of nucleation.

1. Introduction

The Skaergaard Intrusion, east Greenland, is host to the Platinova Reef, a magmatic Cu–PGE–Au sulphide deposit that belongs to a relatively rare subclass of magmatic sulphide deposits. These deposits occur as stratiform layers in the upper parts of their host intrusion (e.g. Maier, 2005) and are referred to as "offset reefs" (Godel, 2015).

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Other examples include the Ferguson Reef of the Munni Munni Complex (Barnes, 1993; Barnes and Hoatson, 1994; Barnes et al., 1992), the Main Sulphide Zone of the Great Dyke of Zimbabwe (Wilson and Tredoux, 1990), and the PGE-enriched layers of the Sonju Lake intrusion (Li et al., 2008), the Rincon del Tigre complex (Prendergast, 2000) and the Stella Intrusion, South Africa (Maier et al., 2003). These all display the essential characteristics of metal offsets within the mineralised interval, such as a distinct zonation with a Pt + Pd-rich peak(s) at the base, followed by a Au peak above this, and finally a Cu peak above that. The Cu peak corresponds to an abrupt increase in bulk sulphide content (Andersen et al., 1998; Holwell and Keays, 2014; Holwell et al., 2015; Nielsen et al., 2005; Prendergast, 2000). This sequence typically occupies a stratigraphic thickness ranging from a few metres to tens of metres. The sequence of metal concentration peaks is generally attributed to the relative order of magnitude of sulphide liquid/silicate liquid partition coefficients for the elements in question, i.e. $D_{Pd} = {\sim}D_{Pt} \gg D_{Au} > D_{Cu}$.

Characteristically, the mineralisation of the Platinova Reef consists largely of Pd(+Pt) and Au alloys intimately associated with sulphide globules composed of bornite and digenite/chalcocite with no significant Ni or Fe sulphides (e.g. Andersen et al., 1998; Holwell et al., 2015; Nielsen et al., 2005, 2015). This mineralisation is largely thought to have formed from the accumulation of very small droplets of Cu-rich magmatic sulphide liquids. These contain the highest recorded tenors of Pd (~10,000 ppm), Au (~15,000 ppm) and Se (<1200 ppm), and the lowest S/Se ratios (190–800) of any known magmatic sulphides (Holwell and Keays, 2014; Holwell et al., 2015). This factor alone makes the Platinova Reef an extremely important example, and possible end-member, of a magmatic system wherein certain processes have led to the formation of ultra-high tenor sulphides. In addition to the extreme tenors, the textures of the sulphides offer the opportunity to investigate extreme processes of metal enrichment in magmatic sulphides. Further to this, the extremely small size of the sulphides and their apparent trapping *in situ* present an opportunity not only to study sulphide microdroplets close to the point of nucleation; but also to investigate a problem when attempting to apply conventional mechanisms of metal concentration by sulphide–silicate interaction (the R factor; e.g. Campbell and Naldrett, 1979). The extreme tenors require mechanisms whereby tiny droplets can effectively extract Pd and Au from magma volumes of the order of hundreds of thousands to millions of times their own volume to satisfy simple mass balance criteria, regardless of the precise mechanism.

Whilst the relationship of offset reefs to the onset of sulphide saturation in their host magmas may be clear, the processes responsible for some of the particularities of these reefs, including the metal offsets, the mineralogy, and the sulphide metal tenors are less clear and currently subject to a range of interpretations. Essentially, most of these processes are orthomagmatic, although the importance of late- and post magmatic fluids on the mobility and distribution of precious metals, and the possibility of S-loss through syn-magmatic dissolution or post-magmatic alteration remain subject to debate (Andersen et al., 1998; Bird et al., 1991; Godel et al., 2014; Holwell and Keays, 2014; Keays and Tegner, 2015; Maier et al., 2003; Nielsen et al., 2005, 2015; Prendergast, 2000; Rudashevsky et al., 2014, 2015; Wohlgemuth-Ueberwasser et al., 2013).

Whilst there have been a number of recent studies on the textures of the silicate and oxide phases in the Skaergaard Intrusion (e.g. Godel et al., 2014; Holness et al., 2007, 2011; Namur et al., 2014), this paper specifically focusses on the textures of the sulphides, precious metal minerals, and their relationship to each other and to the host gabbro cumulate minerals within the Platinova Reef. This study builds on previous work by Godel et al. (2014) in having a larger number of samples, from a drill hole located closer to the side-wall of the intrusion and putting a greater emphasis on the gold-rich layer. We use an integrated approach of high-resolution X-ray computed tomography (HRXCT), SEM, synchrotron and desktop microbeam XRF mapping and thin section petrography to comprehensively classify the textural relations of the precious metal-bearing sulphides of the Platinova Reef. In particular, we focus on the three dimensional textures of the sulphides, precious metal minerals, and their relationship to each other. The combination of these techniques allows us to draw meaningful conclusions about the spatial distribution and relative compositional variation of composite precious metal–sulphide aggregates within an offset reef deposit.

2. Mechanisms of extreme precious metal enrichment in magmatic sulphide liquids

The processes involved in generating PGE-rich magmatic sulphide deposits are well established and summarised by Naldrett (2011) and references therein. Once a mafic/ultramafic magma has become saturated in sulphide, the enrichment of the sulphide in chalcophile elements such as PGE is determined by: (1) the initial concentration of the metals in the magma, which is in part a function of the degree of partial melting at the mantle source; (2) the ability of the sulphide to interact with, and thus sequester chalcophile elements from large volumes of mafic magma; and (3) the relative partitioning of each element into sulphide liquid ($D_{sul/sil}$), which varies from several hundreds for Ni and Cu, through to tens or hundreds of thousands for some of the PGE (Mungall and Brenan, 2014). All these factors can all be related through the equation of Campbell and Naldrett (1979).

$$Y_i = [D_i * Y_{oi} * (R+1)]/(R + D_i) \quad (1)$$

where Y_i is the concentration of metal in the sulphide, D_i is the distribution coefficient between sulphide liquid and silicate magma of the metal, Y_{oi} is the original concentration of the metal in the magma, and R is the ratio between silicate magma and sulphide liquid. Attainment of high metal tenors requires equilibration of the sulphide with large amounts of silicate magma, i.e. high values of R. Mungall (2002) showed that this equilibration is limited by relative rates of magmatic diffusion of the various chemical components of the sulphide melt, including S, and that very high tenor and very high effective R factors are the expected result when very small, approaching infinitesimal, amounts of sulphide first nucleate from a magma.

The Pd and Au tenors of the Platinova Reef are very high, in the region of 10^4 ppm (Holwell and Keays, 2014) (the average Pd tenor of the main Pd peak in the drill hole (PRL-08-35A) from which samples were taken for this study, is 7780 ppm). Assuming that the Pd content of the magma at the time of formation of the Platinova Reef was 43 ppb, as estimated by Keays and Tegner (2015), and that the D_{Pd} is 540,000 (Mungall and Brenan, 2014), Eq. (1) can be used to derive an R-factor value of 2.7×10^5. A single stage batch equilibration model would require a highly unusual mechanism to attain such a very high R-factor.

Several processes can explain very high precious metal tenors in sulphides in addition to the simple batch equilibrium model to which the R factor model applies. Syn-magmatic processes include pre-formation of platinum-group minerals (PGM) prior to collection by sulphide liquids or chromite crystals (Ballhaus and Sylvester, 2000; Helmy et al., 2013; Ohnenstetter et al., 1999; Tredoux et al., 1995). Direct precipitation of PGM from a silicate melt caused by the saturation in certain phases has also been proposed as a possible mechanism for producing PGE-enriched layers with little to no associated sulphide (e.g. Barnes et al., 2016; Maier et al., 2015). Another syn-magmatic process was proposed by Mungall (2002), who showed that the concentration of any element in sulphide liquid is a function not only of how chalcophile that element is (the equilibrium metal partitioning coefficient, $D_{sul/sil}$) but also the relative diffusivities of the most chalcophile elements. He showed that the interplay of fractional sulphide segregation with diffusion-controlled disequilibrium can produce a remarkably faithful duplication of offset metal profiles, using the example of the PGE-enriched offset sulphide reef in the Munni