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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).

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

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

Munni intrusion. At the point of nucleation, sulphide droplets can attain exceedingly high metal tenors however, under conditions where R ≫ D, the maximum metal tenor of any increment of sulphide can never exceed the limit determined by the D value. Hence, for this mechanism to apply in the Platinova Reef, effective D values must still have been extreme.

A number of syn- and post-magmatic processes may occur to modify sulphide droplets once they have formed. This includes partial dissolution upgrading, whereby sulphides partially re-dissolve back into sulphide-undersaturated magma, thus greatly increasing R factors and hence creating sulphides with very high tenors (Kerr and Leitch, 2005). Godel et al. (2014) found textural evidence in the Platinova Reef consistent with this model. Wohlgemuth-Ueberwasser et al. (2013) proposed selective postcumulus oxidation of Fe sulphides giving rise to a reduction in sulphide volume through incongruent dissolution and a consequent increase in Cu content. Finally, post-magmatic hydrothermal alteration of sulphides has the potential to remove sulphide preferentially over precious metals, which would also increase the metal tenor of the sulphides.

Nielsen et al. (2015) proposed a complex model for the Platinova Reef specifically, in which high precious metal (PM) tenors are the result of pre-concentration of PM in a segregated and internally differentiated mush layer at the base of intrusion, followed by partial redissolution in a migrating intercumulus Fe-rich immiscible melt, and upward migration of Au due to interaction with a late-exsolving free volatile phase. This model predicts that the paragenetic association of Au with sulphides in the Au-rich component of the Platinova package should be distinctly different from the equivalent Pd sulphide association.

3. The Platinova Reef

The Skaergaard Intrusion, Kangerlussuaq region, east Greenland (Fig. 1A) was emplaced at 56.02 Ma (Wotzlaw et al., 2012) during widespread Paleogene magmatic activity associated with the opening of the north Atlantic Ocean and passage of Greenland over the proto-Iceland plume (e.g. Brooks and Nielsen, 1982; Momme et al., 2002; Saunders et al., 1997; Tegner et al., 1998). One of the key characteristics of the Skaergaard Intrusion is that it crystallised under closed system conditions from a single, homogeneous body of magma and has thus become the type example for studies of magmatic layering and differentiation (e.g. Holness et al., 2007, 2011; Irvine et al., 1998; Keays and Tegner, 2015; McBirney, 1989; McKenzie, 2011; Nielsen et al., 2015; Tegner et al., 2009; Thy et al., 2009; Wager and Brown, 1968).

The Skaergaard Intrusion consists of three main units, viz.: the Layered Series, formed through crystallisation from the floor up; the Upper Border Series, a mirrored sequence of the Layered Series that crystallised from the roof down; and the Marginal Border Series that crystallised inwards from the outer walls of the intrusion. The Layered Series is split into zones according to cumulus mineralogy and consists of the Hidden, Lower, Middle and Upper Zones (Fig. 1B). The Platinova Reef is located in the uppermost part of the Middle Zone in the Triple Group: a 100 m-thick unit of modally layered plagioclase–clinopyroxene–Fe/Ti–oxide gabbros with three prominent leucocratic layers (Fig. 1C) visible in the field that give the unit its name.

Sulphide mineralisation is present as tiny sub-millimetre grains of bornite–digenite/chalcocite with associated precious metal-bearing minerals that are dominantly Pd–Pt–Au–Cu–Fe-alloys (Andersen et al., 1998; Bird et al., 1991; Cabri et al., 2005; Godel et al., 2014; Holwell

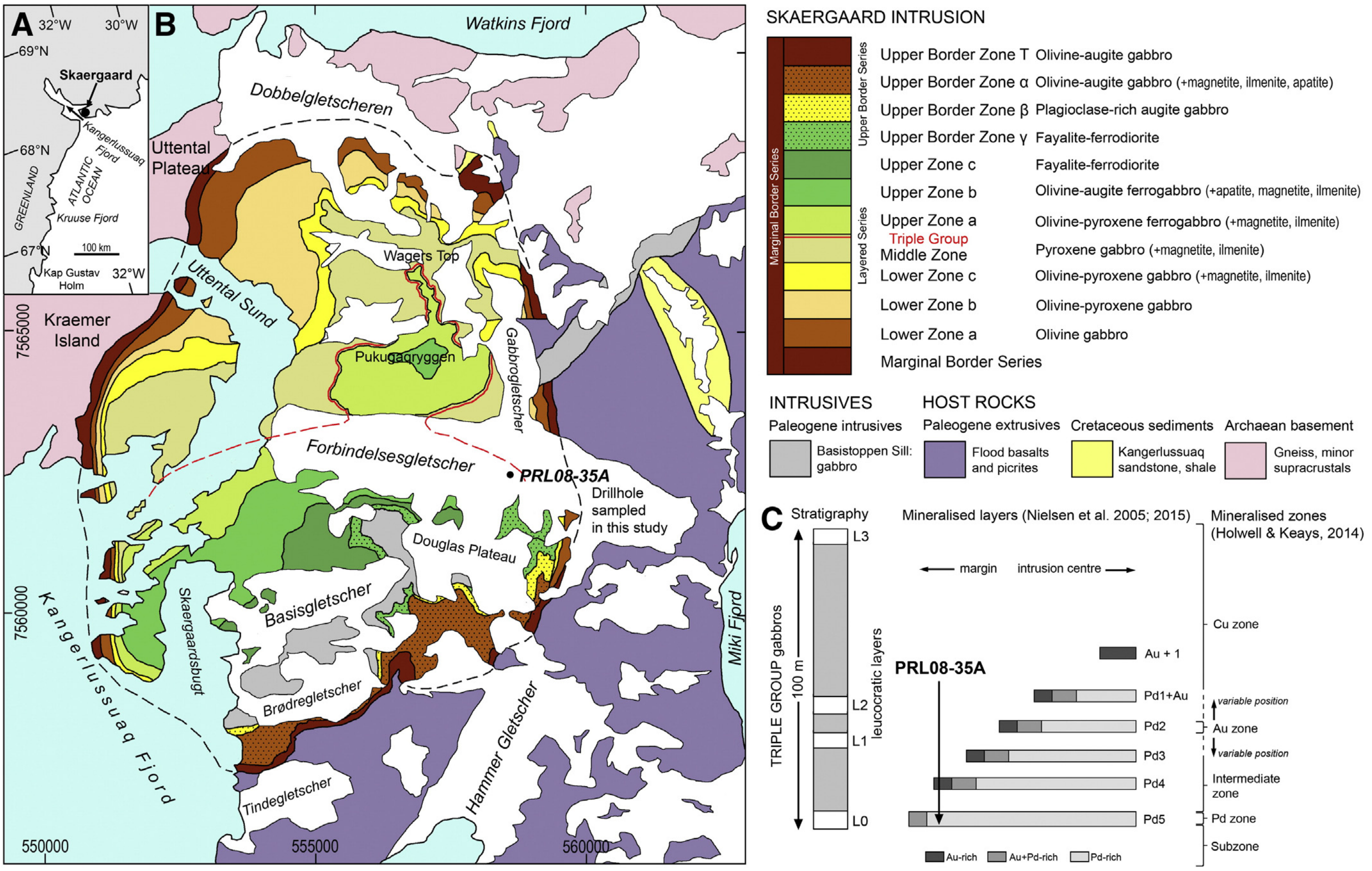

Fig. 1. A: Location of the Skaergaard Intrusion in east Greenland. B: Generalised statigraphic column of the Skaergaard Intrusion. The Platinova Reef is located within the Triple Group, which makes up the upper 100 m of the Middle Zone. C: schematic representation of the Triple Group and its mineralised layers. The relative location of PRL08-35A is shown as being close to the margins of the intrusion, thus only containing two main mineralised layers.

et al., in press; McDonald et al., 2009; Nielsen et al., 2005, 2015; Rudashevsky et al., 2004, 2014, 2015). Precious metals are enriched in a series of stratiform layers, the lowermost precious metal layer is the main Pd-bearing layer (designated Pd5 by Nielsen et al., 2015), and is present across the entire intrusion. Further layers are then present above this, which reduce their lateral extent upwards, and appear to have Au-rich edges (Fig. 1C). This means that in any one location there is a lower Pd rich zone and a Au-rich layer above it, up to 40 m above it in the central parts of the intrusion, and only a few metres above it at the margins. Previous authors have made an analogy to a stack of gold-rimmed plates; Pd rich in the centre and Au rich at the edge, becoming smaller up-section such that the Au-rich edge of the upper plate overlies the Pd-rich interior of a lower one (Andersen et al., 1998; Nielsen et al., 2015). The top of the stack of precious metal-enriched zones is marked by a sharp increase in modal Cu-rich sulphide content across the entire complex. The principal Au peak occurs at the base of this Cu-rich layer, exactly at the sharp transition to higher volumes of sulphide, where Cu contents increase from a few tens to a few hundreds of ppm (Holwell and Keays, 2014).

Here we use the simplified zonation for the mineralised zone based on the relative metal enrichments (Holwell and Keays, 2014; Fig. 1C): the Subzone is stratiform and concordant and present beneath the lowermost leucocratic layer of the Triple Group, L0, where PGE concentrations start to increase upwards; the Pd zone (Pd >1 ppm; Pd5 of Nielsen et al., 2005, 2015) is stratiform and concordant, and located within the L0 unit; the Intermediate zone which is a weakly mineralised (Pd 0.1–1 ppm) zone with multiple small Pd peaks is of variable thickness and is bounded at its base by the stratiform Pd zone; a thin Au zone (Au > 1 ppm; UAuM of Nielsen et al., 2015) which is present within a few metres of the Pd zone at the intrusion margins, and up to 40 m above it in the centre and is thought to be discordant (Nielsen et al., 2015); and the Cu zone, where the Cu contents are consistently >200 ppm and precious metals contents are <1 ppm. This constitutes all rocks in the Triple Group above the Au zone. The mineralization below the Cu zone consists of microdroplets of sulphide (typically <100 μm) with Pd and Au tenors of 10^{3-4} ppm, Pd/Au ratios >1, S/Se ratios 500–800 and low Cu/Pd ratios, whereas the sulphides in the Cu zone are larger (100–1000 μm), have considerably lower tenors (10^{1-2} ppm Pd), Pd/Au ratios of <1, S/Se ratios as low as 190 and high Cu/Pd ratios (Holwell and Keays, 2014; Holwell et al., 2015). However, the sulphide mineralogy in all zones is consistent, being composed of bornite–digenite/chalcocite exsolution intergrowths (Nielsen et al., 2015).

Previous studies have attributed some of the characteristic features of the mineralisation to (1) fractionation of sulphide liquids (Andersen et al., 1998); (2) the presence of immiscible Au-rich melts and sulphide liquids (Bird et al., 1991); (3) filter pressing of sulphide liquid (Andersen et al., 1998); (4) Rayleigh fractionation processes (Prendergast, 2000); (5) oxidation of sulphides (Wohlgemuth-Ueberwasser et al., 2013); (6) late stage redistribution of metals by a volatile phase with deposition at redox boundaries (Andersen, 2006; Nielsen et al., 2015; Rudashevsky et al., 2015); (7) major post-magmatic S loss by fluids (Andersen, 2006); (8) syn-magmatic dissolution of sulphide droplets (Godel et al., 2014; Holwell and Keays, 2014; Nielsen, 2013; Nielsen et al., 2015); and (9) redox fluctuations linked to magnetite formation converting sulphate to sulphide (Keays and Tegner, 2015).

4. Sampling and methods

Fourteen samples were taken from the diamond drillhole PRL08-35A, drilled by Platina Resources Limited in 2008 (Fig. 1A). The core intersects the Subzone, Pd zone, Intermediate zone, Au zone and lower parts of the Cu zone without interruption from dykes or offsets due to faults (Fig. 1C). Samples were selected to cover a range of mineralised zones including two from the subzone (at 335 and 332 m), four from the Pd zone (328, 327, 326, and 325 m), one from the thin Intermediate zone (322 m), five from the Au zone (at 20 cm intervals from 319.0 m) and two from the Cu zone (306 and 297 m). Bulk rock geochemistry on 20 cm intervals through the entire section was provided by Platina Resources, and was generated at Genalysis Laboratory Services, Western Australia using Pb collection fire assay followed by inductively coupled plasma-mass spectrometry for the precious metals and X-ray fluorescence on fusion discs for Fe_2O_3, TiO_2 and V.

Sulphide and precious metal mineralogy and their textures were observed and documented in reflected light and by scanning electron microscope (SEM) at the University of Leicester using a Hitachi S-3600N SEM, coupled with an Oxford Instruments INCA 350 energy dispersive X-ray analysis system.

High resolution X-ray computed tomography (HRXCT) 3D analysis was performed on three representative samples: 327 (Pd zone), 319.2 (Au zone) and 306 (Cu zone) to observe the textural relationships and the distribution of sulphides and precious metal minerals within the samples. The samples were 3 mm cores, of 30 mm length. They were analysed using the XRADIA XRM high-resolution 3D X-Ray microscope system at the Australian Resources Research Centre (ARRC, Perth, Australia). The analytical technique and data processing protocol is described in detail in Godel (2013). The parameters used for the analysis were a voltage of 110 kV, a power of 10 W and a pixel size between 1.523 and 1.533 μm. A total of 2000 2D projections were collected per 360° rotation of the sample, which were used to reconstruct the 3D volumes using the AvizoFire® (Visualization Sciences Group) software coupled with dedicated CSIRO-developed workflows and software designed for ore materials.

X-ray fluorescence (XRF) microscopy was performed on the XFM beamline at the Australian Synchrotron (Paterson et al., 2011) using the Kirkpatrick Baez mirror microprobe end-station. Further details of the analytical procedure can be found in the Supplementary Material.

Thin-section scale mapping was carried out on conventional polished thin sections using a Bruker M4 Tornado™ desktop scanning X-ray fluorescence spectrometer (μ-XRF), with a 40 μm polychromatic beam generated from a Rh tube operating at 50 kV and 500 nA, and signal collection using an Xflash™ silicon drift detector. The maps were scanned at 40 μm resolution using a dwell time of 10 ms/pixel, and processed initially using Bruker's proprietary Esprit™ software. Phase maps were generated using a clustering algorithm within the CSIRO proprietary Chimage™ software (Wilson and MacRae, 2005).

5. Petrology of the mineralised zones

The Triple Group is made up of modally layered Ti-rich gabbros containing lath-like plagioclases, with clinopyroxene, orthopyroxene after inverted pigeonite, ilmenite, and titanomagnetite (Andersen et al., 1998). The reactive symplectites and olivine reaction rims observed by Holness et al. (2011) that are most common in the central parts of the intrusion, interpreted by them to be evidence for immiscible Fe- and Si-rich melts, are absent in our samples from closer to the intrusion margin. Here we show further petrological information gained from desktop XRF mapping to illustrate the distribution of sulphide blebs, interstitial melt pockets and the modal petrology of the rocks.

5.1. Desktop XRF mapping of sulphide distribution

Desktop “tornado” maps were collected over eight thin sections, and converted to phase maps. The results from three selected samples, one each from the Cu, Au and Pd zones, are shown in Figs. 2 and 3. A distinct fabric caused by the alignment of plagioclase is evident in all three samples and is parallel to layering in the intrusion (Fig. 2A). Plagioclase is coarser grained than the oxide and pyroxene phases, which together form clustered interconnecting networks, which is particularly evident in the Au zone sample 319.4 (Fig. 2B). Both ilmenite and titanomagnetite are clearly cumulus phases, forming chains of equant,

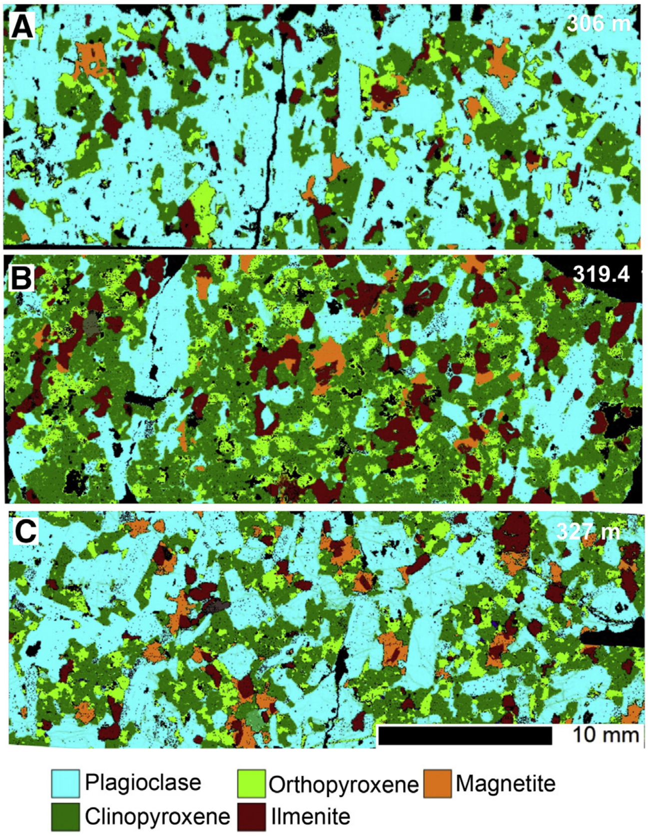

Fig. 2. Chimage tornado maps showing spatial distribution of modal mineralogy through samples from the A: Cu zone (306 m), B: Au zone (319.4 m) and C: Pd zone (327 m). Sections are orientated with their long axis perpendicular to the modal layering, so the alignment of plagioclase is seen to run parallel to the model layering (N–S in the illustrated views).

anhedral grains, corresponding to the P1 paragenesis of Nielsen et al. (2015).

The distribution of sulphide minerals (a complex exsolution texture of bornite and digenite/chalcocite in all zones) in relation to the cumulus silicate-oxide framework can be ascertained from the four-element maps of Cu, K, P and Fe distribution (Fig. 3). These maps show the spatial distribution of sulphides (red), K-feldspar (green) and apatite (blue) in relation to plagioclase, pyroxenes and oxides, which have different shades of grey determined by their respective Fe contents. The proportion of sulphide aggregates that occur at different types of cumulus grain boundaries are shown in the associated pie charts in Fig. 3, which refer to all eight sections imaged. Sulphide grains appear bigger than they are in Tornado images because of the greater penetration of the Cu X-rays through the silicate matrix. The Pd and Au zone have very similar sulphide associations, with around 75% of the sulphides occurring at the boundaries of pyroxene grains (either with other pyroxenes, or with plagioclase), and a quarter associated with oxides. The slightly higher proportion of plagioclase-associated sulphides in the Pd zone compared with the Cu zone (Fig. 3D, F) is reflective of the higher modal proportion of plagioclase (Fig. 3C, D, E), with the Pd zone located in the L0 layer, which has 50% modal plagioclase (Andersen et al., 1998), and the Au zone in our samples located within a more melanocratic unit. This 2D spatial analysis indicates that the great majority of sulphide blebs are located at or within a few microns of grain boundaries of cumulus silicates and oxides, and in most cases are randomly located along different boundary types in rough proportion to the modal abundance of the phases.

The Cu zone samples (one of which was taken from the plagioclase-rich L1 layer at 306 m) show a somewhat greater proportion of sulphides present at oxide grain boundaries, with 49% of sulphide aggregates attached to Fe–Ti oxides in the two samples studied (from 306 to 297 m). Even taking into account the modal mineralogy, there is a slightly higher preference for sulphides to be associated with oxide grain boundaries in this zone than there is in the Au and Pd zones.

The distributions of K and P are significant in recording the final disposition of trapped intercumulus components. It might be expected that K-feldspar (imaged by the K abundance in Fig. 3) and apatite (imaged by P) would show a strong spatial association, as both are postcumulus phases that would be expected to have crystallised from the last segregated dregs of the intercumulus liquid. However, this is not observed; except for one small pocket in section 306 (Fig. 3A) these components are randomly distributed, with K-feldspar showing a strong preference for plagioclase grain margins (presumably reflecting reaction of plagioclase with trapped liquid), including around the edges of poly-grain aggregates, which gives the false appearance in Fig. 3 of there being inclusions of K-feldspar in plagioclase.

5.2. Sulphide–silicate inclusions in oxides

An interesting feature observed in several of our samples, from all zones, is the presence of rounded sulphide–silicate inclusions within ilmenite (Fig. 4). This apparently shows the entrapment of droplets of silicate magma with sulphide droplets. The sulphides and their associated PMM are identical to those found elsewhere (Fig. 4). The silicates are largely hydrous assemblages of biotite, quartz and amphibole, similar to the population of entirely hydrous silicates identified by Godel et al. (2014). Fig. 4C shows a trail of very small silicate inclusions identical to some of those imaged in 3D by Godel et al. (2014).

6. Bulk rock geochemical profiles

Fig. 5 and Table 1 show the detailed metal profiles through drill hole PRL08-35A, including the well-established Pd, Au and Cu patterns defining the various mineralisation zones (Fig. 5A), and thin section photographs to illustrate the modal mineralogy. Previous studies have used samples on a 1 m spacing (e.g. Holwell and Keays, 2014) or 25 cm spacing (Nielsen et al., 2015). We show, for the first time, a profile through the Platinova Reef using continuous 20 cm samples to show the geochemical profiles on a resolution not previously possible. This shows that the Au zone is entirely contained within a single metre intersection, with a very sharp peak on this scale, showing the highest grade to be within a few tens of centimetres.

A number of studies invoke magnetite crystallisation as an important trigger for sulphide saturation in offset deposits (e.g. Andersen, 2006; Keays and Tegner, 2015; Maier et al., 2003; Prendergast, 2000). Holwell and Keays (2014) also suggest this as a possible mechanism in Skaergaard, by demonstrating a general, but loose, correlation between Pd and V as proxies for sulphide and magnetite, respectively, on a 1 m sample scale. Using the higher resolution dataset here, it can be seen that there is a distinct peak in V and TiO_2 at the base of the Pd zone (Fig. 5B). The increase in Pd at the base of the Pd zone matches very closely the point where there is a particularly oxide-rich layer (~9 wt.% TiO_2 and >1000 ppm V), illustrated by the differences in thin sections from 328 m and 325 m (Fig. 5C). Note how the proportion of plagioclase is similar in these two samples, with the major difference being the pyroxene:oxide ratio, with the sample from 325 m containing only a few modal percent oxide corresponding to the TiO_2 and V minima in Fig. 5B. The relationship of a consistent, thin (<1 m) peak in TiO_2 and V located immediately below the main Pd peak has been tested in other drill holes and proven to be a consistent feature of the Platinova Reef (Prasser et al., 2015).

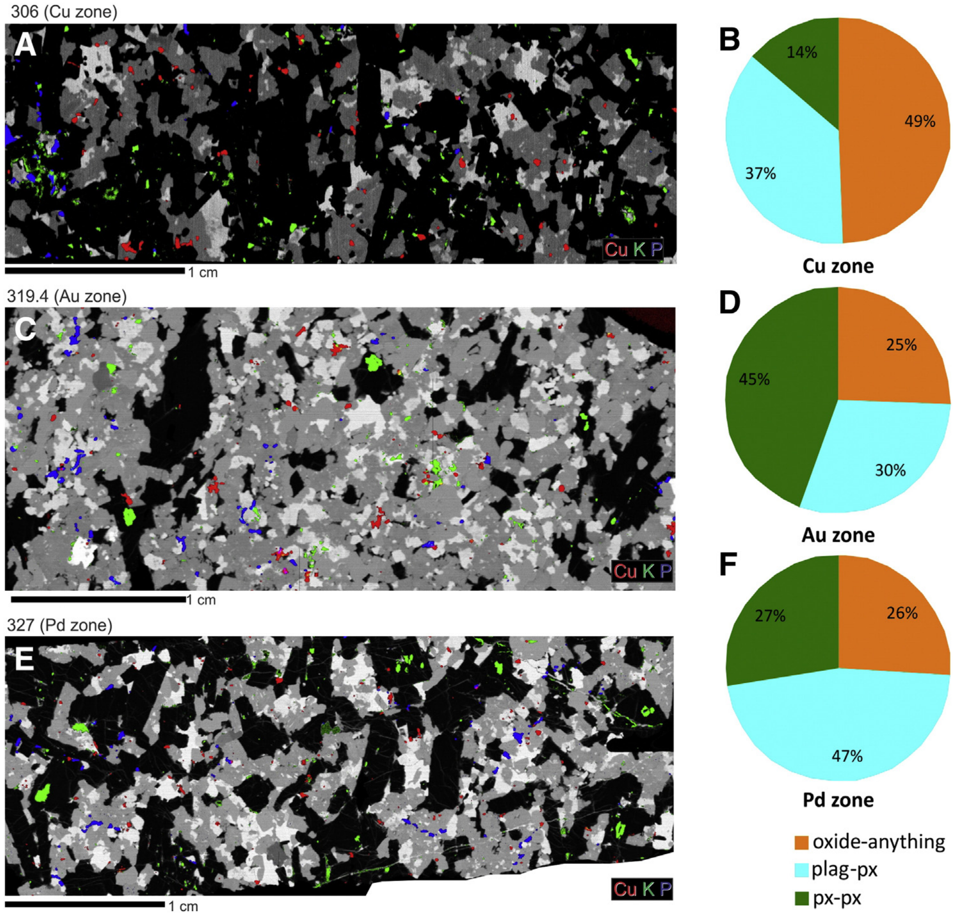

Fig. 3. Tornado XRF element maps showing the spatial distribution of sulphides (red), K-feldspar (green) and apatite (blue) in relation to plagioclase (black), pyroxenes (mid grey) and oxides (pale grey) represented by different Fe contents shown in shades of grey, for samples from the A: Cu zone (306 m), C: Au zone (319.4 m) and E: Pd zone (327 m). Note that the sulphide aggregates appear much larger than they actually are in this representation. Textural associations are summarised in the pie charts (B, D, F), which show the relative proportions of sulphide grain aggregates/blebs (by number of grains) in relation to silicate/oxide grain boundary type, e.g. 49% of sulphides in the Cu zone are located at grain boundaries between oxide minerals and any other phase. Pie charts refer to all samples analysed from the specified zone. Abbreviations: px: pyroxene; plag: plagioclase.

7. Precious metal mineralogy

The mineralogy of the PGE and Au minerals of the Platinova Reef has been described in detail elsewhere (e.g. Cabri et al., 2005; Nielsen et al., 2005, 2015 and references therein) and so here we only report the minerals identified in the samples we have studied that are thus directly relevant to our textural observations on the same samples. Table 2 lists 100 precious metal minerals (PMMs) identified within our samples from the various zones within the Platinova Reef, and Fig. 6A shows the varying proportions of different PMM type in each of the samples.

Our samples are taken from close to the margin of the intrusion, where the PMM mineralogy is known to include a wider range of minerals than the more Pd–Au–Cu alloy dominant central portion (Nielsen et al., 2015). In our samples, the subzone contains a varied assemblage of zvyagintsevite (Pd_3Pb), Pd tellurides, arsenides and the sulphide vysotskite (PdS). The apparently high proportion of PGE sulphides (Fig. 6A) is due to a single large grain skewing the percentage by area. The Pd zone is dominated by the Pd–Cu alloy Skaergaardite (PdCu); with some zvyagintsevite, sulphides including vysotskite and braggite ((Pt,Pd)S), and atokite (Pd_3Sn). Fig. 6B shows an example of an altered sulphide bleb, with secondary silicates cutting across both sulphide and zvyagintsevite, with the latter apparently present prior to alteration. The Au zone is dominated by Au–(Pd)Cu alloys and electrum, with some Pd arsenides such as vincentite (Pd_3As). The majority of the Au–Cu alloys in our samples are Au_3Cu, rather than tetra-auricupride (AuCu), which is reported to be the most common Au mineral in other studies (e.g. Nielsen et al., 2005). However, Nielsen et al. (2015) also note the Au_3Cu increases in abundance close to the intrusion margins. Texturally, the Au_3Cu is located within the margins of the sulphide blebs in the same way most other PMM are (Fig. 6C). The base of the Cu zone includes some PMM, including electrum, tetra-auricupride and some Pd arsenides such as palarstanide ($Pd_5(As,Sn)_2$).

8. Textural associations of the sulphides and precious metal minerals

The 2D and 3D textural relationships of the sulphides have been analysed by synchrotron XFM and high resolution X-ray CT techniques, respectively.

8.1. Synchrotron data

Synchrotron XFM mapping located 195 individual precious metal grains associated with about 67 Cu–Fe sulphide blebs (or their alteration products) in seven 100 μm-thick polished sections: three from the Pd zone and four from the Au zone. The high energy of the X-ray beam used in this technique results in complete penetration of the 100 μm thick section, such that the maps record the position of PM and Cu-rich grains anywhere within the section, in contrast to SEM and optical images that only show grains on the surface. Examples of the squared centimetre and squared millimetre scale detailed maps of one sample each from the Pd and Au zone are given in Figs. 7 and 8, respectively. The results are tabulated in Table 3, showing details of the textural association, location in relation to cumulus mineral species

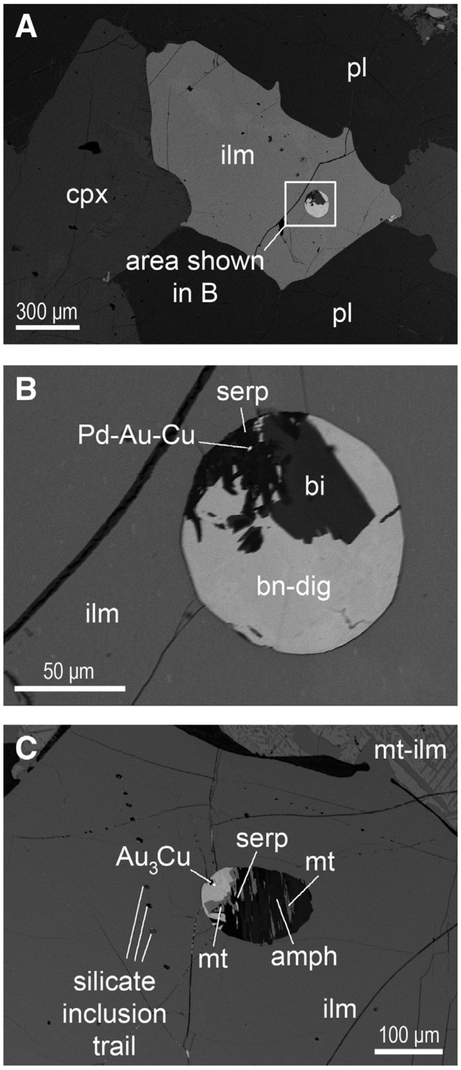

Fig. 4. Backscattered SEM images of sulphide–silicate inclusions hosted by Fe–Ti oxides in A: example of a rounded sulphide inclusion with hydrous silicates in ilmenite from the Pd zone (327 m); B: close up view of the inclusion in A, showing a Pd–Au–Cu alloy associated with hydrous silicates and bornite–digenite; C: example of a rounded sulphide-bearing hydrous silicate inclusion in ilmenite from the Au zone (319.8 m), with a grain of Au$_3$Cu present within the sulphide. Also present is a silicate inclusion trail like those shown by Godel et al. (2014). some of these contain some sulphide. Abbreviations: ilm: ilmenite; cpx: clinopyroxene; pl: plagioclase; serp: serpentine; bi: biotite; bn–dg: bornite–digenite; mt: magnetite.

and degree of alteration of the associated sulphide droplet for all identified PM grains. The relative proportion of PMM, the degree of alteration of the blebs, and the textural association between PMM and the immediately associated phase in Table 3, are plotted as pie charts in Fig. 9.

The major point to emerge from the high resolution synchrotron XFM results is that the textural relationships of the sulphide blebs (Fig. 9A, B) and the relationships between PMM grains and sulphide blebs (Fig. 9C, D) are similar between the Au and Pd zones. The sulphides in both zones have similar and roughly equal proportions that are included in primary minerals, at oxide grain boundaries, and at silicate grain boundaries (Fig. 9.A, B). Almost all of the sulphide blebs that were imaged showed a close spatial association with PMM grains. Between 70% and 80% of all PMM were observed to be in direct contact with sulphide (Fig. 9C, D). In most cases PMM grains were observed to be at the margin of a sulphide bleb, or lying a few microns outside; the latter association tends to apply to the more ragged blebs (e.g. Figs. 7B and 8B), implying that some sulphide has been lost in this setting to alteration, but that the PMM remained. Typically multiple PMM grains were found within each sulphide bleb, although one or two larger ones usually dominate (e.g. Figs. 7H and 8). The synchrotron XFM maps confirm the strong association of these composite grains with the contacts between cumulus minerals, most commonly between pyroxene grains and either other pyroxene grains or oxides (e.g. Figs. 7F and 8A, F, G). Distinct "eyeballs" with a single PMM associated with a subrounded bleb were most commonly observed within Au zone samples (e.g. Fig. 8A) but are not exclusive to this zone. The lack of any systematic correlation between textural associations and hydrothermal alteration implies that alteration was a purely superimposed effect that had no significant impact on the distribution of the PMM.

8.2. High resolution 3D X-ray microtomography

High resolution X-ray microtomographic images were collected on 3 samples, one each from the Pd, Au and Cu zones, and representative images are shown in Figs. 10 and 11.

8.2.1. Sulphide–silicate–oxide relationships

Fig. 10 shows a number of slices through the 3D reconstructions of the samples from the Pd zone (Fig. 10A–C), the Au zone (Fig. 10D–F) and the Cu zone (Fig. 10G–I). Movies showing sequential time slice animations through each of the samples are included in the Supplementary Material (Figs. A1–A3). In agreement with the 2D techniques, most sulphides are located at, or near grain boundaries. Sulphide droplets in the Pd zone are the smallest (<100 μm) and are almost always associated with at least one PMM. The sulphides are variably altered as seen by a continuum from very fresh, rounded sulphides, through slightly altered sulphides (Fig. 10A) to patches of almost totally replaced sulphides, seen as small patches of fine grained sulphides overprinted by secondary silicates (Fig. 10B). Sulphide droplets within oxide grains have not undergone as much alteration, and are usually present as rounded droplets of sulphide; however we have observed a number of rounded inclusions within oxides that are made up of sulphide, PMM and silicates, and appear to represent trapped droplets of sulphide and silicate (Fig. 10C). The sequential slice movies (Supplementary material Figs. A1-A3) prove without doubt that these are rounded droplets entirely enclosed by oxide and do not represent fracture fills or fortuitously sectioned tubular embayments.

The Au zone displays almost identical textures, with sulphides present associated with pyroxenes (Fig. 10D) and oxides in general, with a continuum of textures from rounded and unaltered (Fig. 10D), to examples where the sulphide has been variably altered to secondary silicates (Fig. 10E). There is a slight increase in the size of some of the sulphide blebs compared with the Pd zone, as seen in Fig. 10E, with some blebs up to 200 μm in diameter. In addition to examples of rounded inclusions of sulphide and silicate in oxides, there are also examples of rounded silicate inclusions without any sulphide (Figs. 10F and 4C), as seen by Godel et al. (2014).

The sample from the base of the Cu zone shows a marked increase in the size of the sulphide droplets (typically >200 μm), with mostly rounded blebs present associated with pyroxenes and oxides (Fig. 10G), though many show similar alteration around their margins to those in the other zones (Fig. 10H). This alteration is less pronounced due to the original larger size of the grains, and thus the alteration around the margins is proportionately less pervasive than it is for a much smaller grain. Some small PMMs are observed (Fig. 10H). Sulphides are present within oxides as rounded droplets with silicate, as they are in the other zones. However, unlike in the other zones, sulphides display a tendency to preferentially attach themselves to the surfaces of oxides grains such as ilmenite (Figs. 10I and A3).

8.2.2. Sulphide–precious metal mineral relationships

Fig. 11 illustrates a number of typical variants of sulphides in the Cu (Fig. 11A–C), Au (Fig. 11D–F) and Pd zones (Fig. 11G–I): (1) "eyeballs",

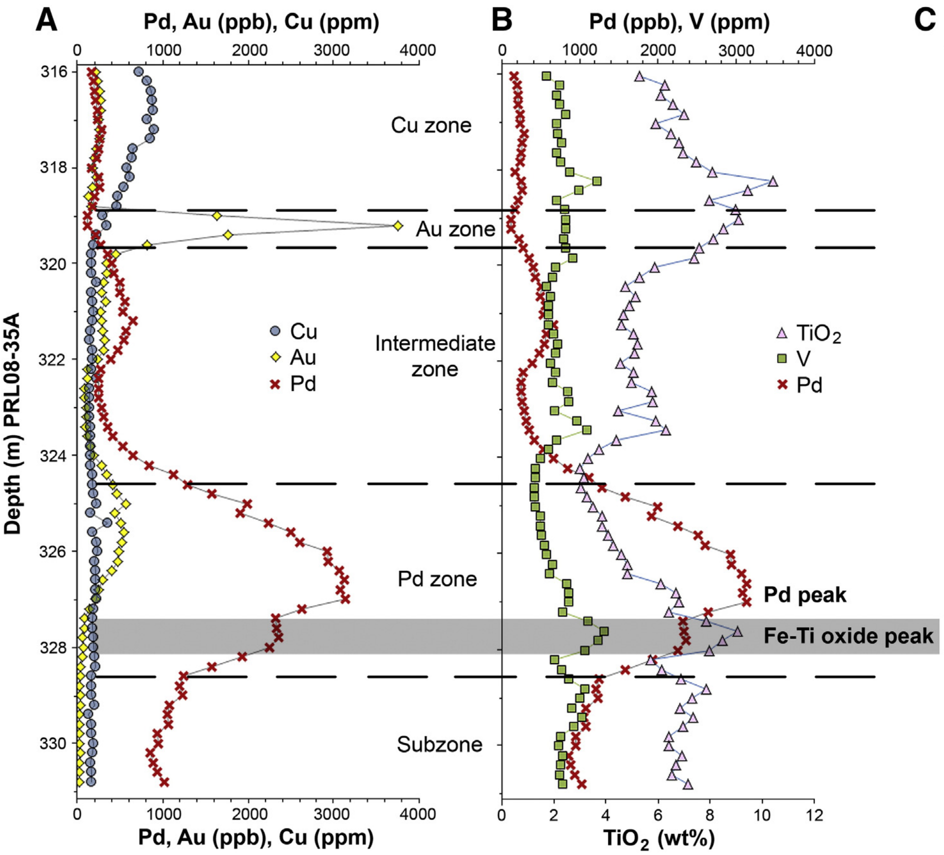

Fig. 5. Downhole bulk rock geochemistry through the Platinova Reef in drill hole PRL08-35A. A: Cu, Pd and Au; B: TiO_2, V and Pd; C: thin section scans from 319, 322, 325 and 328 m showing the difference in Fe–Ti oxide content within the gabbro. Data can be found in Table 2.

where single PMM grains lie at the edges of much larger Cu–Fe sulphide droplets (Fig. 11A, B, G), which form a continuum with; (2) smaller blebs with spherical to irregular morphologies containing a high proportion of PMM to Cu–Fe sulphide (Fig. 11D, G), or in some cases being almost entirely composed of PM with very little sulphide (Fig. 11C, I); and (3) irregular sulphide aggregates with multiple PMs of variable size (Fig. 11E, H). In some cases the irregular multi-PM blebs appear to be the result of alteration of more regular magmatic blebs, but this is not universal.

The 3D data allow firm conclusions to be drawn about textural associations without the usual stereological ambiguities and biases arising from 2D sections. The statistics are compared in Fig. 12 on observations on 137 grains from the 3D-scanned samples from all three zones. We compared the distribution of sulphide–PMM blebs after dividing them into three categories—high Cu/PMM blebs with a volume ratio of PM/sulphides between 10^{-5} and 0.01; small PMM-dominated (low Cu/PMM) blebs with a volume ratio of PM/sulphides between 0.01 and 1, and isolated PMs with little or no associated sulphides (Fig. 12) with a volume ratio of PM/sulphides between 1 and 1.10^5. All three types are equally likely to be sited at any of the various grain boundary types (allowing for the fact that some of these types, such as pyroxenes, are more common than others; Fig. 12B, D, F). The proportion of larger sulphide blebs increases from the Pd zone, through Au to the Cu zone, with a concurrent reduction in PMM with little to no sulphide (Fig. 12A, C, E), and the Au zone represents a transition between small, PMM dominant blebs in the Pd zone, and the large sulphide blebs of the Cu zone.

The size and ratios of PMM and sulphide grains are presented in Fig. 13, as equivalent sphere diameter (ESD), determined by the 3D HRXCT analysis. The size of the PMM within the sulphide droplets is generally similar in the Au and Pd zones (Fig. 13B, C), and smaller in the PMM-poor Cu zone (Fig. 13A). Fig. 13D and E shows the ratio of PMM to sulphide sizes as a ratio of their respective ESD and volumes. This clearly shows that there is a systematic progression of proportionally increasing sulphide up through the three zones. From Fig. 13B and C, there is no difference in the size of the PMM in the Pd and Au zones, thus the effect shown in Fig. 13D and E is entirely due to the increased sulphide volume in the Au zone, in comparison to the Pd zone. Fig. 13F confirms this and shows that volumetrically, there is more sulphide in the Au zone than the Pd zone.

9. Discussion

As noted in Section 1, the characteristic, sequential offsets in PGE, Au and Cu peaks are not unique to the Skaergaard Intrusion. This pattern is exactly the same as is observed in other offset PGE Reefs: e.g. Stella, Rincon del Tigre, Sonju Lake, Munni Munni, and the Great Dyke (Table 1 of Maier et al., 2003, Fig. 4 of Prendergast, 2000, Fig. 6 of Li et al., 2007; Fig. 6 of Barnes, 1993; Fig. 12 of Wilson and Tredoux, 1990, respectively). This similarity exists notwithstanding substantial difference in detail, such as the multiple sub-layers within the Platinova package (Fig. 1C), and a wide variability in thickness (a few metres at Munni Munni, several tens of metres at Rincon del Tigre), and a magnetite association in some cases (Stella and Rincon del Tigre) but not others (Munni Munni and the Great Dyke). On this basis, it is hard to believe that the Platinova system represents a fundamentally different set of processes than these other examples. Therefore, whilst we discuss our textural observations specifically for the Platinova Reef, we extend the inference that some of the fundamental physical and geochemical processes are ones that must apply to similar magmatic systems anywhere.

Table 1
Geochemical data for the main mineralised portion of PRL08-35A, as plotted in Fig. 5.

From (m)	To (m)	Zone	Au (ppm)	Pd (ppb)	Cu (ppm)	V (ppm)	Fe_2O_3 (wt.%)	TiO_2 (wt.%)
316.0	316.2	Cu	0.211	158	719	572	18.88	5.28
316.2	316.4	Cu	0.232	190	812	731	20.36	6.23
316.4	316.6	Cu	0.257	201	867	703	20.48	6.08
316.6	316.8	Cu	0.271	209	873	733	21.51	6.57
316.8	317.0	Cu	0.265	229	890	821	22.74	6.97
317.0	317.2	Cu	0.246	235	813	703	20.47	5.91
317.2	317.4	Cu	0.254	287	895	708	21.64	6.49
317.4	317.6	Cu	0.257	264	857	761	22.14	6.78
317.6	317.8	Cu	0.217	246	650	703	21.88	6.94
317.8	318.0	Cu	0.201	228	638	749	22.23	7.46
318.0	318.2	Cu	0.174	162	583	860	23.16	8.06
318.2	318.4	Cu	0.217	246	613	1213	26.84	10.41
318.4	318.6	Cu	0.173	253	540	988	24.92	9.42
318.6	318.8	Cu	0.123	201	477	703	21.9	7.95
318.8	319.0	Cu	0.160	170	462	808	23.7	8.98
319.0	319.2	Au	1.631	120	291	812	23.95	9.07
319.2	319.4	Au	3.753	115	346	821	23.93	8.48
319.4	319.6	Au	1.770	216	221	793	23.51	8.1
319.6	319.8	Au	0.819	269	192	809	23.22	7.57
319.8	320.0	Au	0.449	348	161	906	23.92	7.38
320.0	320.2	Au	0.346	399	168	691	20.98	5.87
320.2	320.4	Intermediate	0.339	421	164	652	20.46	5.27
320.4	320.6	Intermediate	0.303	498	225	570	18.91	4.73
320.6	320.8	Intermediate	0.281	492	164	625	20.55	5.14
320.8	321.0	Intermediate	0.328	555	176	596	20.03	4.87
321.0	321.2	Intermediate	0.273	532	193	598	20.09	4.65
321.2	321.4	Intermediate	0.283	655	178	595	19.95	4.59
321.4	321.6	Intermediate	0.292	568	157	665	20.86	5.05
321.6	321.8	Intermediate	0.323	544	140	711	21.31	5.19
321.8	322.0	Intermediate	0.301	474	175	686	21.18	5.1
322.0	322.2	Intermediate	0.234	393	174	616	20.03	4.55
322.2	322.4	Intermediate	0.116	271	169	686	21.42	5.03
322.4	322.6	Intermediate	0.120	246	220	652	21.47	4.95
322.6	322.8	Intermediate	0.077	244	134	841	23.03	5.74
322.8	323.0	Intermediate	0.076	252	137	851	23.49	5.79
323.0	323.2	Intermediate	0.106	278	136	668	20.16	4.47
323.2	323.4	Intermediate	0.100	306	139	952	23.89	5.89
323.4	323.6	Intermediate	0.098	352	154	1088	24.59	6.28
323.6	323.8	Intermediate	0.121	416	149	698	20.17	4.4
323.8	324.0	Intermediate	0.152	527	152	589	18.52	3.73
324.0	324.2	Intermediate	0.191	655	149	496	17.17	3.28
324.2	324.4	Intermediate	0.287	845	155	432	16.06	2.98
324.4	324.6	Pd	0.345	1118	180	426	15.71	3.13
324.6	324.8	Pd	0.414	1285	177	408	15.79	3.01
324.8	325.0	Pd	0.457	1578	182	418	16.21	3.24
325.0	325.2	Pd	0.563	1987	221	427	15.56	3.5
325.2	325.4	Pd	0.431	1909	152	493	17.39	3.84
325.4	325.6	Pd	0.510	2244	359	489	16.85	3.84
325.6	325.8	Pd	0.548	2505	177	498	17.22	4.08
325.8	326.0	Pd	0.518	2603	218	541	17.26	4.25
326.0	326.2	Pd	0.487	2921	233	568	17.03	4.56
326.2	326.4	Pd	0.466	2935	196	642	18.09	4.81
326.4	326.6	Pd	0.395	3068	216	613	16.56	4.82
326.6	326.8	Pd	0.298	3132	213	823	20.32	6.09
326.8	327.0	Pd	0.250	3084	214	857	20.83	6.68
327.0	327.2	Pd	0.216	3135	225	858	20.94	6.79
327.2	327.4	Pd	0.137	2634	188	777	18.83	6.4
327.4	327.6	Pd	0.080	2318	170	1102	22.27	7.83
327.6	327.8	Pd	0.082	2329	180	1311	26.04	9.05
327.8	328.0	Pd	0.062	2354	186	1223	24.18	8.47
328.0	328.2	Pd	0.071	2247	189	1066	23.63	7.97
328.2	328.4	Pd	0.059	1933	196	666	19.24	5.72
328.4	328.6	Pd	0.038	1580	211	758	20.28	6.13
328.6	328.8	Subzone	0.028	1244	166	854	21.8	6.87
328.8	329.0	Subzone	0.026	1198	166	1061	24.34	7.83
329.0	329.2	Subzone	0.029	1231	160	998	22.84	7.31
329.2	329.4	Subzone	0.030	1073	194	889	22.17	6.82
329.4	329.6	Subzone	0.025	1052	132	1021	23.81	7.34
329.6	329.8	Subzone	0.026	1067	160	923	22.43	6.95
329.8	330.0	Subzone	0.022	938	162	753	21.08	6.42
330.0	330.2	Subzone	0.022	948	182	719	20.79	6.4
330.2	330.4	Subzone	0.029	856	174	779	21.89	6.89
330.4	330.6	Subzone	0.022	885	154	753	21.41	6.69
330.6	330.8	Subzone	0.024	933	161	732	21.15	6.51
330.8	331.0	Subzone	0.024	1015	158	773	21.94	7.14

9.1. Textural relationships between sulphides and host phases: sulphide droplet formation

9.1.1. The precious metal enriched zones

Texturally, the sulphide blebs (with associated PMM) in the Au and Pd zones display no significant differences in terms of their association with host cumulus phases and importantly, there is no spatial association between sulphides with what are interpreted to be late intercumulus phases (Fig. 3). There is an increase in the number of larger sulphide blebs in the Au zone, compared with the Pd zone (Figs. 12 and 13), in line with Au enrichment occurring as the sulphide volume starts to increase; common to all offset reefs. The presence of a very small modal proportion of intercumulus phases (Fig. 3) is interpreted to mirror the presence of only very small volumes of trapped interstitial melt; consistent with the results from Tegner et al. (2009) who calculated the amount of trapped melt within the Triple Group to be around 2%–5%. These observations together imply that sulphides were not derived from a late-crystallising intercumulus liquid, but instead are a genuinely cumulus phase; a conclusion also favoured by Godel et al. (2014). Trapping of these very small cumulus droplets in the Pd zone almost certainly happened very close to where they initially became incorporated into the cumulus crystal mush, given that the size of the droplets is likely to preclude the possibility of any significant gravity-driven percolation through the intercumulus porosity (Chung and Mungall, 2009; Holwell and Keays, 2014; Nielsen et al., 2015).

This raises the question of how the tiny, extremely PMM enriched sulphide droplets of the Pd and Au zones became incorporated into the cumulus pile. An argument has been in progress for many years on the relative roles in cumulate formation of mechanical accumulation of crystals nucleated elsewhere, relative to *in situ* nucleation and growth of crystals in the location where they are now observed. For example, recent observations on the Bushveld Complex and Rum Intrusion (Latypov et al., 2013, 2015) provide strong support to the hypothesis that PGE Reefs, containing extremely PGE enriched sulphide droplets, can form by an *in situ* nucleation and growth mechanism. In such models, high R factors are attained as a result of the reaction between sulphide droplets that are nucleated within a static mush layer at the interface between the magma and the cumulus pile, and magma convecting over that interface. This process is referred to as *in situ* reef formation by Latypov et al. (2013), and we consider it here as a possible explanation for our observations.

9.1.2. The precious metal-poor Cu zone and the transition in sulphide volume

The larger sulphides in the Cu zone show a slight preference to be located at cumulus oxide grain boundaries (Figs. 3B, 10I, and A3). The relationship of the sulphides with oxides in this zone may reflect mild preferential wetting properties of sulphides on the oxides (e.g. Brenan and Rose, 2002). Holwell and Keays (2014) suggested that the sulphides in this zone had undergone some degree of gravitational settling from the overlying magma column, and thus the ability to grow. Again there is no spatial preference to intercumulus/late cumulus phases (Fig. 3E), and the sulphides of the Cu zone are interpreted as being a mechanically sedimented cumulus phase. The low PM content of the Cu zone reflects PM depletion in the main magma body as a result of extraction into the lower PM-rich layers of the reef, in line with the previously proposed models of PGE depletion by progressive fractional sulphide segregation in offset-type reefs (e.g. Barnes, 1993).

We suggest that the stratigraphic transition to higher volumes of sulphide records the onset of chamber-wide sulphide saturation. The very small size of the sulphide droplets below the transition reflects *in situ* nucleation in the crystal mush at the floor. These droplets are trapped, as microdroplets, *without* coalescing or growing more than a few tens of microns. Droplets in the main part of the chamber have the ability to grow from the convecting magma and accumulate at the floor. The transition to higher volume, PM-poor Cu sulphides seen in all offset reef deposits thus marks the point where the first arrival of this wave of allochthonous (i.e. nucleated elsewhere) chamber-derived sulphides hits the floor. Therefore, it reflects a transition from *in situ* nucleatation to mechanical accumulation of sulphides. This would also imply a high R factor for the larger sulphides, but the low tenor indicates precious metals had been depleted before they formed. Depletion of the magma in high D value elements like the PGE could be explained by the mechanism of convecting magma interacting with a static mush layer as mentioned above (Latypov et al., 2013).

This transition also appears to coincide with the main Au peak, which in all such deposits coincides with an increase in the volume of sulphide, before the first Cu peak. Our size data shows this transition in sulphide size accordingly (Fig. 13F), and thus Au enrichment occurs at precisely to the point where the sulphide volumes start to increase, but do so over a very thin interval. This is shown in Fig. 5, with the very thin (<1 m) Au peak coinciding precisely with the increase in sulphide as traced by Cu.

Table 2
Summary of precious metal minerals identified through the Platinova Reef in samples from drill hole PRL08-35A. Area is calculated by assuming an ellipse around the longest and perpendicular axes of each grain in section (Holwell et al., 2006).

			Cu zone		Au zone		Pd zone		Subzone		Total	Total
Mineral	Formula	Classification	*n*	Area	*n*	Area	n	Area	*n*	Area	*n*	Area
Skaergaardite	PdCu	PM–Cu alloy					23	599			23	599
Zvyaginsevite	Pd_3Pb	Pd plumbide					14	240	2	539	16	779
Unnamed	Au_3Cu	PM–Cu alloy			11	326					11	326
Vysotskite	PdS	PGE sulphide					7	112	1	91	8	203
Unconstrained	Pd–Te–As	PGE arsenide			2	45			5	630	7	675
Electrum	(Au,Ag)	Electrum	1	1	4	333			1	30	6	364
Vincentite	Pd_3As	PGE arsenide			3	195	1	156			4	351
Tetra-aurocupride	AuCu	PM–Cu alloy	4	48							4	48
Atokite	Pd_3Sn	Pd stannide					4	280			4	280
Braggite	(Pd,Pt)S	PGE sulphide					3	234			3	234
Palarstanide	$Pd_5(As,Sn)_2$	PGE arsenide	3	3							3	3
Keithconnite	Pd_3Te	Pd telluride					1	80	1	35	2	115
Kotulskite	PdTe	Pd telluride			1	9			1	0	2	9
Cabriite	Pd_2CuSn	Pd stannide	2	2							2	2
Unconstrained	Pt–Pd–As	PGE arsenide							1	0	1	0
Majakite	PdNiAs	PGE arsenide	1	2							1	2
Isomerteite	$Pd_{11}Sb_2As_2$	PGE antimo-arsenide			1	120					1	120
Unnamed	Pd–Ge–Cu	Pd germanide					1	60			1	60
Unconstrained	Pt–Pd–Fe	PGE–Fe alloy					1	6			1	6

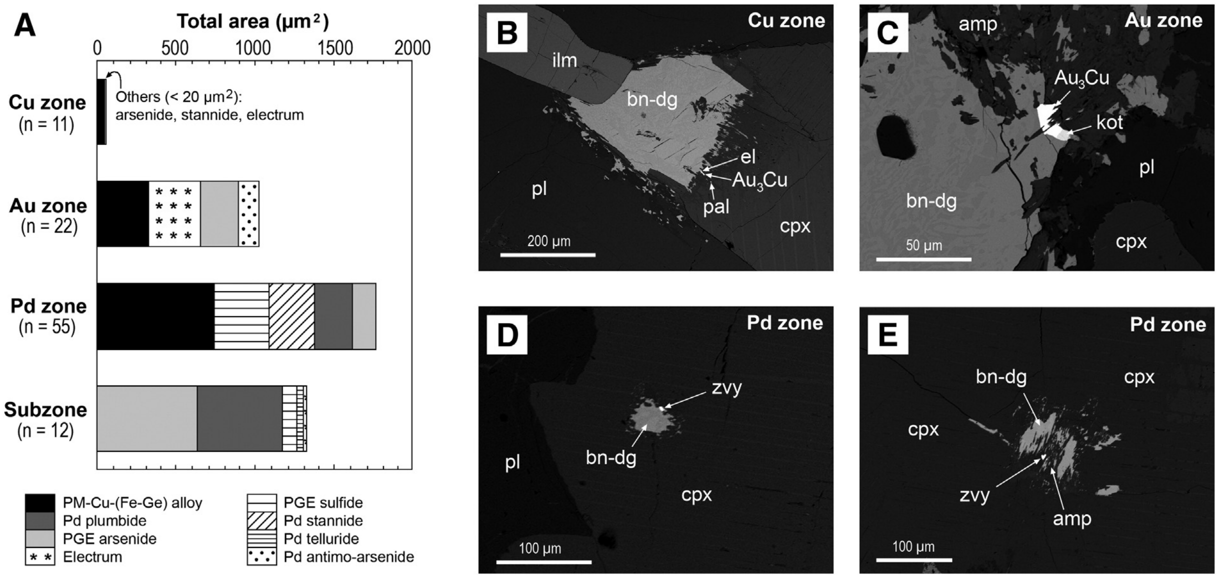

Fig. 6. A: Summary of precious metal mineral types found through the subzone, Pd, Au and Cu zones of PRL0835A. See Table 1 for the individual mineral compositions and data; B: example of a relatively large sulphide bleb, attached to an Fe–Ti oxide grain from the Cu zone. Very small PM minerals are also associated with the sulphide; C: example of Au_3Cu and Pd telluride at the margin of a sulphide grain that is partially replaced by amphibole; D and E: examples of zvagintsevite associated with sub-rounded and altered sulphide from the Pd zone. Abbreviations: cpx: clinopyroxene; pl: plagioclase; ilm: ilmenite; amp: amphibole; bn–dg: bornite–digenite; el: electrum; pal: palarstenide; kot: kotulskite; zvy: zvyagintsevite.

9.2. Textural relationships between PMM and sulphides: Precious metal enrichment

There is an extremely strong spatial association between PMM grains and Cu-rich sulphide blebs, which attests to the original collection of PGE and Au by immiscible Cu–Fe sulphide liquid throughout the Platinova Reef. Furthermore, the textural relationship of PMM (as Pd–Pt–Cu of Pd–Pb alloys in the case of the Pd zone, and Au–Cu alloys in the Au zone) with their associated sulphide droplets is essentially identical between the Pd and Au zones, implying a similar physical mode of accumulation in both zones, but with different resultant geochemical characters.

At the broadest scale, the relationship between sulphide volume and PM tenor is inverse (Fig. 13E), which would be expected if the growing droplets start at very high R factors and evolve to grow progressively and thus reduce the R factor. However, our work shows that there is a wide variability of more than two orders of magnitude in the proportions of Pd or Au minerals to Cu sulphide within individual sulphide blebs in the same few cubic milimetres, as determined by full 3D imaging (Figs. 13, A1–A3; Table A1). Such apparent variation in PMM to sulphide ratio on a droplet-by-droplet scale can be seen in Fig. 9 of Cabri et al. (2005) in 2D, though this could be a function of where each grain was sectioned. The confidence that the 3D information affords (Figs. A1–A3; and Godel et al., 2014) means that we can state unequivocally that the variability is real, and not a function of the 2D sectioning effects that can restrict traditional mineralogical deportment studies. This means that whilst the metal tenors calculated by Holwell and Keays (2014) in the range 10^3 to 10^4 ppm Pd and Au are average tenors on a metre sample scale, each individual droplet, however, may have tenors ranging from a few ppm to tens of percent. Whilst in the altered sulphides, this can easily be explained by the reduction in volume of the sulphide, this relationship holds true for the rounded, ‘eyeball’ types and rounded to irregular grains with high PMM contents (e.g. Fig. 11A, C, D, F, J).

This variability in PM tenor of the sulphide component at the individual bleb scale is not associated with particular textural microenvironments, with the exception of blebs enclosed within cumulus oxide phases in the Pd zone, which were shown by Godel et al. (2014) to have systematically lower tenors relative to those outside. These enclosed blebs were very rare in the samples studied in this investigation, and we conclude that they make up a very small contribution to the overall sulphide population. Here we assess three possible explanations for the wide variability in individual metal tenor that can potentially be tested with the data we present above, in the context of current knowledge of magmatic PM geochemistry.

1. Separate nucleation of PMM and sulphide droplets
2. Formation of extremely PM-enriched Cu sulphide with subsequent modification
3. The effect of equilibrium and kinetic partitioning around growing sulphide droplets

9.2.1. Separate nucleation of PMM and sulphide droplets

In this model, Cu-rich sulphide liquid and PMMs grew independently from a Pd–Cu (or Au–Cu, Pd–Pb, etc.) metal-saturated silicate magma and are physically associated by some process. Given the very strong spatial association between them, if separate nucleation did happen, then the two phases must have had an extremely strong affinity to each other after initial formation. The generation of PMM directly from a magma has been suggested as a possible mechanism for producing PGE-enriched horizons with little to no base metal sulphides, such as Pt phases in the Monts de Cristal intrusion, Gabon (e.g. Barnes et al., 2016; Maier et al., 2015). This model, initially proposed to explain extreme PGE enrichment in trace sulphides in the Munni Munni Complex (Barnes, 1993), may provide an explanation as to how the sulphide droplets became so highly enriched in precious metals, if the PGE and Au were effectively pre-concentrated by formation of metal alloys.

There are few experimental studies that report the solubility of Pd in silicate magma but they are known to be much higher than Pt (Mungall and Brenan, 2014). A number of recent studies have shown that direct crystallisation of PMM, particularly Pt arsenide phases, can occur prior to sulphide saturation (Brenan et al., 2015; Helmy et al., 2013, 2015). There is almost no As whatsoever in the Platinova Reef sulphides and the only semi metals present in any consistently detectable amount in the laser ablation study of Holwell et al. (2015) were Te, Bi (as minor PMM) and Se (in solid solution in sulphide). However, the PMMs are primarily alloys of Cu, or in our samples, also Pb. Therefore if separate saturation of PMM took place, it would imply that the magma became

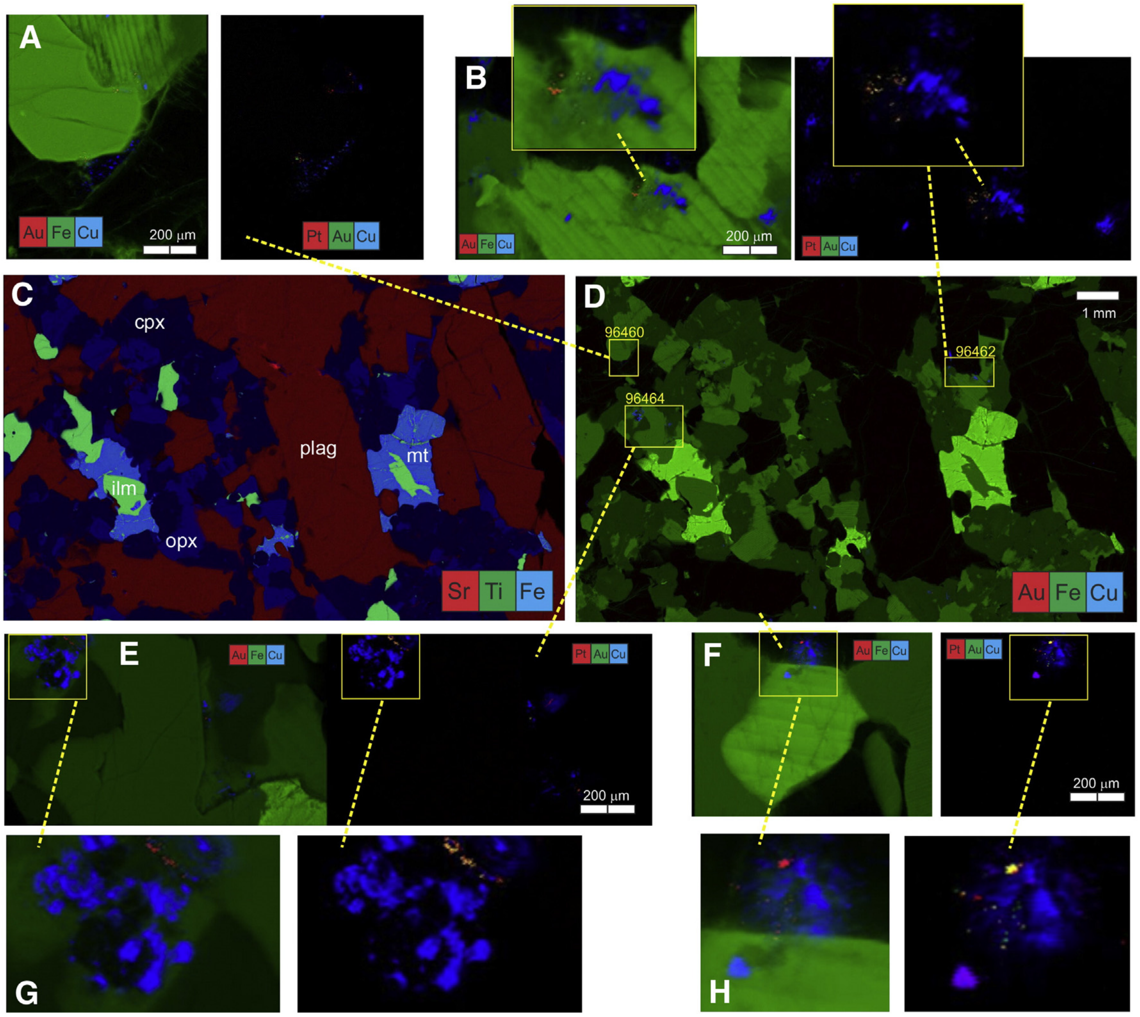

Fig. 7. Synchrotron XRF element maps from the Pd zone. C and D show an area of one of the sections mapped, with Sr (red) highlighting plagioclase, Ti (green) highlighting ilmenite, and Fe (blue) highlighting magnetite (pale blue) and pyroxenes (dark blue). A, B, E and F show magnified areas containing Cu sulphide and PMM, with G and H showing further magnified areas of E and F, respectively. Each magnified section is shown with Au–Fe–Cu (left hand side) and Pt–Au–Cu (right hand side) as the RGB colour set. Abbreviations: plag = plagioclase, ilm = ilmenite, mt = magnetite, cpx = clinopyroxene, opx = orthopyroxene.

saturated in Pd–Au–Cu and Pd–Pb alloys, that then acted as a nucleation point for the Cu sulphides, and then saturated in Au–Cu alloy at a slightly later stage.

Whilst this is an attractive mechanism for producing the extremely high metal tenors and the variable PMM–Cu sulphide ratios on a droplet scale, it would require the somewhat coincidental saturation of the magma in PGM and sulphide liquids almost instantaneously, followed by saturation in AuCu (which has a liquidus of ~920 °C; Okamoto et al., 1987), and whilst this does not preclude this mechanism, we view it as very unlikely. Furthermore, two immiscible melts in equilibrium with one another must be in equilibrium with the same solid phase. So if the silicate melt was saturated in Pd–Cu alloy, then the sulphide must have been too. The solubility of PdCu in the Cu–Fe–S melt is in the order of tens of percent (Karup-Møller et al., 2008), and so the silicate melt cannot have been saturated with PdCu at the time the low tenor sulphide droplets formed. Therefore, we suggest that the sulphide droplets in the Pd-rich zones must have nucleated as Cu–Fe–S liquid with very high Pd contents, but not Pd–metal saturated.

9.2.2. Formation of extremely PM-enriched Cu sulphide and subsequent modification

One major characteristic of the Platinova Reef sulphides is that the metal tenors are much higher than in any of the similar offset reef style deposits. One possible reason for this was proposed by Holwell and Keays (2014) and Nielsen et al. (2015) who advocate mechanisms by which the basal layer of magma from which the Platinova Reef formed was anomalously enriched in chalcophile elements. The proposed mechanisms differ somewhat, but essentially involve the addition of PM-enriched sulphides or silicate liquids derived from elsewhere in the chamber to a sulphide-undersaturated liquid layer at the floor, generating PGE enrichment in this liquid layer, which then becomes sulphide saturated to form high tenor sulphide microdroplets. Given some degree of Pd pre-enrichment, the high Pd tenors of some of the observed droplets could be explained in relation to the known extremely high partition coefficient for Pd (Mungall and Brenan, 2014). However, given the similar tenors for Au in the Au zone, this does not appear to be a possibility for Au (which has a much lower partition coefficient of ~1000); unless particular circumstances have led to anomalously high partition coefficients. With that said, the positioning of a Au-rich zone above the PGE-rich zone is a consistent general feature of offset reef deposits, and as pointed out above the relative positioning of the Pd, Au and Cu peaks in Platinova is essentially identical to that in numerous other offset reefs with widely varying host cumulus mineralogy.

Assuming the formation of PM-enriched sulphide droplets, the observed variations in PMM sulphide ratio could be formed if the droplets underwent subsequent modification. Possible mechanisms are: a) redissolution in a migrating sulphide-undersaturated or Fe-rich

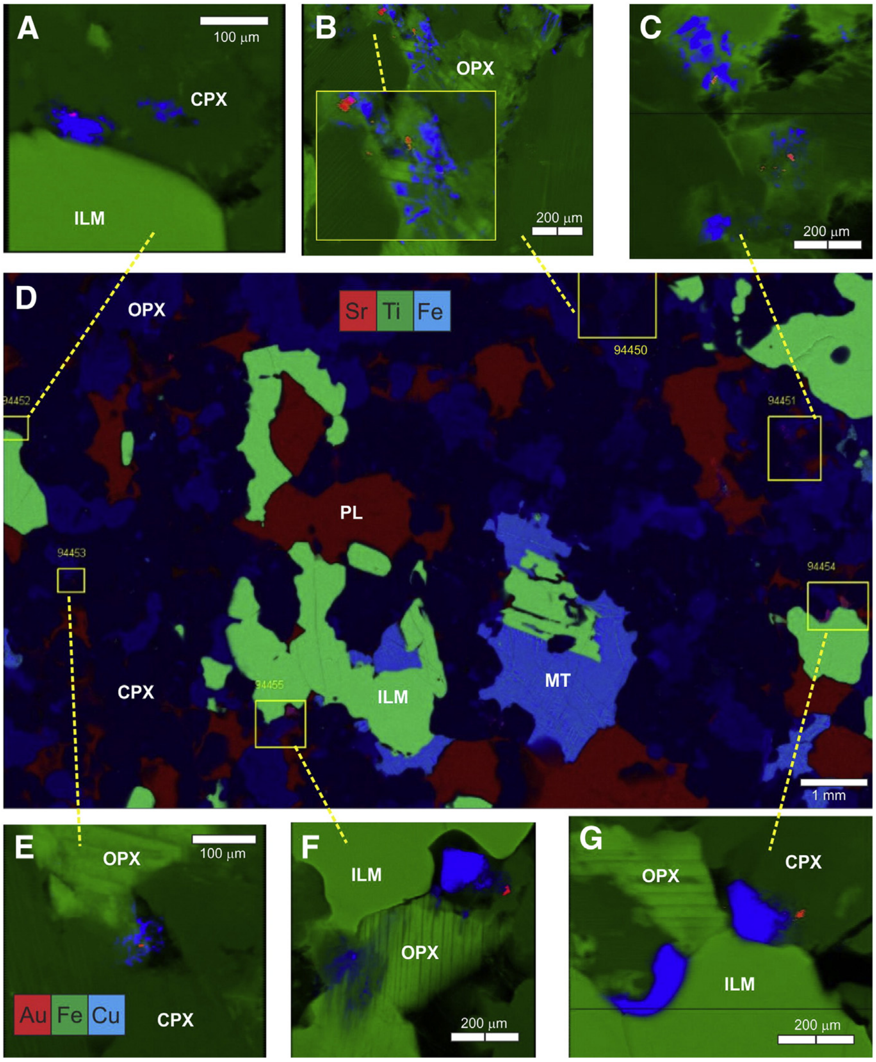

Fig. 8. Synchrotron XRF element maps from the Au zone. D shows an area of the thin section mapped with Sr (red) highlighting plagioclase, Ti (green) highlighting ilmenite, and Fe (blue) highlighting magnetite (pale blue) and pyroxenes (dark blue). A–C and E–G show magnified areas containing Cu sulphide and PMM, with the Au bearing PMM picked out in red (Au), with the Cu sulphides shown in blue (Cu).

melt (Godel et al., 2014; Nielsen et al., 2015); b) incongruent destruction by oxidation (Wohlgemuth-Ueberwasser et al., 2012) selectively removing Fe–Ni sulphide, or c) physical mechanicals driven by late stage solidification and compaction such as separation of sulphide from solid PM phases during percolation through the crystal mush, or preferential attachment to migrating vapour bubbles. Essentially all these mechanisms alter the PM tenor by removing or decoupling sulphide and PM, post-formation.

Godel et al. (2014) and Nielsen et al. (2015) interpret the higher Pd tenors in sulphides outside of oxide grains to be a result of partial dissolution of sulphides not protected by entrapment in oxide. If partial dissolution took place after the *in situ* growth and trapping of the sulphides, it would require a change from sulphide saturated to undersaturated conditions. Nielsen et al. (2015) attribute this dissolution to be caused by interaction with the immiscible Fe-rich liquids derived from the intercumulus melt within their postulated crystal mush layer. The variability we observe in silicate hosted blebs could be explained by the variable interaction with such a liquid. However our samples are close to the margin of the intrusion and do not show evidence of significant silicate liquid immiscibility in the form of the characteristic symplectites; and yet the sulphide population is no different to that recorded from the more central parts (Godel et al., 2014; Nielsen et al., 2015). Thus this mechanism does not fully explain the intrusion-wide features.

Wohlgemuth-Ueberwasser et al. (2012) showed experimentally that the Cu/Fe ratio of sulphide melt increases as a function of oxygen fugacity due to the preferential conversion of FeS into FeO and $FeO_{1.5}$, and used this as an explanation for the low-volume Cu-rich sulphides in deposits such as the Platinova Reef. However, we suggest that this is unlikely to be the case for the Platinova Reef. Firstly, the oxidation model would require the Skaergaard magma to be highly oxidised at the point of the Platinova Reef formation, which is unlikely given that magnetite had been crystallising for some time. Secondly, and most convincingly, experimental work by Ripley et al. (2002) showed that the first exsolution of sulphide liquid from strongly fractionated silicate melt involves saturation in a Cu–Fe–S liquid phase, resulting in S-poor bornite solid-solution; precisely the assemblage observed in the Platinova Reef. Thus an increase in Cu/Fe due to oxidation of sulphide, whilst possible, is considered as unnecessary.

It is possible that sulphide liquid may have mechanically separated from the PMM, for example due to necking and squeezing as the surrounding cumulates crystallised. This could produce a population with variable PM tenors (as the nuggety PMM may be preferentially retained by one portion of the split droplet). It could also explain the apparent consistency in Se tenor (Holwell et al., 2015), which contrasts to the variability in PM tenor, as Se substitutes for S in the sulphide portion and hence would not be fractionated by this process. However, if this was

Table 3
Summary of PGE mineral associations from the synchrotron XRF mapping.

		Au zone		Pd zone	
		Totals	%	Totals	%
Total grain count of sulphide blebs		37		30	
Total grain count of PMM		55		140	
Sulphide association	Inclusion in oxide	1	2.7	0	
	Inclusion in clinopyroxene	9	24.3	8	26.7
	Inclusion in plagioclase	0		3	10.0
	Grain boundary: ox–ox	1	2.7	0	
	Grain boundary: ox–cpx	5	13.5	6	20.0
	Grain boundary: ox–plag	7	18.9	2	6.7
	Grain boundary: cpx–cpx	11	29.7	5	16.7
	Grain boundary: cpx–plag	3	8.1	5	16.7
	Grain boundary: plag–plag	0		1	3.3
PMM associations	Inclusion in sulphide	4	7.3	18	12.9
	Inclusion in oxide	1	1.8	4	2.9
	Inclusion in clinopyroxene	4	7.3	8	5.8
	Inclusion in plagioclase	0		7	5.0
	Grain boundary: sulphide	44	80.0	98	70.5
	Grain boundary: ox–cpx	1	1.8	4	2.9
	Grain boundary: cpx–plag	1	1.8	0	
PMM composition	Au–Cu	30	54.5	20	14.3
	Pd–Cu	0		52	37.1
	Pd other	0		28	20.0
	Au other	25	45.5	40	28.6
Sulphide alteration	<10%	13	35.1	4	13.8
	10–50%	17	45.9	11	37.9
	>50%	7	18.9	14	48.3

Abbreviations: ox = oxide, cpx = clinopyroxene, plag = plagioclase, PMM = precious metal mineral.

the case, one might expect to observe more clustered populations of sulphide blebs, which are not particularly obvious (Figs. 2, A1–A3), although there is some evidence of squeezing along grain boundaries (Fig. 6E). Most importantly, the 3D textural relationships presented in Fig. 11 show unambiguously that the sulphide liquid is very strongly wetting with respect to the PMM grains, making it very unlikely that these phases could be physically separated during postcumulus processes.

9.2.3. The effect of equilibrium and kinetic partitioning around growing sulphide droplets

The consistent sequence of PGE, Au and Cu peaks in offset reefs has been modelled in several examples by sequential fractional segregation of sulphide, and in all these cases the sequence can be predicted in terms of the relative values of the sulphide-silicate partition coefficient—highest for Pd, which is much higher than that for Au, which is slightly higher than Cu. Holwell et al. (2015) show a detailed series of peaks at the Au–Cu zone transition in the Platinova Reef of Au > Te > Se > Cu, upwards over a thickness of a few metres, entirely consistent with relative $D_{\text{sul/sil}}$ values. Thus, relative $D_{\text{sul/sil}}$ is likely to be the key control over the sequence of metal enrichment, though this does not in itself explain the high tenors.

Mungall (2002) states that at the point of nucleation, the effective R factor is extremely high, and thus the initial formation of sulphide droplets can produce very high tenors through kinetic effects. For an extreme example like the Platinova Reef, with exceedingly small sulphide droplets, the relative offsets may well be due to differences in $D_{\text{sul/sil}}$ value, but the tenors could also be explained by kinetic effects at the point of sulphide nucleation. Each droplet will initially be surrounded by a boundary layer depleted in those highly chalcophile elements that partition into the droplet. As such the very first, tiny droplets will be gain extremely high tenors immediately. However, this also has the effect of reducing the effective partition coefficient between the droplet and the far-field magma outside the boundary layer (or to decrease the effective R factor for each element). Mungall (2002) explains that the tenor variation at different stratigraphic heights is due to the interplay between the degree of supersaturation of the sulphide, which determines how fast the droplets grow, and the diffusivity of the PM species in question. Therefore, it is entirely possible that the extreme tenors in the smallest sulphides (in the Pd zone) are caused by these kinetic

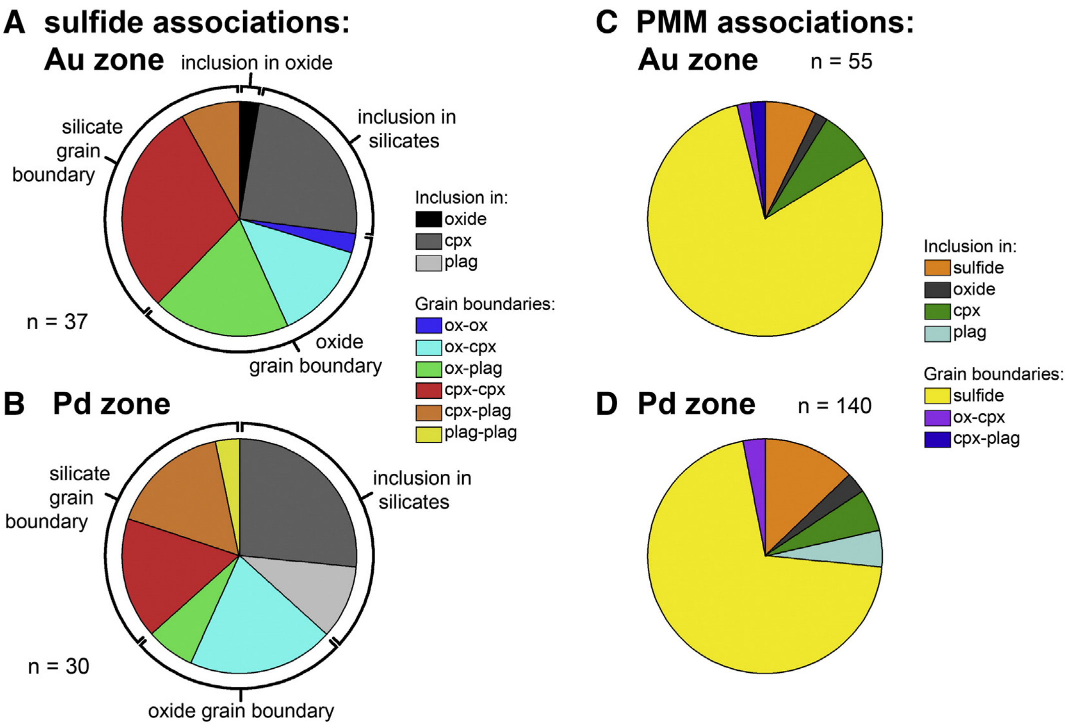

Fig. 9. Summary of association data for sulphide belbs and precious metal minerals (PMMs) from the synchrotron XRF mapping data shown in Table 3. A: sulphide associations in the Au zone; B: sulphide associations in the Pd zone; C: PMM associations in the Au zone; and D: PMM associations in the Pd zone.

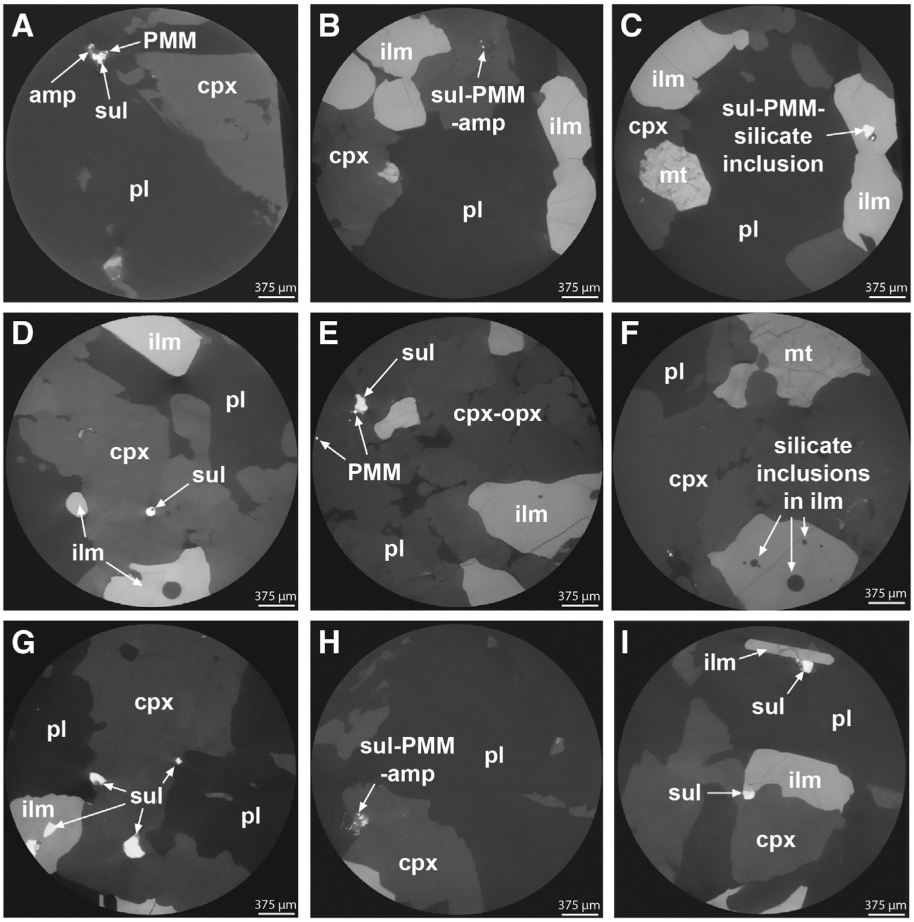

Fig. 10. Slices through HRXCT reconstruction of samples from the Pd (A–C), Au (D–F) and Cu (G–I) zones showing textural relationships of PMM, sulphides (sul), alteration amphiboles (amp) and host clinopyroxene (cpx), plagioclase (pl), orthopyroxene (opx), ilmenite (ilm) and titanomagnetite (mt). See text for description of features. Full sequential slice movies through each sample are included in the Supplementary Material.

effects primarily, and the reduction in tenor with greater sulphide droplet size (Fig. 13) can be a result of sulphide growth.

9.3. Implications for the formation of offset reef deposits

The consistent sequence of metal offsets present in all offset reef deposits is compelling. On this basis, it is hard to believe that the Platinova system represents a fundamentally different set of processes than these other examples, and observed patterns are generally consistent with $D_{\text{sul/sil}}$ values at least in terms of their relative position. Kinetic effects on top of this are also likely to play a part. Mungall (2002) obtained a highly refined fit for the Munni Munni offset profile by including terms for diffusivity as well as for partition coefficients. The order of magnitude and order of peaks was essentially the same as that obtained by Barnes (1993) and Wilson and Tredoux (1990) for the Great Dyke using variation in partition coefficients only. A number of parallels from Mungall's (2002) modelling can be made with the Platinova Reef, including the peaks in PGE being prior to the peak in Cu. Most interestingly, his modelling also shows a distinct peak in Au at the same point as where Cu increases: exactly where the main Au peak occurs in the Platinova Reef. The latter has much higher concentrations of Au, though this is likely in part to be a consequence of the more fractionated nature of the Skaergaard magma at the time of sulphide formation (also seen by the lack of any Ni or IPGE). As such, the primary control on the order of metal peaks in offset deposits appears to the relative $D_{\text{sul/sil}}$ value of the chalcophile element; although the kinetic effects also play a role, in particular in allowing the very first droplets to become very high tenor at the point of nucleation. As sulphide segregation progresses, alongside fractionation, depletion of the magma in PGE (e.g. through the mechanism proposed by Latypov et al., 2013) will compound the reduction in tenor up through the sequence.

Our textural data supports an analogous physical mechanism of sulphide formation in the irrespective of the dominant PM (Pd or Au). We therefore favour models for the formation of the Platinova Reef and other offset reefs that allow for the formation of microdroplets of Cu sulphide that become enriched in precious and semi metals according to their relative $D_{\text{sul/sil}}$ value, but that may also be affected by diffusion of those cations, which is related to the time available for equilibratation, and the degree of sulphide supersaturation. Clearly, the change to higher sulphide volumes affects the ability for Au to partition into sulphide as this is a common feature of all such deposits, but this gives an *apparent* increase in its $D_{\text{sul/sil}}$ value. There may be some change in the speciation of Au in the melt which causes a big change in its D value (and perhaps diffusivity as well), with this happening at the same time as the degree of supersaturation in Cu(Fe)S liquid is changing at the point of the chamber-wide onset of sulphide saturation. Whatever the mechanism, this transition marks a fundamental change in partitioning behaviour, but not the physical mechanism of formation.

9.3.1. Implications for the formation of the Platinova Reef

This work implies a similar physical mechanism for PM sulphide bleb formation, irrespective of the dominant PM, and confirms the conclusions of previous studies that suggest *in situ* growth and trapping of tiny PM-enriched cumulus sulphide droplets (Godel et al., 2014; Holwell and Keays, 2014; Nielsen et al., 2015). In addition to these aspects, our geochemical and mineralogical data have a number of other

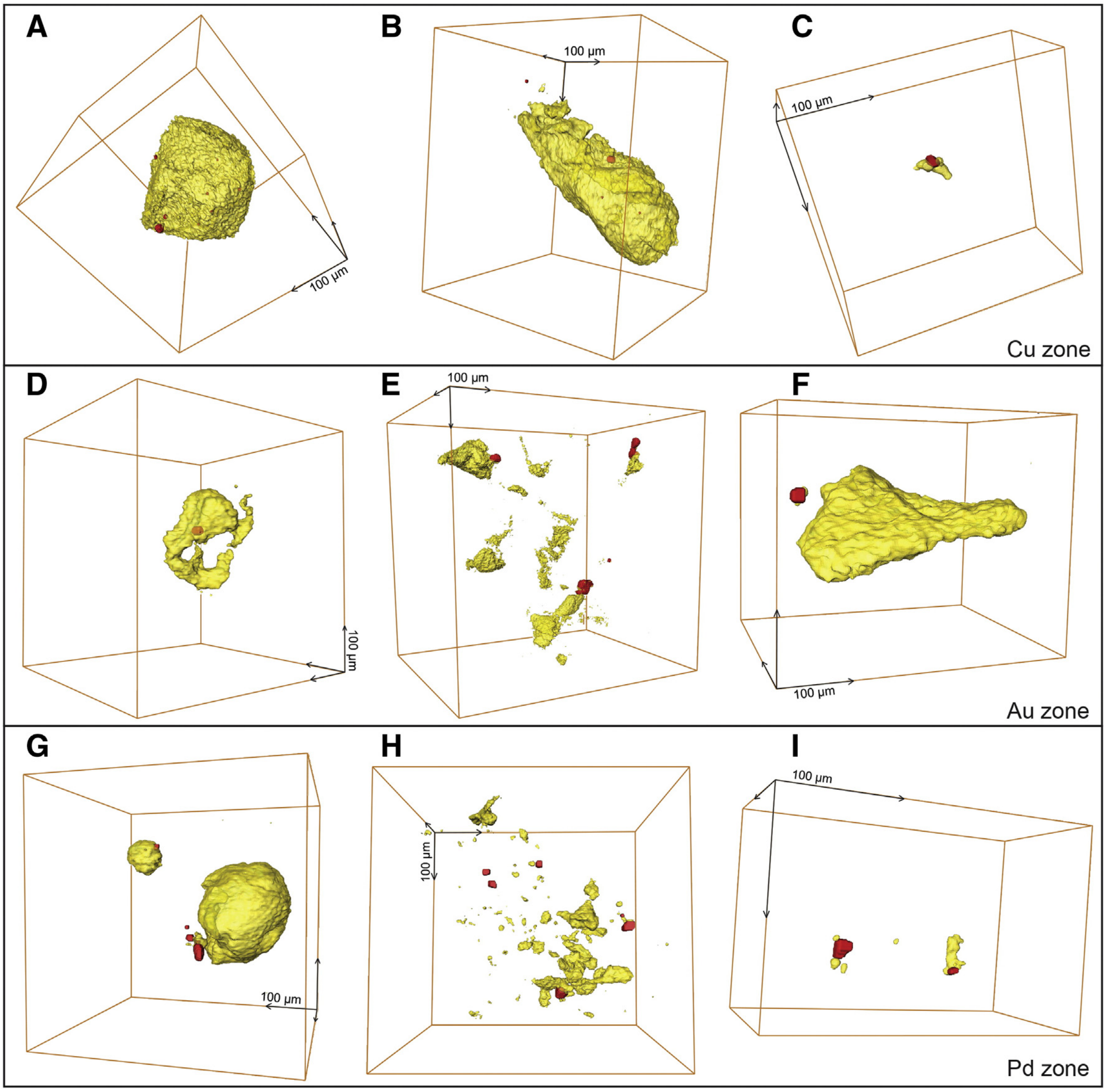

Fig. 11. 3D isosurfaces showing the relationship between PMM (red) and sulphide (yellow) blebs from A–C: the Cu zone (306 m), showing very small PMM associated with relatively large sulphides; D–F: the Au zone showing a variety of PMM to sulphide ratios, and examples of rounded droplets (D and F) and altered and ragged morphologies (E); G–I: the Pd zone showing both rounded (G) and ragged, altered (H, I) sulphide morphologies. Note that there are multiple PMMs associated with the sulphides. 3D visualisations of the images shown in B, E, and I can be found at, respectively: https://data.csiro.au/dap/SupportingAttachment?collectionId=16932&fileId=1065 https://data.csiro.au/dap/SupportingAttachment?collectionId=16932&fileId=1066 https://data.csiro.au/dap/SupportingAttachment?collectionId=16932&fileId=1067

implications that can be applied to models for the formation of the Platinova Reef, including the role of magnetite, and hydrothermal activity.

The role of magnetite crystallisation in driving the Skaergaard magma to sulphide saturation has been explored by a number of authors (Andersen, 2006; Holwell and Keays, 2014; Keays and Tegner, 2015), with analogies made to other offset layers located in the upper parts of their host intrusions, where the reefs are located where massive magnetite layers come in (Maier et al., 2003; Prendergast, 2000). Although there are no massive magnetite layers in the Triple Group, the trigger for the Platinova Reef sulphides may still have been as a response to a more subtle pulse of oxide crystallisation that pushed the magma to sulphide saturation. Keays and Tegner (2015) show that cumulus sulphides in the Skaergaard Intrusion started to form at around 300 m below the Platinova Reef, as a response to the first appearance of magnetite. These sulphides formed at the crystal–magma interface, and it was not until the level of the Triple Group that sulphide saturation took place in the whole-chamber. The fine resolution geochemical profiles shown in Fig. 5 show a significant peak in TiO_2 (a proxy for ilmenite) and V (magnetite) that corresponds closely with the point where Pd starts to increase. This is a consistent feature of the Platinova Reef sections studied by Prasser et al. (2015) and is also shown by Nielsen et al. (2015). However, in detail, Pd actually starts to increase 40 cm below the point where TiO_2 and V increase. If magnetite did trigger the sulphide formation, this would imply a small scale decoupling, and possible evidence of some minor downward percolation of sulphide droplets. Or it could simply mean that the close association is the result of some other factor that could have led to oxide and sulphide formation.

We emphasise that magnetite crystallisation is not critical to forming all offset reef-type deposits. As noted above, Munni Munni and the Great Dyke both contain offset deposits in magnetite-free cumulates that formed before onset of magnetite saturation. However the distinct correlation shown here implies that magnetite crystallisation contributed to the culmination of factors that triggered the Platinova Reef formation (e.g. Keays and Tegner, 2015).

Andersen (2006) and Nielsen et al. (2015) have, to varying extents, advocated the role of syn or post-magmatic hydrous fluids transporting

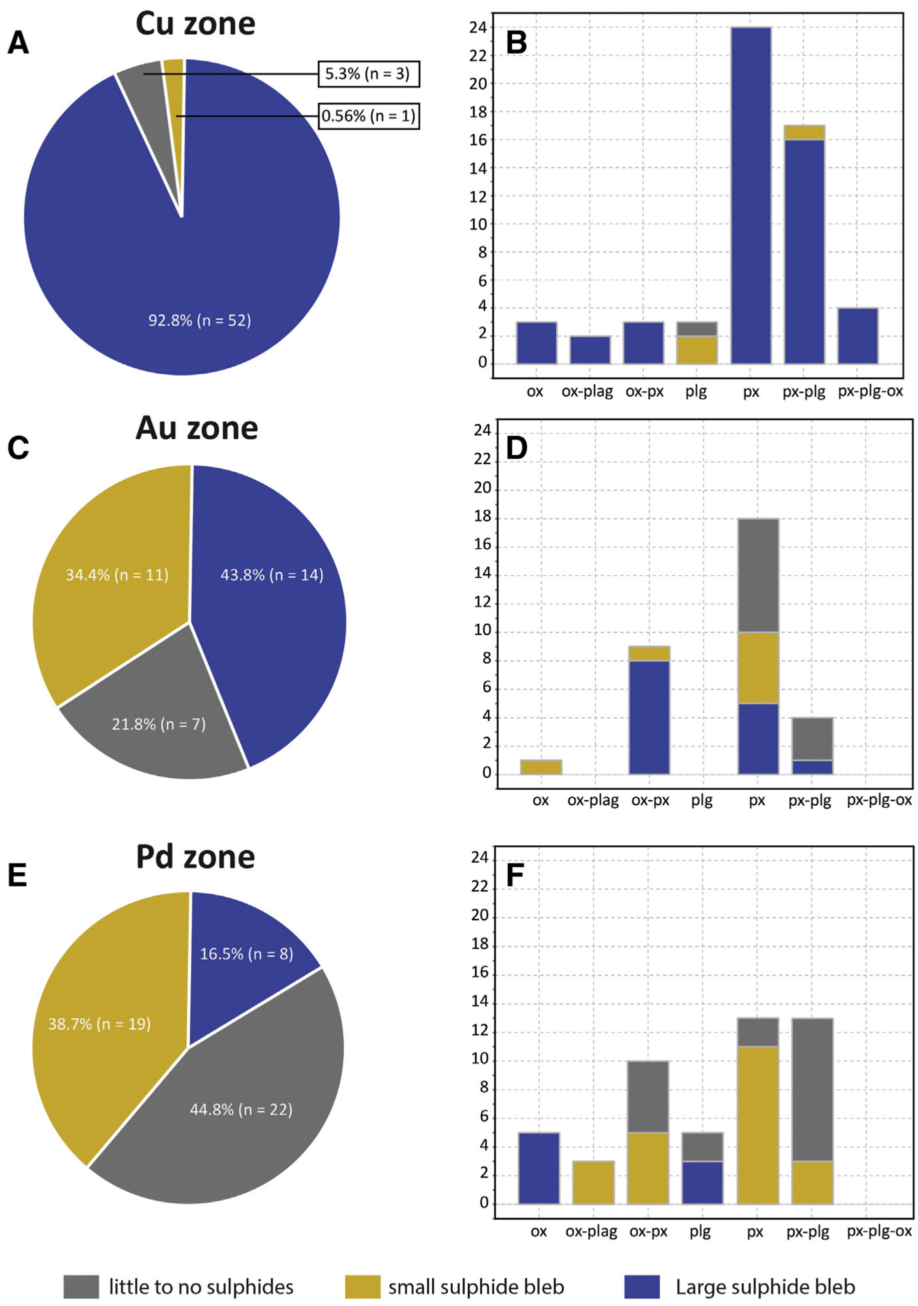

Fig. 12. A, C, E: proportion by number of grains of small sulphide blebs with high PM/Cu ratios, large sulphide blebs with low PM/Cu ratios in Cu zone and PGM with little or no sulphide in the Cu, Au and Pd zones; B, D, F: numbers of these blebs within plagioclase (plag), pyroxene (px) and oxides (ox) as well as at contacts of plagioclase and pyroxene grains and contact of oxides with other minerals in the Cu zone.

precious and other metals. Our data shows no systematic difference in the nature and intensity of alteration between the Au and Pd zones or between blebs of high and low sulphide to precious metal ratio; this precludes any significant late hydrothermal component to the PM concentration mechanism. However, there are a number of features that show hydrous melts or fluids were present during or after formation of the primary sulphides, such as the presence of hydrous silicates with sulphides and PMM that are trapped within Fe–Ti oxides (Fig. 4). Godel et al. (2014) interpreted these to be a product of the low-temperature equilibration of trapped silicate melt and trapped vapour or fluids by diffusive exchange with evolved trapped interstitial liquid during the late stages of solidification. Critically, the inclusions are not restricted to a particular zone, and thus not related to the different PM contents in different zones.

Rudashevsky et al. (2014, 2015) and Nielsen et al. (2015) suggest that the Au zone represents a late mineralisation event formed in already crystallised gabbro, caused by the migration of the volatile-bearing residual of Fe-rich immiscible silicate melt enriched in Au, with Au deposited on grain boundaries. We find no 3D textural evidence for any significant differences between the formation of the Au and Pd zone sulphides and associated PM, and very little evidence of Fe-rich silicate immiscibility in our samples. However, the Au mineralogy does show some evidence of low temperature formation. The most common Au-bearing mineral in the Au zone in our samples, and those from other drillholes in the vicinity (Nielsen et al., 2015), is the unnamed mineral Au_3Cu, whereas it is tetra-auricupride (AuCu) in the more central areas. Cabri et al. (2005) and Rudashevsky et al. (2004) also note the presence of this phase in their studies of the Platinova Reef. Outside

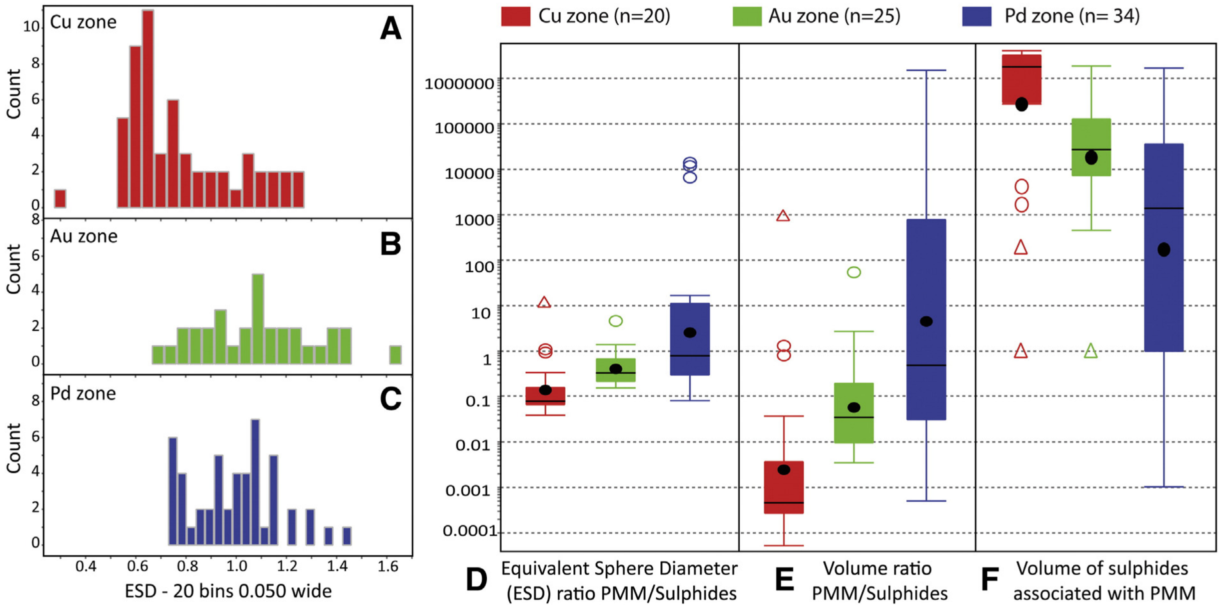

Fig. 13. A–C: PMM sizes as equivalent sphere diameters (ESDs) in the Cu, Au and Pd zones, respectively. D–F: Turkey box plots of (D) the ratio of PMM/sulphide ratio, by ESD, showing an increase from Cu, through Au to Pd zones; (E) the ratio of PMM/sulphide ratio, by volume, showing an increase from Cu, through Au to Pd zones; (F) the volume of sulphides associated with the PMM, showing a clear increase in sulphide volume from the Pd, through Au, to Cu zone. Tukey Box Plots divide the ordered values of the data into four equal parts by finding the median and then the 25th and 75th percentiles (~inter quartile range depending on duplicate values—IQR). The median is defined by a horizontal line within a box that spans the ~IQR and contains approximately 50% of the data. The mean is represented by a large black circle. The fence is defined here as the central box (IQR) extended by 1.5 times the length of the box towards the maximum and the minimum.

the Skaergaard Intrusion, Au_3Cu is very rare, but in all other cases where it is found, it is thought to have a low-temperature hydrothermal origin (Knipe and Fleet, 1997; Stumpfl and Clark, 1965; Verryn et al., 1991). Okamoto et al. (1987) show experimentally that Au_3Cu is stable at temperatures below 240 °C; consistent with its presence as a low temperature hydrothermal phase. At Skaergaard, its presence may indicate *in situ* recrystallisation at low temperatures, rather than fluid remobilisation of PMM. Alternatively, the Au_3Cu in the Platinova Reef may simply be a low temperature alloy formed during recrystallisation on cooling of the PM sulphide blebs without mediation by hydrothermal fluid. Therefore whilst some alteration is present to varying degrees, we do not believe that fluid activity mobilised precious metals, but may have produced some S-loss from some sulphides and recrystallized some PMM to low-temperature phases. More generally, we argue that a fluid-driven mechanism requires a highly improbable coincidence in depositing Au at a precise and very specific stratigraphic level in textural associations identical to those in the Pd-rich zone; in all offset reef style deposits.

10. Conclusions

The relative position of the Pd, Au and Cu peaks in the Platinova package is essentially the same as that in numerous other examples of offset PGE reefs, notwithstanding many differences in finer detail. This is unlikely to be a coincidence and thus we suggest that the same overarching processes are responsible for the enrichment in metals, and relative offsets in peak metal concentrations in all offset reef deposits worldwide. The Platinova Reef is important in this respect as it is an extreme example of such a deposit which records the extreme enrichment of precious metals via equilibrium and diffusive partitioning into sulphide liquid microdroplets very close to their point of nucleation. Concentration of the majority of precious metals is by cumulus droplets of Cu sulphide nucleated and grown *in situ* at the interface between the magma and the crystal pile; and occurs prior to the appearance of more abundant and larger gravitationally settled sulphide droplets. This feature is common in other 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 textures and mineralogy show the physical mechanisms of concentration are the same in all zones indicating a similar physical method of concentration. The fundamental geochemical and kinetic controls on the sequence and extent of metal enrichment are their relative $D_{sul/sil}$ values and diffusivities. In the case of the Platinova Reef, the increase in Pd concentration is located at a major Ti–V peak suggestive of a link between magnetite crystallisation and the nucleation of tiny Cu sulphide liquid droplets, although the existence of magnetite-free offset reefs in other intrusions implies that the role of magnetite is not universal. Thus, offset reefs can form in settings corresponding to the first onset of sulphide saturation in an evolving magma chamber, regardless of the precise mechanism that triggers attainment of sulphide liquid saturation, and record the process of sequential metal enrichment subsequent to the intial nucleation of sulphide droplets in the magma.

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