

Processes controlling the distribution of Te, As, Bi, Sb, and Sn, and the formation of platinum-group minerals in sulphide ores in the Noril'sk mining district (Russia)

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Abstract. The distribution of TABS (Te, As, Bi, Sb, and Sn) in magmatic sulphide ore deposits have been neglected despite their critical role in forming platinum-group minerals (PGM). Investigating the primary processes controlling the TABS distribution is a challenge as TABS are generally volatile, present at low levels, and mobile with alteration. Magmatic sulphide ore bodies in the Noril'sk mining district (Siberia, Russia) offer an exceptional opportunity to investigate the behaviour of TABS during fractional crystallisation of sulphide liquids and PGM formation as the primary features of the ore bodies have been relatively well preserved. We show that the distribution of Pt, Pd, and TABS is controlled by their partitioning behaviour during sulphide liquid fractional crystallisation, prior to PGM formation. In Cu-poor massive sulphides the PGM formed as the result of exsolution from sulphide minerals, whereas in Cu-rich massive sulphides the PGM formed by crystallisation from late-stage fractionated liquids.

1 Introduction

The distribution of platinum-group elements (PGE) within zoned magmatic ore bodies has been extensively studied and appears to be controlled by the partitioning behaviour of the PGE during fractional crystallisation of magmatic sulphide liquids (monosulphide solid solution (MSS) – intermediate solid solution (ISS) crystallisation sequence). However, other chalcophile elements, especially TABS (Te, As, Bi, Sb, and Sn) have been neglected despite their critical role in forming platinum-group minerals (PGM). TABS are considered to be mobile elements so investigating their primary distribution may be challenging in magmatic ore bodies that have been somewhat altered. Furthermore, determining their concentrations is a challenge as they are generally volatile and present at low levels.

Magmatic sulphide ore bodies in the Noril'sk mining district (Siberia, Russia) offer an exceptional opportunity to investigate the behaviour of TABS during fractional crystallisation of sulphide liquids and PGM formation as the primary features of the ore bodies have been relatively well preserved. In contrast to a number of previous studies on specific aspects of the geology, petrography, platinum-group mineralogy, whole-rock and isotopic compositions of the ores in the Noril'sk mining district, our study focusses on integrating the textural, mineralogical, and

geochemical variations. We combine optical and secondary electron microscopy, electron probe micro-analysis (EPMA) of PGM and precious metal minerals (PMM), high-resolution X-ray computed tomography (HRXRCT), and whole-rock geochemical analyses to address the main differences between the various ore types. We show that textural, mineralogical, and geochemical variations are consistent with variable interaction of sulphide liquid droplets with silicate magma followed by sulphide liquid ponding, MSS-ISS fractional crystallisation, and in some cases injection of Cu-rich liquid into surrounding rocks. Using the median disseminated sulphide composition as initial sulphide liquid composition and recent partition coefficients ($D^{\text{MSS/liq}}$ and $D^{\text{ISS/liq}}$), numerical modelling predicts the compositional variations observed in the massive sulphides, especially in terms of Pt, Pd, and TABS. We also discuss the origin of PGM and PMM (i.e., exsolution versus crystallisation).

2 Petrography and geochemistry of the sulphide ores

Based on textures, sulphide-mineral proportions, and whole-rock compositions, the sulphide ores were divided into four main groups. The main characteristics of these groups are described below.

Disseminated sulphides: This ore type essentially consists of millimetric to centimetric spherical to ellipsoidal droplets in olivine-gabbro-norites. The typical droplets are characterized by a pyrrhotite-rich base and a chalcopyrite-rich top with pentlandite in-between (Fig. 1). Recalculated to 100% sulphides, disseminated sulphides have primitive mantle normalized multielement patterns enriched in most elements (Fig. 1). The petrography and geochemistry suggest that disseminated sulphides have initial sulphide liquid compositions and higher concentrations in most elements can be explained by strong interaction of sulphide liquid droplets with silicate magma.

Cu-poor massive sulphides: This ore type essentially consists of accumulation of sulphides at the base of the intrusions and is characterized by high abundances of pyrrhotite (>70%), variable abundances of pentlandite, and low abundances of chalcopyrite (< 10%). Pyrrhotite occurs as centimetric anhedral patches. Pentlandite occurs in

three forms: as large subhedral grains (a few hundred μm to a few mm in apparent diameter), as chain-like polycrystalline aggregates around Po grains, and as exsolution flames within Po grains (Fig. 1). Chalcopyrite occurs either as small anhedral grains randomly dispersed between pyrrhotite and pentlandite grains or as centimetric patches. The Cu-poor massive sulphides have primitive mantle multielement patterns (Fig. 1) depleted in elements incompatible with MSS (Sn, In, Tl, As, Sb, Pb, Bi, Cd, Ag, Cu, Au, Te, Pd, Pt) and enriched in elements compatible with MSS (Mo, Re, Rh, Ru, Ir, Os, Co). The petrography and geochemistry suggest that Cu-poor massive sulphides consist of cumulus MSS \pm Cu-rich fractionated liquid.

Cu-rich massive sulphides: This ore type essentially consists of accumulation of sulphides at the base of the intrusions or of sulphide impregnations in surrounding rocks (veins and breccias). Most Cu-rich massive sulphides are characterized by high abundances of chalcopyrite (>50%; Fig. 5a-i) and variable abundances of pentlandite and pyrrhotite, with pyrrhotite being minor (<10%) or absent. Chalcopyrite occurs as centimetric anhedral patches and in some samples, it hosts cubanite exsolutions. Cubanite exsolutions either occur as large bands (Fig. 1) or as tiny patches. Pentlandite mainly occurs as large grains (hundreds of μm to several mm in apparent diameter) associated with chalcopyrite and/or with pyrrhotite where present. Despite the texture variability observed in the Cu-rich samples, the geochemical compositions are the same. Similar geochemical compositions are suggestive of a common origin for all the Cu-rich samples. Differences in textures may simply reflect variations in kinetic processes. In contrast to Cu-poor massive sulphides, the Cu-rich massive sulphides have primitive mantle multielement patterns (Fig. 1) enriched in elements incompatible with MSS (Sn, In, Tl, As, Sb, Pb, Bi, Cd, Ag, Cu, Au, Te, Pd, Pt) and depleted in elements compatible with MSS (Mo, Re, Rh, Ru, Ir, Os, Co). The petrography and geochemistry suggest that Cu-rich massive sulphides represent cumulus ISS \pm late-stage fractionated liquid.

Transitional massive sulphides: The transitional massive sulphides have the appearance of a mixture between Cu-poor and Cu-rich sulphides. Pyrrhotite proportions vary between 40 and 60%, chalcopyrite proportions vary between 10 and 50%, and pentlandite proportions vary between 10 and 30%. Pentlandite occurs as exsolution flames in pyrrhotite (Fig. 1) and/or as polycrystalline aggregates at the pyrrhotite/chalcopyrite interface (Fig. 1). The transitional massive sulphides have intermediate primitive mantle multielement patterns (Fig. 1) in that they share geochemical characteristics with both Cu-poor and Cu-rich ores. The petrography and geochemistry suggest that transitional massive sulphides represent accumulation of sulphides in which MSS, ISS, and late-stage fractionated liquid have not been dissociated.

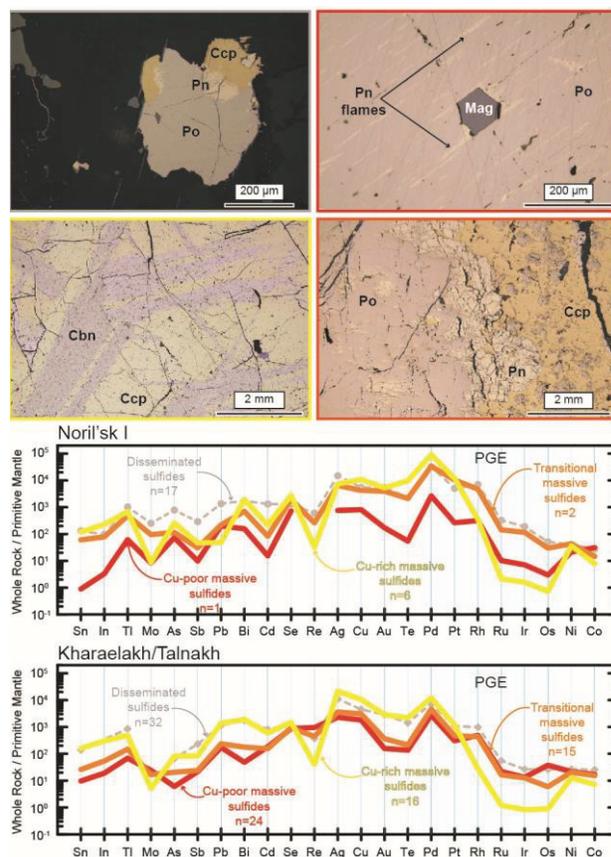


Figure 1. Typical examples of the petrography of each ore type (colour coded) and primitive mantle normalized multielement patterns of each ore type recalculated to 100% sulphides for the Noril'sk I and Kharaelakh + Talnakh intrusions of the Noril'sk mining district. Po = pyrrhotite; Pn = pentlandite; Ccp = chalcopyrite; Cbn = cubanite; Mag = magnetite.

3 Platinum-group and precious-metal mineralogy

In our investigated samples PGM and PMM consist of Pt-, Pd-, and Au-bearing minerals. No IPGE-, Rh-, or Re-bearing minerals were observed. The PGM and/or PMM were identified in all ore types, however the vast majority were found in the Cu-rich samples. In the disseminated sulphides and Cu-poor and transitional massive sulphides, the PGM and PMM essentially consist of Pt-PGM (Fig. 2) and minor electrum. No Pd-PGM was observed in these ore types. In the Cu-rich massive sulphides, Pt only-PGM were rarely observed. Most PGM in this ore type consist of Pt-Pd-PGM and Pd-PGM. Composite grains consisting of stannides and/or bismuthotellurides and/or arsenides and/or alloys were also commonly observed. Most grains were observed at sulphide grain boundaries (sulphide-sulphide, sulphide-silicate, sulphide-carbonate interfaces) or included within sulphide grains. The texture of the PGM and PMM varies from euhedral grains with well-defined crystal faces to anhedral grains with ragged boundaries.

High-resolution X-ray computed tomography (Fig. 2)

performed on samples from each ore types shows that PGM and PMM from the disseminated sulphides have the highest median sphericity (0.677) followed by those from the Cu-rich massive sulphides (0.669), transitional massive sulphides (0.584), and Cu-poor massive sulphides (0.569). This indicates that in general the PGM and PMM in disseminated sulphides and Cu-rich massive sulphides have more rounded shapes, whereas those in transitional and Cu-poor massive sulphides have more elongated shapes. The PGM and PMM from the Cu-rich massive sulphides have the highest median specific surface area (9.851 mm^{-1}) followed by those from the transitional massive sulphides (4.780 mm^{-1}), disseminated sulphides (2.874 mm^{-1}), and Cu-poor massive sulphides (1.893 mm^{-1}). This indicates that in general the PGM and PMM in Cu-rich and transitional massive sulphides have rougher surfaces whereas those in disseminated sulphides and Cu-poor massive sulphides have smoother surfaces.

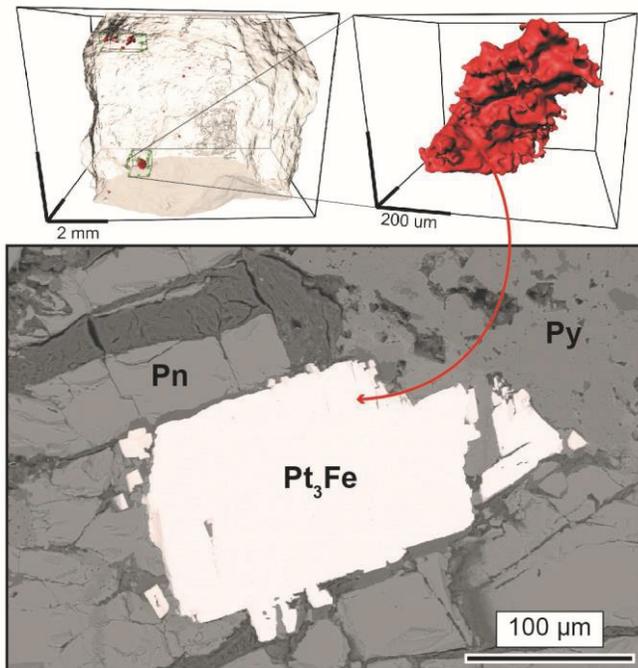


Figure 2. Example of HRXRCT 3D reconstruction of a PGM showing isosurfaces and 3D relationships. The same PGM grain is shown a backscattered electron image and electron-probe micro-analysis indicate that it consists of isoferroplatinum (Pt_3Fe).

Considering that Cu-poor ore crystallized early, when the sulphide liquid was likely unsaturated in Pt, Pd, Au, and TABS, PGM and PMM in this ore type could not have crystallized from sulphide liquids. Elongated morphologies and smooth crystal faces rather suggest that PGM and PMM in the Cu-poor ore formed by exsolution from the sulphide minerals. Ballhaus and Ulmer (1995) showed that at high temperature, Pt and Pd could substitute for Fe in MSS when vacancies surround the Fe sites, and that solubilities of Pt and Pd drastically decrease with decreasing temperature and $f\text{S}_2$, leading to exsolution of Pt

and Pd initially present in solid solution in MSS as it recrystallized to form Po and Pn ($< 650^\circ\text{C}$). The lack of Pd-PMM in the Cu-poor ore also suggests that Pd did not exsolve from MSS along with Pt and was rather incorporated into Pn as demonstrated by Barnes et al. (2006). In contrast to the Cu-poor ore, the Cu-rich ore crystallized later and late-stage fractionated sulphide liquids enriched in Pt, Pd, Au, and TABS formed after ISS crystallisation ($< 880^\circ\text{C}$). Such liquids have low melting points and droplets of these residual liquids were likely trapped among ISS grains in the late stages of crystallisation prior to crystallize as composite PGM and PMM. This interpretation is supported by the spherical morphology of composite grains. As transitional massive sulphides represent mixtures of Cu-poor and Cu-rich ores, the intermediate median sphericity and specific surface area suggest that in this ore type PGM and PMM consist of a combination of exsolutions and trapped droplets of late-stage fractionated sulphide liquid.

4 Modelling the composition of massive sulphides

Upon sulphide segregation from, and interaction with silicate liquid, sulphide liquid droplets tend to accumulate downwards due to higher density relative to silicate liquid. Once pools of sulphide liquid have accumulated, the composition of massive sulphides is believed to be controlled by the partitioning behaviour of the elements during the course of fractional crystallisation of sulphide liquids (i.e., $D^{\text{MSS}/\text{liq}}$ and $D^{\text{ISS}/\text{liq}}$; see discussion in Liu and Brenan (2015) for further insights). To test whether the partitioning behaviour of the elements is the essential parameter in controlling the composition of massive sulphides, compatible elements in MSS (e.g., Ir and Rh) and incompatible elements in MSS (e.g., Pt, Pd, and Cu) have been plotted against each other. Commonly, massive sulphides lie along the evolution lines of predicted MSS and complementary fractionated liquid calculated from assumed initial liquid composition on the basis of Rayleigh fractionation.

To further assess the role of fractional crystallisation, we present the massive sulphide data and the result of the modelling on Pd, Pt, and TABS versus Cu plots (Fig. 3), in which Cu is used as an index of sulphide evolution. For clarity and due to limited massive sulphide samples from Noril'sk I, we only present the data from Kharaelakh and Talnakh. Assuming that disseminated sulphides represent initial sulphide liquids from which massive sulphide accumulated, the composition of the modelled MSS and complementary fractionated liquids derived from these initial liquids can be calculated using the Rayleigh fractionation equations:

$$C_L = C_0 * F^{(D-1)} \quad \text{eq (1)}$$

$$C_S = C_L * C_0 * F^{(D-1)} \quad \text{eq (2)}$$

in which C_L is the concentration of an element in the fractionated sulphide liquid; C_S is the concentration of an element in the solid crystallizing from the sulphide liquid; C_0 is the concentration of an element in the initial sulphide liquid; F is the fraction of liquid; and D is the partition coefficient between the solid and liquid. In addition, the modelled ISS and fractionated liquid after ISS crystallisation are plotted. The same Rayleigh fractionation equations were used and in this case C_0 was assumed to be the composition of the fractionated liquid after reaching >20 wt.% Cu (i.e., after ca. 60% fractionation), which is consistent with the experimental work of Ebel and Naldrett (1996) and Liu and Brenan (2015). The modelling was performed using the experimental range of partition coefficients for Pd, Pt, and TABS, and the best fits for the evolution lines were obtained with the lowest partition coefficients (Barnes and Ripley 2016).

Most Cu-poor and transitional massive samples plot between the evolution lines of modelled MSS and sulphide liquid crystallizing MSS, whereas most Cu-rich massive sulphides plot along the evolution lines of modelled ISS and fractionated liquid crystallizing ISS. Overall, the Pd, Pt, TABS, and Cu compositions of the massive sulphides from Kharaelakh and Talnakh are in agreement with the MSS-ISS crystallisation sequence and sulphide liquid enrichment in incompatible elements. The fact that TABS are concentrated in evolved sulphide liquids along with Pt and Pd is of high importance for magmatic sulphide deposits, as these elements play a key role in the formation of PGM and PMM. The partitioning behaviour of these elements during sulphide liquid differentiation was likely the main parameter driving the changes in composition observed in massive sulphides, leading to concentration of these elements in the residual liquids until PGM and PMM crystallisation in the Cu-rich ore.

5 Concluding remarks

The petrographic and geochemical variations in sulphide ores from the Noril'sk mining district are consistent with fractional crystallisation of sulphide liquids. Platinum-group minerals mainly exsolved from sulphide minerals in the Cu-poor ore whereas in the Cu-rich ore PGM mainly crystallised from late-stage fractionated liquids. Numerical modelling predicts the compositional variations observed in the massive sulphides, especially in terms of Pt, Pd, and TABS, in agreement with our observations and interpretations.

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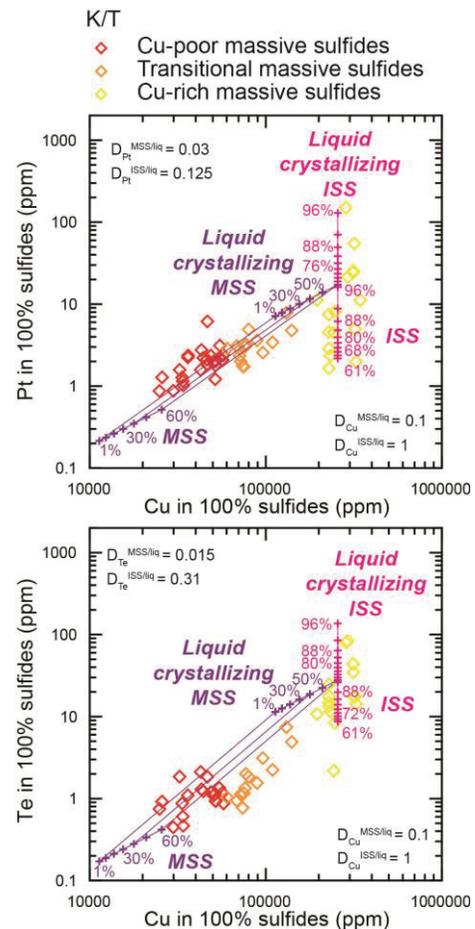


Figure 3. Binary diagram of Cu versus Pt and Te for massive sulphides from Kharaelakh and Talnakh (recalculated to 100% sulphides). The purple lines represent model compositions of the evolving MSS and liquids. The numbers represent the degree of fractionation in percent. After 60% fractionation, ISS would crystallise (i.e., when the liquid reached ca. 20 wt.% Cu). The pink lines represent the compositions of the evolving ISS and liquids. Note that Pd, As, Bi, Sb, and Sn show the same distribution.

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