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# The importance of volatiles in the formation of magmatic sulphide ore deposits: experimental constraints

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## Abstract.

Research studies provide growing evidence for the presence of fluids within magmatic mineral systems of mafic-ultramafic composition, although these ore-forming magmas are generally considered volatile-poor. Here we summarise the results of two experimental studies that clarify the role of volatiles in the formation of magmatic sulphide ore deposits in mafic-ultramafic magmas: (i) interaction experiments simulating magmatic assimilation of sulfate and/or organic compounds (Iacono-Marziano et al. 2017); (ii) a more recent experimental study shedding light on previously unnoticed physical processes ensuing from the association between sulphide melt and fluid phase (Iacono-Marziano et al. 2022). The silicate melt composition used for both studies is similar to the parental melt of Noril'sk-Talnakh ore bearing intrusions in Polar Siberia, and the starting materials of the experiments were samples in Noril'sk region. Moreover, the experiments were conducted at magmatic conditions relevant to emplacement pressures and temperatures of Noril'sk-Talnakh intrusions. Experimental findings are therefore directly applicable to these world-class ores, suggesting that volatiles may have played a crucial role in their formation. Several other magmatic sulphide ores present evidence of the occurrence of a fluid phase during ore formation; hence the mechanisms illustrated by the experiments are likely to be more common than currently considered.

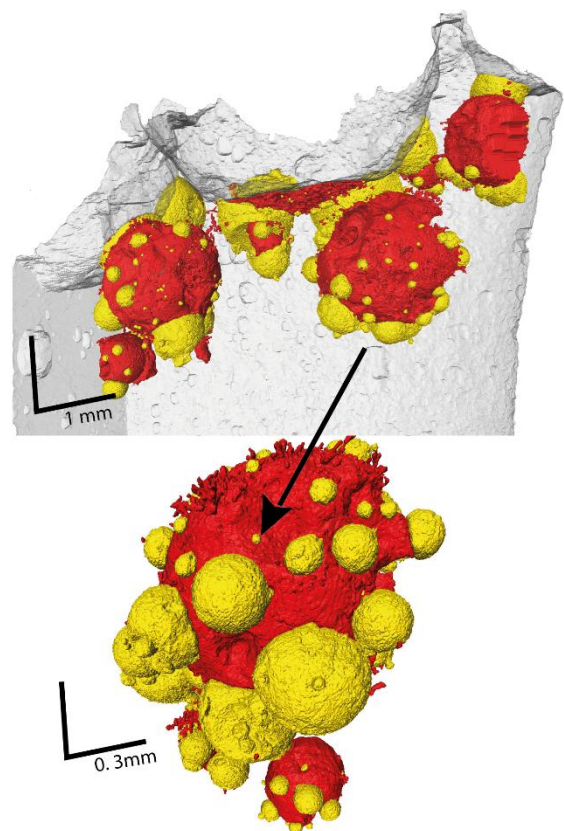
## 1 Triggering sulphide saturation

The addition of external sulphur to the magma is one of the most common ore-forming processes invoked for magmatic sulphide deposits (e.g. Naldrett 2004). Sulphur can be introduced into the magma by several processes: those that have been experimentally documented are anhydrite dissolution (Iacono-Marziano et al. 2017), black shale devolatilization (Virtanen et al. 2021), and black shale assimilation (Deegan et al. 2022). Our experiments at magmatic conditions (1200°C, 80 MPa) show that anhydrite assimilation in the presence of a reducing agent, i.e. organic matter-rich rocks such as coal, is extremely efficient in producing high sulphide supersaturation in the magma (Iacono-Marziano et al. 2017).

## 2 Accumulation of the sulphide melt

The association between the sulphide melt and the fluid phase has been shown to allow the upward transfer of the sulphide melt (Mungall et al. 2015). Our recent experimental results illustrate another physical process that occurs when the proportion

of fluid phase in the magma is low: the sulphide-fluid association favours the accumulation of the sulphide liquid, by facilitating the coalescence of the sulphide droplets that are attached to the same fluid bubble (Iacono-Marziano et al. 2022). This consents the accumulation of the sulphide melt in the upper part of the experimental samples (Fig. 1).



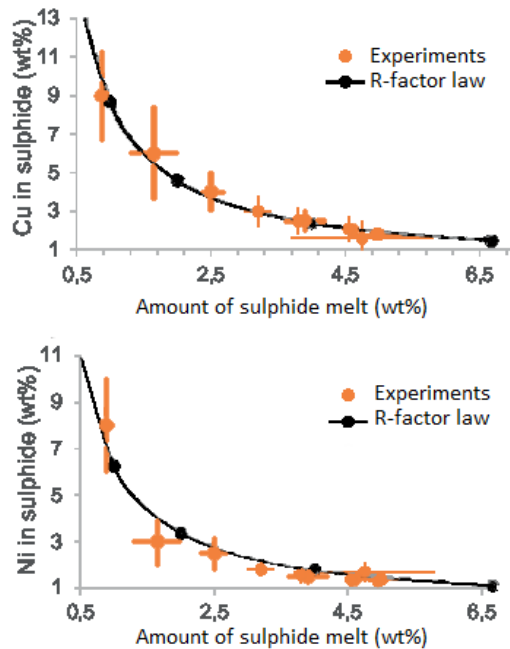
**Figure 1.** High-resolution X-ray computed tomography rendering of a representative experimental sample showing 3D distribution of sulphide droplets in yellow and fluid bubbles in red (the silicate glass is in grey). The upper image shows a general view of the upper part of the experimental sample, whereas the lower image shows a detail of sulphide-fluid associations, with several sulphide droplets attached to the same fluid bubble. Modified from Iacono-Marziano et al. (2022).

Coalescence of sulphide droplets may be facilitated by the lowering of their interfacial tension induced by the bubble. However, the main driver

for coalescence to occur is likely to be the fact that connection to the bubbles keeps the droplets in contact for a long enough time to allow drainage of the melt film between them, as opposed to the situation in a flowing magma where adjacent droplets are sheared apart before the melt film has time to drain (Robertson et al. 2015). This process may enable sulphide droplets coalescence and deposition in flowing magma, which otherwise have been shown to be unlikely processes (Robertson et al. 2015).

### 3 Metal enrichment of the sulphide melt

Experimental results indicate that sulphur degassing to the fluid phase increases with increasing proportion of fluid phase, concurrently reducing sulphide melt stability. Consequently, the sulphide melt is consumed and its metal content augments, due to the preferential partitioning of metals into the sulphide melt (Iacono-Marziano et al. 2022). Experimental samples with increasing fluid contents present increasingly Ni and Cu-rich sulphide melts, illustrating how the metal enrichment of the sulphide melt can be attained by sulphur degassing (Fig. 2). Sulphide upgrading can therefore be achieved by magma degassing.

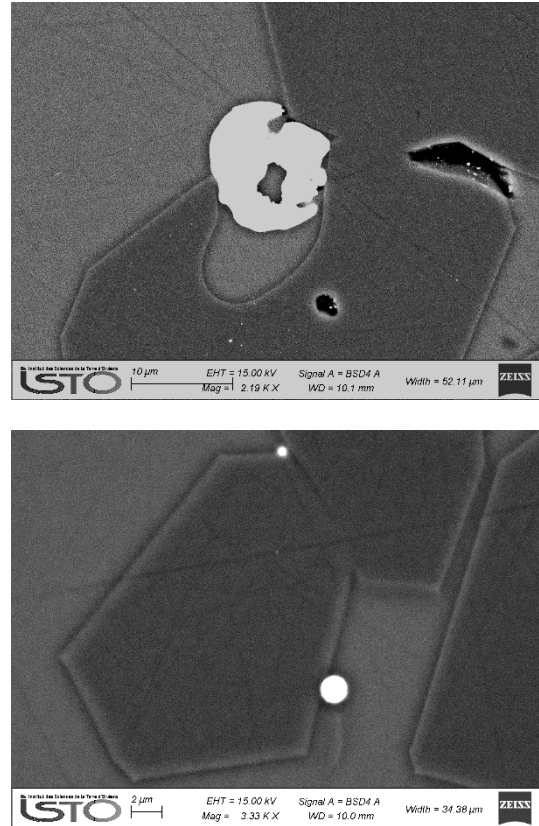


**Figure 2.** Cu and Ni content of the sulphide melt versus its amount in experimental samples (orange dots) and in theoretical calculations (black line) using the R-factor law of Campbell & Naldrett (1979). Modified from Iacono-Marziano et al. (2022).

### 4 PGM formation by desulphurisation

Extensive sulphur degassing may completely consume the sulphide melt and form platinum

group minerals (PGMs) at relatively high temperatures (1150°C in the experiments of Iacono-Marziano et al. 2022). PGM formation in the experimental samples (Fig. 3) occurs by desulphurisation of the sulphide melt, while Ni and Cu are partitioned between the silicate melt and the fluid phase. This suggests an unconventional mechanism of PGM formation at temperatures higher than those typical of sulphide melt crystallization.



**Figure 3.** BSE images of an experimental sample with a high proportion of fluid phase (2.2 wt%), which experienced an extensive sulphur degassing. The upper image shows a partially corroded sulphide bleb observed in the upper part of the sample. The lower image shows the Pt-rich, Fe-S-Ni-Cu bearing phase that commonly occurs at the interface between the olivine and the silicate melt.

### 5 Application to Noril'sk-Talnakh ores

The experimental results presented above illustrate how the occurrence of a fluid phase in a mafic-ultramafic magma may represent a significant boost for magmatic sulphide ore forming processes: sulphide melt accumulation, tenor increase, and crystallization of platinum group minerals are indeed key processes in the formation of magmatic Ni-Cu-Co-PGE ore deposits. We use the world-class Noril'sk-Talnakh ore deposits, in Polar Siberia as a case study.

Noril'sk-Talnakh ores are hosted in mafic-ultramafic subvolcanic ribbon-shaped intrusions. Extensive interaction of the ore-forming magmas with evaporitic and carbonaceous rocks has been

proposed to be at the origin of the mineralisation and the coexisting abundant fluid phase (e.g. Iacono-Marziano et al. 2017).

The three main ore types are described in ore-bearing intrusions: (i) massive sulphides in the lower part of the intrusion and largely in the country rocks, (ii) disseminated sulphides (also called globular ores) inside picritic and taxitic rocks, also in the lower part of the intrusion, (iii) low-sulphide PGE ores in the upper part of the intrusion (e.g. Naldrett 2004; Le Vaillant et al. 2017; Schoneveld et al. 2020).

In the second and third ore-types subspherical structures within the crystalline framework have been interpreted as fluid bubbles filled with late magmatic phases or hydrothermal minerals (e.g. Le Vaillant et al. 2017; Schoneveld et al. 2020). In the lower part of the intrusion, these structures are systematically associated with sulphide minerals suggesting they represent sulphide-fluid associations preserved in the olivine-rich magmatic rocks (Le Vaillant et al. 2017). In the upper part of the intrusion, these subspherical structures are even more common and generally contain lower amounts of sulphide minerals but abundant PGMs (Schoneveld et al. 2020), suggesting higher extents of sulphur degassing and sulphide dissolution. On the contrary, massive sulphides are proposed to have experienced low extents of sulphur degassing, attested by the lower metal contents with respect to disseminated sulphides (Iacono-Marziano et al. 2022).

Ore type distribution in Noril'sk-Talnakh intrusions therefore strongly suggests an increasing extent of degassing from the bottom toward the top of the intrusions, implying increasing sulphide melt consumption and metal enrichment. Although a role for volatiles is less clear in other magmatic sulphide deposits, an increasing number of examples of sulphide-fluid associations is reported, as summarised in Iacono-Marziano et al. (2022). This suggests that the role of volatiles in the formation of magmatic sulphide deposits should probably be re-evaluated.

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