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

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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 as volatile-poor. Here we summarize the results of two experimental studies that clarify the role of volatiles in the formation of magmatic sulfide 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 sulfide melt and fluid phase (Iacono-Marziano et al. 2022). The silicate melt composition used for both studies is similar to the parental melt of the Noril´sk-Talnakh ore bearing intrusions in Polar Siberia and all materials used in the experiments were sampled from the Noril´sk region. Moreover, the experiments were conducted at magmatic conditions relevant to the emplacement pressures and temperatures of the Noril´sk-Talnakh intrusions, so that experimental findings are directly applicable to these world-class ores.

The addition of external sulfur to the magma is one of the most common ore-forming processes invoked for magmatic sulfide deposits. Sulphur can be introduced into the magma by several process, 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 sulfide supersaturation in the magma.

The association between the sulfide melt and the fluid phase has been shown to allow the upward transfer of the sulfide 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 sulfide-fluid association favors the accumulation of sulfide liquid by facilitating the coalescence of the sulfide droplets that are attached to the same fluid bubble. This leads to the accumulation of the sulfide melt in the upper part of the experimental samples. Coalescence of sulfide 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 long enough 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 sulfide droplets coalescence and deposition in flowing magma, which otherwise have been shown to be unlikely processes (Robertson et al. 2015).

Experimental results indicate that sulfur degassing to the fluid phase increases with increasing proportion of fluid phase, concurrently reducing sulfide melt stability. Consequently, the sulfide melt is consumed and its metal content augments. Experimental samples with increasing fluid contents present increasingly Ni- and Cu-rich sulfide melts, illustrating how metal enrichment of sulfide melt can be attained by sulfur degassing. Magma degassing can therefore lead to sulfide upgrading.

Extensive sulfur degassing may completely consume the sulfide melt and form platinum-group minerals (PGMs) at relatively high temperatures (1150 ˚C in our experiments). Platinum-group mineral formation in the experimental samples occurs by desulfurisation of the sulfide 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 sulfide melt crystallization.

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 sulfide ore forming processes: sulfide melt accumulation, tenor increase, and crystallization of PGMs 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 mineralization 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 sulfides in the lower part of the intrusion and largely in the country rocks; (ii) disseminated sulfides (also called globular ores) inside picritic and taxitic rocks, also in the lower part of the intrusion; (iii) low-sulfide PGE ores in the upper part of the intrusion (e.g. 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 (segregation vesicles) and/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 sulfide minerals suggesting they represent sulfide-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, typically associated with oxide mineral coatings, and generally containing lower amounts of sulfide minerals but abundant PGMs (Schoneveld et al. 2020), suggesting higher extents of sulfur degassing and sulfide dissolution. In contrast, massive sulfides are proposed to have experienced low extents of sulfur degassing, attested by the lower metal contents with respect to disseminated sulfides.

The distribution of ore types in Noril'sk-Talnakh intrusions therefore strongly suggests an increasing extent of degassing toward the top of the intrusions, implying increasing sulfide melt consumption and metal enrichment. Several other magmatic sulfide ores present evidence of the occurrence of a fluid phase during ore formation (relevant information can be found in Iacono-Marziano et al. 2022). Although a role for volatiles is less clear in other deposits, an increasing number of examples of sulfide-fluid associations is reported, suggesting that the mechanisms illustrated by the experiments may be more common than currently considered. We conclude that the role of volatiles in the formation of magmatic sulfide deposits should probably be re-evaluated.

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