

Role of carbon in the formation of Ni-Cu-PGE mineralization in the Valmaggia ultramafic pipe: Insights from laser-ablation-time-of-flight ICP-MS

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Abstract. Understanding the processes that control sulfide transport and deposition in the deep lithosphere is a critical step in the search for ore deposits in lower crustal rocks. The magmatic sulfide ore-bearing Valmaggia pipe in the Ivrea-Verbano Zone (Italy), an exposed cross section of the subcontinental lithospheric mantle and overlying crust, allows for unique insight into ore-forming processes in the lower crust. Sulfides in the pipe are spatially associated with carbonates and hydrous silicates. Previous studies suggested that the sulfides were physically introduced into the pipe via a bubble-pair transport model, i.e., upward flotation of sulfide droplets attached to vapor bubbles. To further evaluate sulfide ore-forming processes, we integrate new petrographic observations with laser-ablation time-of-flight-ICP-MS trace element mapping of sulfide-carbonate-hydrous silicate relationships. We show that carbonates and hydrous silicates exist in varying sizes, compositions, textures and orientations in relation to sulfide phases, and are not restricted to a singular textural or chemical relationship. Similarly, sulfide textures vary and may or may not exhibit rimming by volatile phases. Our data show that bubble-pair transport cannot fully explain the textural relationships between sulfides and volatile-rich minerals, but rather suggest that at least some of the sulfides and carbonates co-precipitated from the same fluid/melt.

1 Introduction

The number of new and significant ore deposit discoveries is declining (Schodde, 2020). One possible way to increase the discovery of magmatic Ni-Cu-platinum-group element (PGE) sulfide deposits is to open new exploration space in (exhumed) lower crustal rocks that are often neglected in exploration models. However, the chemical and physical processes that form magmatic sulfide deposits in the lower crust remain elusive.

One key area to study the formation of lower crustal magmatic sulfide deposits is the Ivrea-Verbano Zone (IVZ) in northwest Italy (Fig. 1A). The IVZ is a rare example of an exposed cross section of the subcontinental lithospheric mantle and overlying crust (Mehnert, 1975; Garuti et al. 1980). The IVZ hosts five variably metasomatized ultramafic pipes (Fig. 1B) containing Ni-Cu-PGE mineralization with grades of up to 11.9% Cu, 10.7% Ni, and 5 ppm PGE (Zaccarini et al. 2014). The sulfide mineralization appears to be spatially associated with carbonate minerals and hydrous silicates such as phlogopite

and amphibole. However, the relationship between volatile-rich minerals and sulfides, and to what extent (carbonated) hydrous fluids played a role in ore genesis, remains to be fully understood.

Previous studies suggested that the sulfides were physically introduced into the pipes via a bubble-pair transport model wherein SCLM sulfides attached to supercritical CO₂ bubbles migrated upwards into the pipes (Blanks et al. 2020; Locmelis et al. 2021). To further test this hypothesis, we integrate new petrographic observations with laser-ablation time-of-flight inductively coupled mass spectrometry (LA-ICP-TOF-MS) trace element mapping of sulfide-carbonate-hydrous silicate relationships for the best preserved IVZ pipe at Valmaggia. The data are used to evaluate whether 1) sulfides were introduced into the Valmaggia pipe attached to CO₂ bubbles, or whether 2) sulfides and carbonates co-precipitated from a high temperature fluid or melt rich in S and CO₂/CaCO₃.

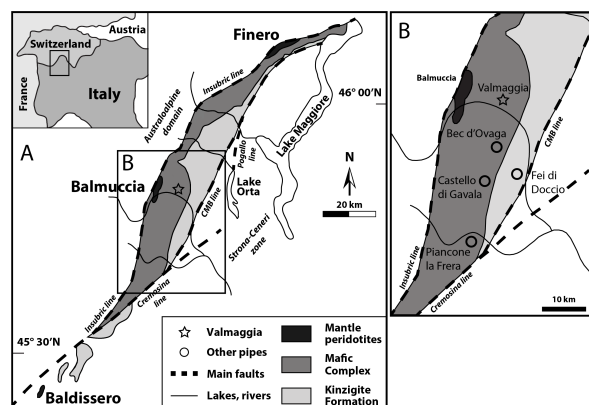


Figure 1. A: Simplified geologic map of the Ivrea-Verbano Zone. B: Location of the ultramafic pipes, including Valmaggia (star). Modified after Fiorentini and Beresford (2008) and Locmelis et al. (2016).

2 Geologic Setting

The IVZ (Fig. 1) in the Western Alps, Italy, hosts five discordant ultramafic pipe-like intrusions hosted by the Mafic Complex and Kinzigite Formation (Fig. 1B). Locmelis et al. (2016) showed that the 249 Ma Valmaggia pipe was initially emplaced as an almost pure dunite. Later metasomatic pulses at 209.4 ± 5.1 Ma and 207.8 ± 2.0 Ma (Sessa et al. 2017;

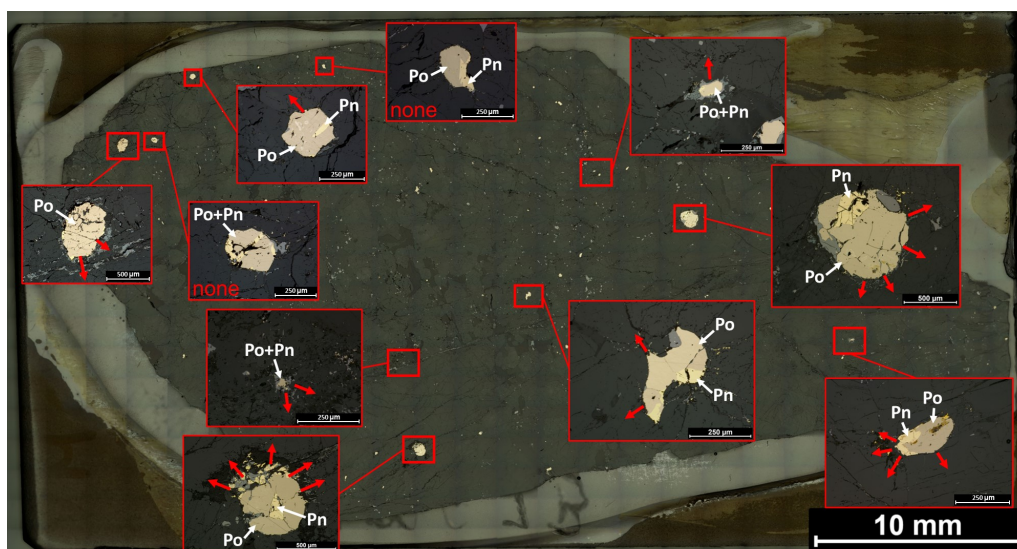


Figure 2. Reflected light image of sample VMG1B from the core domain of the Valmaggia pipe. Insets show zoomed-in reflected light images of pyrrhotite (Po) and pentlandite (Pn) blebs/globules. The red arrows indicate the perpendicular direction of sulfide-carbonate contacts.

Locmelis et al. 2021) produced a secondary hydrous assemblage dominated by phlogopite and amphibole with locally abundant carbonates. The Valmaggia pipe hosts blebby and semi-massive sulfide mineralization in its rim portion, compared to a smaller (< 1 mm) disseminated assemblage in the core. Locally, the sulfides are rimmed by and/or intergrown with carbonates, phlogopite and amphibole, particularly in the rim portion.

3 Samples and Methods

Four polished thin sections from the Valmaggia pipe were investigated, i.e., two from the core (VMG1B and VMG7) and two from the rim (I-6A and I6B). The sections were studied using transmitted and reflected light microscopy using a Leica DVM 6 digital microscope in the Department of Geosciences and Geological and Petroleum Engineering (GGPE) at Missouri University of Science and Technology.

Major and minor element compositions of sulfides, carbonates and silicates were determined using a JEOL JXA-8200 electron microprobe equipped with wavelength and energy dispersive spectrometers (EDS and WDS) in the Department of Earth and Planetary Sciences, Washington University, St. Louis, Missouri, USA. Precision and accuracy were better than 3-5% (2σ).

A total of 27 quantitative sets of maps (^{23}Na to ^{238}U) were generated by time-of-flight LA-ICP-TOF-MS (Savard et al. 2023) using a 7, 9, and 19 μm beam size. The analysis focused on sulfide grains that were in contact and/or spatially close to volatile phases (carbonates and/or hydrous silicates).

4 Sulfide – Carbonate Relationships

Sulfide mineralization in the core of the Valmaggia pipe is commonly disseminated, consisting of < 1 mm patches and composite blebs of pyrrhotite + pentlandite \pm chalcopyrite (Fig. 2). Sulfide mineralization in the rim is semi-massive, consisting of polyphase blebs composed of pyrrhotite + pentlandite \pm chalcopyrite several microns up to 1 cm in the longest direction (Fig. 3A). In both domains, sulfides are commonly embayed with, or rimmed by, carbonate phases (Fig. 3) and/or hydrous silicates (phlogopite, amphibole). The TOF-LA-ICP-MS data show that sulfides spatially related to carbonates are variably enriched in lithophile elements in the rim (< 20-370 ppm Na, 100-7400 ppm Mg, < 40-390 ppm Al, and < 330-676 ppm Ca) and the core (< 20-530 ppm Na, < 50-1100 ppm Mg, < 40-280 ppm Al, < 330-580 ppm Ca).

Carbonates in the studied samples are generally dolomitic, with less common calcite and Ca-Mg-Fe carbonate phases. The Ca-rich carbonate phases commonly occur adjacent to, or in direct contact with sulfides (Figs. 3A and 4A). Conversely, Ca-poor and Fe-rich phases are mostly surrounded by and intermixed with silicate phases and restricted to sulfide-poor or -absent areas.

Three distinct carbonate groups were identified in this study:

- 1) Carbonates in direct contact with sulfide grains/blebs in sulfide-rich areas. These grains contain 15-20 wt.% Mg, 20-30 wt.% Ca, 2-3 wt.% Fe, with 1500-2000 ppm Mn, 40-60 ppm Pb, < 90-2780 ppm Ni, and < 30-170 Cu;

- 2) Carbonates not in direct contact with sulfides, but near small, disseminated sulfide grains (<150 μm) in sulfide-poor areas. These grains contain 34-50 wt.% Mg, < 0.5 wt.% Ca, 10-15 wt.% Fe, 0.5-0.7 wt.% Mn, < 90-120 ppm Ni, and < 30-34 ppm Cu;
- 3) Carbonates within sulfide grains as vein fill (only in sample VMG7). These grains contain 8-9 wt.% Mg, 20-22 wt.% Ca, 2-3 wt.% Fe, 3-6 wt.% Mn, < 90-265 ppm Ni, and < 30-90 ppm of Cu.

5 Bubble transport vs. chemical precipitation of sulfides in the Valmaggia pipe

Two possible models for the origin of sulfide mineralization in the Valmaggia pipe are discussed: physical bubble-pair transport and chemical sulfide-carbonate co-precipitation.

A physical bubble transport mechanism for sulfides from the upper crustal Norilsk-Talnakh deposit in Russia was recently proposed by Barnes et al. (2019). These authors identified several key characteristics that may be indicative of a bubble transport, including:

- 1) Crystalline silicate caps uniformly oriented in the direction of lower lithostatic pressure “above” sulfide blebs or globules (“segregation vesicles”), indicating the buoyant migration of the vapor bubble upwards;
- 2) Flattening of sulfide globules perpendicular to the direction of ascent (gravitational settling);
- 3) Internal differentiation in the sulfide globule;
- 4) Differentiation in the silicate “cap”.

Similarly, studies by Mungall et al (2015) and Yao and Mungall (2020) conducted experimental and natural studies confirming that under certain conditions, vapors can exsolve from a melt and act as a ‘raft’ for immiscible sulfide droplets to migrate upwards through a melt.

Here we further investigate the possibility of bubble transport in the Valmaggia pipe via trace element TOF-LA-ICP-MS mapping. Our observations show several lines of evidence that are not consistent with a simple bubble transport model. For example, the mineral textures observed in the samples studied here do not follow the criteria identified by Barnes et al. (2019). There is no obvious uniform orientation of the volatile-rich components associated with sulfides that would indicate pressure-controlled ascent of sulfide-bubble pairs (Fig. 2). Further, uniform flattening of sulfides is not observed although the effect of flattening should theoretically be stronger considering the emplacement depth and impact of high pressure on crystal settling.

Cusped “embayments” within sulfides are rarely rimmed with carbonates or other volatile-bearing phases. Comb-textured carbonate aggregates

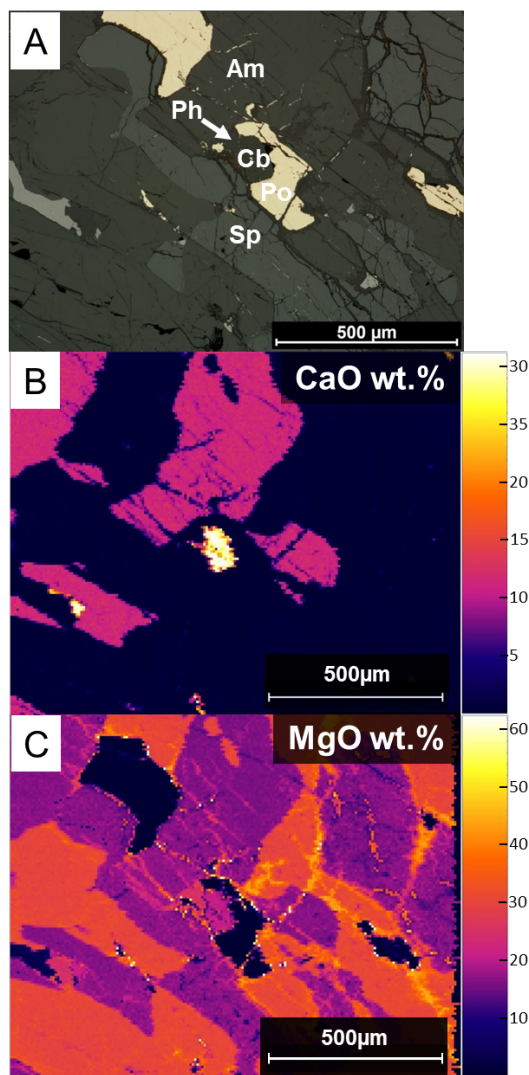


Figure 3. A: Reflected light image of a monophase pyrrhotite grain with a Mg-Ca carbonate grain embayment from sample I6B. B-C: Time-of-flight LA-ICP-MS elemental weight % maps analyzed with a 7 μm beam size. Yellow indicates the highest concentration measured for CaO (B) and MgO (C). Am = amphibole, Cb = carbonate, Po = pyrrhotite, Sp = spinel, Ph = phlogopite.

adjacent to sulfides (which may indicate late-stage carbonate precipitation) were documented by Sessa et al. (2017) and Blanks et al. (2020), but not observed in this study, possibly indicating more than one carbonate mineralization event. The absence of uniform relationships between sulfides and volatile-bearing phases suggests that their formation (or preservation) likely was not uniform throughout the pipe. Furthermore, it is noted that internal differentiation of sulfides and silicate caps (*cf.* Barnes 2019) remain to be fully investigated; however, our currently available data do not show any textural or compositional evidence for mineral-scale differentiation processes.

In contrast to a simple bubble transport model, several textural and geochemical observations appear to favour co-precipitation of sulfides, carbonates, and (metasomatic) silicates. For example, the enrichment of lithophile elements (Ca,

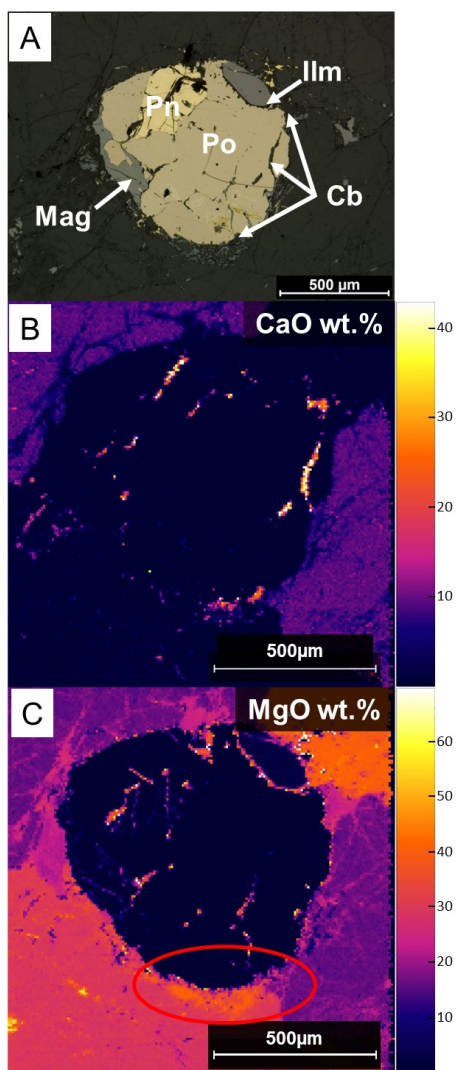


Figure 4. A: Reflected light image of a composite pyrrhotite-pentlandite bleb with accessory ilmenite, magnetite, and carbonate phases surrounding the bleb (center) from sample VMG1B. B-C: Time-of-flight LA-ICP-MS elemental weight % maps analyzed with a 7 μm beam size. Yellow indicates the highest concentration measured for CaO (B) and MgO (C). Am = amphibole, Cb = carbonate, Po = pyrrhotite, Mag = magnetite, Ilm = ilmenite.

Mg, Na, Al) in pyrrhotite and chalcophile elements (Cu, Ni, Fe, Pb) in carbonate phases indicates that the composition of sulfides and carbonates are controlled by the same geochemical process. This is further indicated by the occurrence of varying carbonate compositions (Ca-rich vs Mg- and Fe-rich). Carbonate inclusions in sulfides (Figs. 4B, 4C) have a composition similar to that of the rimming carbonates: this relationship cannot be explained with a simple bubble transport model as it is not physio-chemically compatible. Rather, it indicates that a carbon-rich fluid was present during sulfide ore formation.

The observations presented here possibly indicate co-exsolution of a carbonate phase and sulfide minerals from a S and CO₂ saturated fluid/melt. The findings from this study highlight the

need for more comprehensive research on the roles of volatile phases in the transport and deposition of S and metals in the deep lithosphere.

Acknowledgements

M. L. acknowledges support through the National Science Foundation (NSF) CAREER award #1944552 "Investigating the source, transport and deposition of economically important metals in the lower continental crust".

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