The Role of Arsenide Melts as Collectors of Platinum-group Elements in Ni-Cu Magmatic Sulfide Deposits

/ RUBÉN PIÑA* (1), FERNANDO GERVILLA (2), SARAH-JANE BARNES (3), LORENA ORTEGA (1), ROSARIO LUNAR (1, 4)

(1) Dpt. Cristalografía y Mineralogía. Universidad Complutense de Madrid. c/ José Antonio Novais 2. 28040, Madrid, Spain
(2) Dpt. Mineralogía y Petrología and Instituto Andaluz de Ciencias de la Tierra. Universidad de Granada-CSIC, Av. Fuentenueva s/n, 18002 Granada, Spain
(3) Sciences de la Terre, Université du Ùniversité, Chicoutimi, PQ G7H 2B1, Canada
(4) Instituto de Geociencias (UCM-CSIC), c/José Antonio Novais 2. 28040, Madrid, España.

INTRODUCTION

It is well known that the platinum-group elements (PGE: Os, Ir, Ru, Rh, Pd and Pt) concentrate into sulfide melts segregated from mafic-ultramafic magmas. As a consequence, the distribution of PGE in most magmatic sulfide deposits is mainly controlled by the distribution of base-metal sulfides crystallizing from sulfide melt (i.e., pyrrhotite, pentlandite and chalcopyrite), with PGE occurring in solid solution within pyrrhotite and pentlandite and/or as discrete platinum-group minerals (PGM; e.g., sulfides, arsenides, bismuthotellurides, tellurides) associated with them. However, in a number of As-rich, Ni-Cu sulfide ores, PGE are preferentially concentrated in the most As-rich ore zones, leaving the relatively As-poor, S-rich zones typically depleted in such metals (e.g., Ronda and Beni Bousera ultramafic massifs, Spain and Morocco respectively, Gervilla et al., 1996; Dundonald Beach South deposit, Canada, Hanley 2007; Rosie Nickel prospect, Australia, Godel et al. 2012). In these cases, PGE occur dissolved in trace amounts within arsenide and/or sulfarsenide minerals (e.g., nickeline NiAs, maucherite $Ni_{11}As_8$, gersdorffite NiAsS) formed from an arsenide melt previously segregated by immiscibility from a sulfide melt.

Several experimental studies have demonstrated that As-rich melts can segregate from sulfide melts over a wide range of temperatures scavenging the dissolved PGE (Helmy et al. 2013 and reference therein). However, there are few comprehensive studies quantifying the partition behaviour of PGE among arsenide and sulfide melts. Helmy's experimental study reports sulfide/arsenide partition coefficients (D) for Pt and Pd lower than 2×10^{-5} and 0.01, respectively, and Hanley (2007) and Godel et al. (2012) inferred in natural samples $D_{PGE}^{As/sulf}$ in the order of 10 to 100 and 25 to 400, respectively.

In this contribution, we present the partition coefficients recently determined by Piña et al. (2013) for PGE, Au, Ag, Bi, Te, Sb and Se between arsenide and sulfide melts in natural samples from the Amasined mineralization in Beni Bousera (Morocco) and the PGE distribution among arsenides and sulfides of the chromite-Ni arsenide (Cr-Ni) and sulfide-graphite (S-G) deposits from the Serranía de Ronda (Spain). These results highlight the strong affinity of PGE for arsenide phases.

PARTITION COEFFICIENTS OF PGE, Au, Ag, Se, Bi, Te and Sb BETWEEN ARSENIDE AND SULFIDE MELTS

The Amasined mineralization represents one of the few examples of liquid immiscibility between arsenide and sulfide melts observed in the nature (Gervilla et al., 1996) and thus constitutes an excellent natural laboratory to evaluate the partition coefficients of these elements between both melts. Maucherite crystallized from an As-rich melt coexists in equilibrium with pyrrhotite (fig. 1), pentlandite and chalcopyrite and all these minerals account for the bulk of PGE and chalcophile elements in the samples. By measuring the in situ contents of these elements in each mineral by LA-ICP-MS, Piña et al. (2013) determined that PGE, Au, Bi, Te and Sb are strongly compatible into arsenides, Ag is only weakly compatible and Se is moderately incompatible (Table 1).
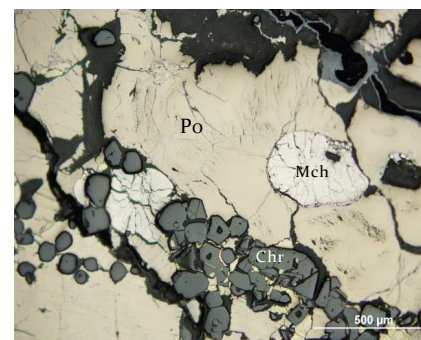

fig 1. Textural relationships between maucherite (Mch), chromite (Chr) and pyrrhotite (Po).

PGE DISTRIBUTION AMONG ARSENIDES AND SULFIDES FROM RONDA, SPAIN

The peridotite massifs of the Serranía de Ronda in the Betic Cordillera (Málaga) host two unusual types of magmatic mineralization: 1) Cr-Ni deposits composed of chromite and nickel arsenides (mainly, nickeline, maucherite and nickeliferous löllingite $FeAs_2$) that represent the crystallization products of an immiscible arsenide melt segregated from an As-rich sulfide melt and crystallized among early-crystallized chromites (fig. 2) and 2) S-G deposits consisting of Fe-Ni-Cu sulfides and graphite representing the crystallization of the remaining sulfide liquid.

The laser ablation ICP-MS analyses reveal that arsenides are enriched in all

	Os	Ir	Ru	Rh	Pt	Pd	Au	Ag	Se	Te	Bi	Sb
D$^{As/sulf}$	140	920	50	620	330	250	310	4	0.6	190	50	890
S.E.	30	500	10	230	200	80	200	2.1	0.1	40	10	260

Table 1. Partition coefficients (D) for PGE, Au, Ag, Se, Te, Bi and Sb between arsenide and sulfide melts determined by Piña et al. (2013) from their abundances in arsenide and sulfide minerals. S.E.: standard mean error.

---

* corresponding author: rpinagar@ucm.es

PGE, but especially in elements with the strongest affinity for the arsenide melt, including Ir, Rh and Pt. In contrast, Se and Ag (with the lowest affinities for the arsenide melt) are preferentially concentrated into the sulfide assemblage. Figure 3 shows that the distribution of PGE and trace elements between arsenide and sulfide phases (interpreted as having crystallized from an arsenide and sulfide melt, respectively) is in agreement with the partition coefficients estimated by Piña et al. (2013).
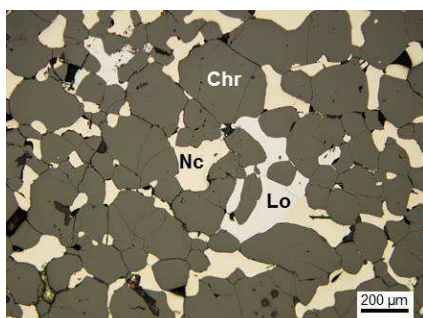

fig 2. *Nickeliferous löllingite (Lo) and nickeline (Nc) filling intergranular spaces between chromite grains (Chr) (Piña et al. 2014).*

CONCLUDING REMARKS

The observed partition behaviour of PGE among arsenide and sulfide melts underlines the importance of arsenide phases as efficient collectors of these noble metals in magmatic Ni-Cu sulfide deposits, highlighting that the best targets for PGE exploration may be the As-richest ore zones. A number of factors such as initial PGE and As content of sulfide melt, arsenide/sulfide melt ratio, efficient concentration of As-PGE-bearing minerals/melt and timing of arsenide melt segregation will notably influence the possible formation of an economic PGE-As-rich deposit.

Specifically, the timing of formation of arsenide melts is an important factor controlling the distribution of PGE. If arsenide melts segregate after extensive fractionation of monosulfide solid solution (mss), arsenide minerals become depleted in Os, Ir, Ru and Rh since these elements are previously concentrated into mss. Consequently, arsenide and sulfarsenide minerals become enriched only in Pt, Pd and Au which are incompatible into mss. In contrast, if arsenide melts segregate before the crystallization of monosulfide solid solution (mss) (~ 1100-1000ºC), they concentrate all PGE leaving the sulfide melt (and sulfide minerals) strongly depleted in such noble metals. The latter case is quite unusual because sulfide melts are usually poor in As. As-rich melts only form from sulfide melts moderately enriched in As (e.g. after assimilation of As-bearing crustal rocks) after considerable crystallization of mss. Thus, the residual melt left by the crystallization of mss from an As-rich sulfide melt becomes enriched in As as well as in all other chalcophile elements (e.g., Bi, Te, Sb) promoting As-saturation on cooling (Tomkins, 2012). Therefore, the early segregation of arsenide melts in Beni Bousera and Ronda implies an abnormal As-rich nature of the parental magmas.

Once formed, arsenide melts tend to migrate downward (they are denser than sulfide melts) and accumulate in the basal zones of magmatic sulfide deposits. The wetting behavior of arsenide melts against previously solidified sulfide minerals plays an important role in the effectiveness of concentration of arsenide melts. Recently, Tomkins (2010) has demonstrated that As-rich melts containing significant proportions of Pd and Pt and exceeding 0.2 % of the rock volume can wet mss and percolate downward through an interconnected network. Thus, the combination of gravitational accumulation and wetting behavior of arsenide melts can drive to the formation of As- and PGE-rich domains within major sulfide orebodies.

REFERENCES

Gervilla, F., Leblanc, M., Torres-Ruiz, J., Fenoll Hach-Alí, P. (1996): Immiscibility between arsenide and sulfide melts: a mechanism for the concentration of noble metals. Can Mineral., **34**, 485-502

Godel, B., González-Álvarez, I., Barnes, SJ., Barnes, S-J., Parker, P., Day, J. (2012): Sulfides and sulfarsenides from the Rosie Nickel Prospect, Duketon Greenstone Belt, Western Australia. Econ. Geol., **107**, 275-294

Hanley, J.J. (2007): The role of arsenic-rich melts and mineral phases in the development of high-grade Pt-Pd mineralization within komatiite-associated magmatic Ni-Cu sulfide horizons at Dundonald Beach South, Abitibi subprovince, Ontario, Canada. Econ. Geol., **102**, 305-317

Helmy, H.M., Ballhaus, C., Fonseca, R.O.C., Nagel, TJ. (2013): Fractionation of platinum, palladium, nickel, and copper in sulfide-arsenide systems at magmatic temperature. Contrib. Mineral. Petrol., **166**, 1725-1737

Piña, R., Gervilla, F., Barnes, S-J., Ortega, L., Lunar, R. (2013): Partition coefficients of platinum-group and chalcophile elements between arsenide and sulfide phases as determined in the Amasined sulfide-graphite mineralization (Beni Bousera, North Morocco). Econ. Geol., **108**, 935-951. DOI: 10.2113/econgeo.108.5.935

—, —, —, —, — (2014): Liquid immiscibility between arsenide and sulfide melts: evidence from a LA-ICP-MS study in magmatic deposits from Serranía de Ronda (Spain). Min. Dep. (in press)

Tomkins, A.G. (2010): Wetting facilitates late-stage segregation of precious metal-enriched sulfosalt melt in magmatic sulfide systems. Geology, **38**, 951-954
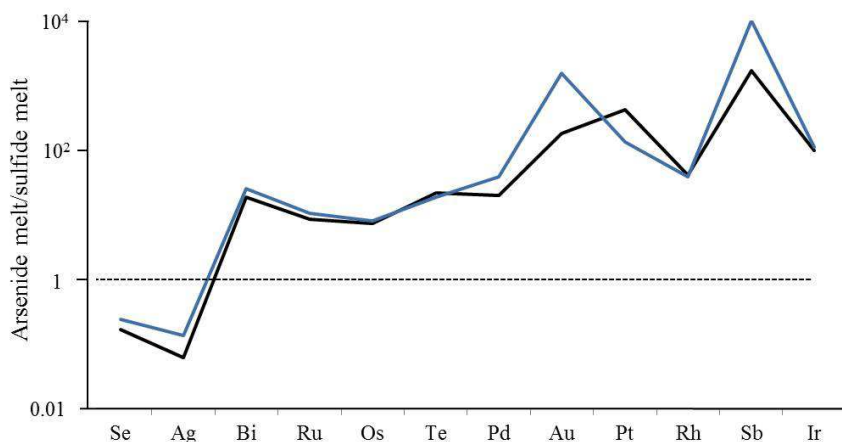
fig 3. *Profiles with the estimated trace element contents for arsenide melt normalized to the concentrations for sulfide melt. The arsenide melt compositions were calculated from in situ contents of individual minerals analyzed by LA-ICP-MS, assuming modal proportion of 85% nickeline-15% maucherite (blue line) and 90% nickeline-10% löllingite (black line) in two different sets of samples. The sulfide melt composition was calculated assuming a modal proportion of 80% pyrrhotite, 15% pentlandite and 5% chalcopyrite. The trace elements are ordered as a function of the partition coefficients estimated by Piña et al. (2013). The elements with values higher than 1 concentrated preferentially into the arsenide melt, whereas those with values lower than 1 concentrated preferentially into the sulfide melt. Pt, Rh and Ir values are probably higher than plotted because these elements occur in sulfides below their detection limits and these detection values were used in the calculation overestimating their abundances (Piña et al. 2014).*