

Partition of Platinum-Group Elements between arsenide and sulfide minerals in magmatic Ni-Cu sulfide systems

R. Piña¹, F. Gervilla², S.-J. Barnes³, L. Ortega¹, R. Lunar¹

¹ *Facultad de Geología, Universidad Complutense de Madrid, Spain*

rpinagar@geo.ucm.es

² *Dpto. Mineralogía and IACT (Universidad de Granada-CSIC) Granada, Spain*

³ *Sciences de la Terre, Université du Québec à Chicoutimi, QC G7H 2B1, Canada*

ABSTRACT. The partition coefficients of platinum-group elements (PGE) between arsenide and sulfide minerals ($D_{\text{PGE}}^{\text{As/sulf}}$) have been calculated by determining in situ concentrations of these elements by LA-ICP-MS in coexisting arsenide (maucherite) and sulfide (pyrrhotite, pentlandite and chalcopyrite) minerals from the Beni Bousera Cr-Ni mineralization (North Morocco). Maucherite contains significant amounts of all PGE (average values, 8.3 ppm Os, 25.8 ppm Ir, 7.5 ppm Ru, 8.6 ppm Rh, 61.7 ppm Pd and 7.5 ppm Pt), whereas sulfides have contents commonly below 0.2 ppm. With the exception of Pt, mass balance calculation indicates that arsenides and sulfides account for the bulk of PGE in the samples. The calculated $D_{\text{PGE}}^{\text{As/sulf}}$ reveal the strong affinity of PGE by arsenide minerals: $D_{\text{Ir}}^{\text{As/sulf}} = 923$, $D_{\text{Rh}}^{\text{As/sulf}} = 540$, $D_{\text{Pt}}^{\text{As/sulf}} = 325$, $D_{\text{Pd}}^{\text{As/sulf}} = 254$, $D_{\text{Os}}^{\text{As/sulf}} = 145$ and $D_{\text{Ru}}^{\text{As/sulf}} = 50$. The maucherite grains, which occur included within the sulfides (mostly pyrrhotite), can attribute to: 1) direct crystallization from sulfide melt before mss crystallization, or 2) crystallization from an arsenide melt segregated by immiscibility from a sulfide melt. Because of maucherite melts incongruently above 830°C, well below the temperature of crystallization of mss (around 1000°C), maucherite probably represents the crystallization product of droplets of arsenide melt and the calculated partition coefficients, the partition values of PGE between arsenide and sulfide melts.

1 INTRODUCTION

The distribution of PGE in magmatic sulfide deposits is typically controlled by the distribution of pyrrhotite, pentlandite and chalcopyrite (e.g., Barnes and Lightfoot 2005). However, in a number of As-rich Ni-Cu sulfide ores, PGE concentrate in the As-richest ore zones leaving the As-poor and S-rich ore zones relatively depleted in such noble metals (Gervilla et al. 1998; Hanley 2007; Dare et al. 2010; Godel et al. 2012). In these As-rich zones, PGE occur either as early crystallized, As-bearing platinum-group minerals from a sulfide melt (e.g., sperrylite, irarsite, hollingworthite) or dissolved in trace amounts within arsenide and/or sulfarsenide minerals (e.g., nickeline, maucherite, gersdorffite) formed from an arsenide melt. Several experimental studies have highlighted the preference of PGE by As-rich melts when these melts separate by immiscibility from a sulfide melt (Makovicky et al. 1990, 1992; Fleet et al. 1993; Gervilla et al. 1994; Tomkins 2010). However, the partition coefficients of these elements between both melts remain to date unknown. The only experimental study by Wood (2003) obtained a minimum $D_{\text{Pd}}^{\text{As/sulf}}$ of 34, whereas Hanley (2007) and Godel et al. (2012) inferred $D_{\text{PGE}}^{\text{As/sulf}}$ in the order of 10 to 100 and 25 to 400, respectively.

In this study, we have analyzed the in situ PGE contents by LA-ICP-MS in coexisting arsenide (maucherite) and sulfide (pyrrhotite, pentlandite and chalcopyrite) minerals from the Beni Bousera Cr-Ni mineralization. Because these phases account for the bulk of PGE in these samples (as indicated by the mass balance calculation), we employ these concentrations to estimate the partition coefficients of these elements between arsenide and sulfide minerals.

2 SAMPLE DESCRIPTIONS AND ANALYTICAL METHODS

The studied samples come from the Amasined Cr-Ni mineralization situated in the northern part of the Beni Bousera lherzolite massif, north Morocco. The mineralization consists of 20-30 meters long and up to one-meter thick lens of massive sulfides hosted by lherzolite rocks. The ore mineralogy comprises pyrrhotite, pentlandite, chalcopyrite, chromite and maucherite, with minor violarite, nickeline, members of the solid solution cobaltite-gersdorffite and graphite (Gervilla et al. 1996). Arsenides are concentrated in a 5-10 cm thick, basal zone along the footwall of the lens. Maucherite is by far the main arsenide. It mostly occurs as radially fractured, lobular or rounded globules within pyrrhotite (Fig. 1A) and along the contact between chromite and pyrrhotite commonly including early-formed chromite crystals (Fig. 1B). Rarely, thin rims of cobaltite-gersdorffite surround to maucherite (Fig. 1C), and nickeline occurs in the maucherite cores. The curved boundaries are not only frequent between maucherite and pyrrhotite but also between maucherite and pentlandite and chalcopyrite (Fig. 1D).

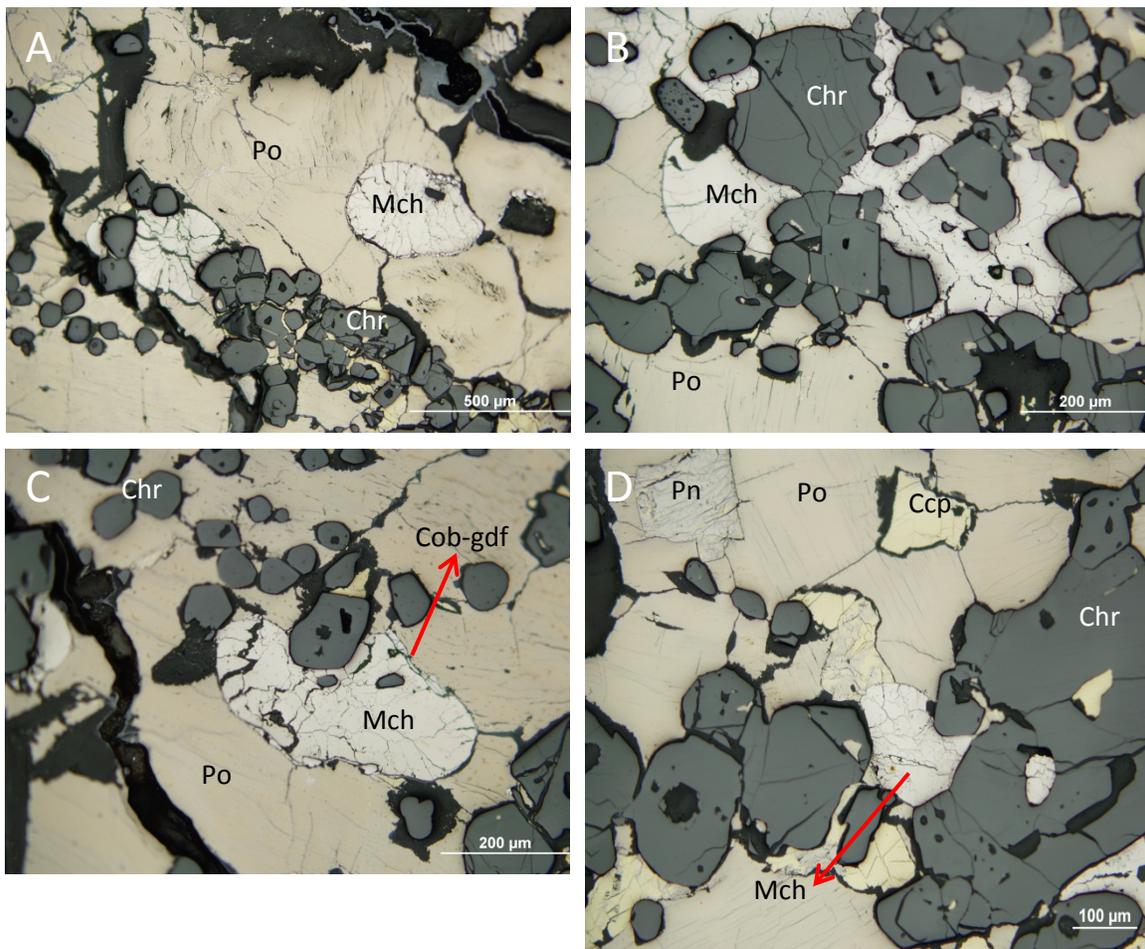


Figure 1. Microphotographs of reflected-light optical microscope showing: A-B. Textural relationships between maucherite (Mch), chromite (Chr) and pyrrhotite (Po); C. Globular maucherite surrounded by a thin rim of cobaltite-gersdorffite (Cob-gdf); D. Curved boundaries between maucherite and pyrrhotite and chalcopyrite (Ccp).

The PGE concentrations in maucherite, pyrrhotite, pentlandite and chalcopyrite were determined by LA-ICP-MS at LabMaTer in the Université du Québec à Chicoutimi (Canada) using an Agilent 7700x mass spectrometer with an Excimer 193nm Resonetics Resolution M-50 laser ablation probe. We did line scans across the grains using a beam of 55 μm , a laser frequency of 15 Hz and a speed

of laser displacement of 5 $\mu\text{m/s}$. ^{101}Ru was corrected for ^{61}Ni interference and ^{103}Rh and ^{105}Pd were corrected for $^{63}\text{Cu}^{40}\text{Ar}$ and $^{65}\text{Cu}^{40}\text{Ar}$, respectively.

3 RESULTS

The laser ablation analyses reveal that maucherite contains important amounts of all PGE (Table 1). In contrast, pyrrhotite, pentlandite and chalcopyrite are significantly depleted in these elements. PGE contents in chromite are invariably below detection limit (0.010-0.001 ppm).

Table 1. Average and standard deviation (in brackets) of PGE contents in arsenide and sulfide minerals from the Amasined mineralization, Beni Bousera

	^{189}Os	^{191}Ir	^{101}Ru	^{103}Rh	^{195}Pt	^{105}Pd
Maucherite	8.3 (2.6)	25.8 (11.6)	7.5 (2.4)	8.6 (4.6)	7.5 (8.4)	61.7 (14.3)
Pyrrhotite	0.059 (0.035)	0.033 (0.057)	0.138 (0.044)	0.014 (0.013)	0.027 (0.040)	0.060 (0.044)
Pentlandite	0.046 (0.021)	< 0.005	0.200 (0.109)	0.014 (0.026)	< 0.010	1.020 (1.177)
Chalcopyrite	0.058 (0.078)	0.033 (0.043)	0.214 (0.174)	0.095 (0.055)	< 0.010	0.120 (0.116)

Values in part per million. Number of analyzed grains for each mineral: 35 for maucherite, 20 for pyrrhotite, 13 for pentlandite and 8 for chalcopyrite. < below detection limit. In chalcopyrite, ^{108}Pd was used instead of ^{105}Pd to avoid Cu interference. ^{108}Pd was corrected for ^{108}Cd .

3.1 Partition coefficients of PGE between arsenide and sulfide minerals

Before calculating the partition coefficients, a mass balance calculation has been carried out to determine whether maucherite, pyrrhotite, pentlandite and chalcopyrite are the only carriers of PGE in the samples. For this calculation we have used the bulk PGE concentration of the samples, previously published by Gervilla et al. (1996), the average content in PGE and the weight fraction of each phase assuming that these are the only sulfide and arsenide minerals presents. This assumption is valid because nickeline and cobaltite-gersdorffite are very minor, being commonly absent in most samples. Mass balance calculation indicates that maucherite and sulfides account for the totality of Os (185.4%), Ir (113.4%), Ru (99.4%), Rh (108.4%) and Pd (92.1%), being maucherite the main carrier of Ir (95.7%), Os (84.9%), Rh (81.5%) and Pd (54.6%) and pyrrhotite the main host for Ru (54.8%). The sum of percentage of Os in arsenide and sulfide minerals is high probably due to loss of Os during whole rock analyses. In contrast, Pt is low, 26.3%, due to the presence of Pt-bearing microinclusions within maucherite (revealed by erratic ICP-MS signal with well-defined Pt peaks) formed probably by exsolution. Thus, maucherite originally hosted more Pt than the obtained value and its calculated partition coefficient represents a minimum estimation.

The $D_{\text{PGE}}^{\text{As/sulf}}$ is given by $C_i^{\text{As}}/C_i^{\text{Sulf}}$, where C_i^{As} corresponds to the content of element i in maucherite and C_i^{Sulf} corresponds to the content of element i in sulfide melt. C_i^{Sulf} is given by $(F_{\text{Po}}C_i^{\text{Po}})/F_{\text{sulf}} + (F_{\text{Pn}}C_i^{\text{Pn}})/F_{\text{sulf}} + (F_{\text{Ccp}}C_i^{\text{Ccp}})/F_{\text{sulf}}$, being C_i^{Po} , C_i^{Pn} and C_i^{Ccp} the average contents of the element i in pyrrhotite, pentlandite and chalcopyrite, respectively, and F_{sulf} the total weight fraction of sulfides defined as the sum of the weight fraction of pyrrhotite (F_{Po}), pentlandite (F_{Pn}) and chalcopyrite (F_{Ccp}). The $D_{\text{PGE}}^{\text{As/sulf}}$ are highly compatible with the arsenide phases: 923 for Ir, 540 for Rh, 325 for Pt, 254 for Pd, 145 for Os and 50 for Ru.

4 CONCLUDING REMARKS

The origin of maucherite is key for the meaning of the calculated partition coefficients. The maucherite grains may represent either solid phases having growth directly from the sulfide melt or droplets of an arsenide melt segregated by immiscibility due to As saturation of the sulfide melt such as suggested by Gervilla et al. (1996). In the first case, the coefficients would represent the partitioning behaviour of PGE between arsenide phenocrysts and sulfide melt and in the second, the partitioning between arsenide and sulfide melt. Because maucherite grains are typically located within pyrrhotite, these grains had to crystallize before mss formation, i.e. above 1000°C. However, maucherite forms typically by a peritectic reaction that replaces to nickeline at around 830°C, after

the crystallization of nickeline from a Ni-As liquid at around 900°C (Yund, 1961). These temperatures are well below the temperature of mss crystallization, so we suggest that maucherite likely represents droplets of an immiscible arsenide melt segregated before/during mss crystallization and the obtained values are thus the partition coefficients of PGE between arsenide and sulfide melts.

Independently to the maucherite origin, the calculated partition coefficients underline the importance of arsenide minerals as collectors of PGE in magmatic Ni-Cu sulfide deposits, demonstrating that the best targets for PGE exploration may be the As-richest ore zones. A number of factors such as initial PGE content of sulfide melt, arsenide/sulfide melt ratio, efficient concentration of As-PGE-bearing minerals/melt and timing of arsenide melt segregation will influence notably in the possible formation of an economic PGE-As-rich deposit. For example, regarding timing of segregation of the arsenide melt, if the arsenide melt segregates before mss crystallization, then it will be able to scavenge the whole of PGE initially dissolved into the sulfide melt, including Os, Ir, Ru and Rh. In contrast, if the arsenide melt segregates after mss crystallization, then the arsenide melt would be only enriched in Pd and Pt, and depleted in Os, Ir, Ru and Rh, because these PGE would be previously concentrated into the crystallizing mss due to their highly compatible behaviour into mss.

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