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IMMISCIBILITY BETWEEN ARSENIDE AND SULFIDE MELTS: A MECHANISM FOR THE CONCENTRATION OF NOBLE METALS

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ABSTRACT

Evidence of immiscibility between arsenide and sulfide melts can be observed locally in the magmatic ores associated with the Carratraca (Serranía de Ronda, southern Spain) and Beni Bousera (northern Morocco) lherzolite massifs. They occur in the form of Fe–Ni–Cu sulfide ores containing arsenide globules. The globules are interpreted as droplets of an immiscible arsenide melt with a composition close to that of maucherite – nickeline, suspended in the sulfide melt. Both arsenide melts depleted in As with respect to maucherite and those with As contents higher than nickeline tend to dissolve increasing amounts of Co, Fe and S. The above lines of evidence support the genetic model for the chromite – Ni arsenide ores and the sulfide – graphite ores described in the Serranía de Ronda and Beni Bousera lherzolite massifs. The model considers that the early cyrstallization of chromite collected most Os, Ir and Ru, while gold and the remaining PGE were partitioned into an immiscible arsenide melt, leaving a sulfide melt depleted in PGE and Au. Thus, although chromite – Ni arsenide ores show higher PGE (0.9–5 ppm) and Au (3–18 ppm) contents than Fe–Ni–Cu sulfide – graphite ores (0.18–0.42 ppm PGE and 0.03–0.07 ppm Au), sulfide ores containing arsenide globules of aproximate maucherite composition display intermediate noble metals abundances (0.6–1.07 ppm PGE and 0.07–0.45 ppm Au). These data suggest that PGE and Au have a higher affinity for arsenide melts than for sulfide melts, remarking their importance as collectors of noble metals in nature.

Keywords: Ni-arsenide melts, sulfide melts, immiscibility, platinum-group elements, mechanism of concentration, Ronda peridotite, Spain, Beni Bousera peridotite, Morocco.

SOMMAIRE

Des preuves de l'immiscibilité des liquides arsenié et sulfuré peuvent être observées localement dans les minéralisations magmatiques des massifs lherzolitiques de Carratraca (Serrania de Ronda, Espagne) et de Beni Bousera (Rif, Maroc). On y trouve des minerais massifs de sulfures Fe–Ni–Cu renfermant des globules d'arséniures. Ces globules sont interprétés comme des goutelettes d'un liquide arsenié immiscible, de composition nickélifère (mauchérite – nickeline), en suspension dans le liquide sulfuré. Qu'ils soient relativement pauvres en arsenic (par rapport à la mauchérite) ou plus riches en arsenic que la nickeline, ces liquides arseniés tendent à s'enrichir en Co, Fe et S. Ces observations confirment le modèle génétique proposé pour les minéralisations à chromite – arséniures de Ni et sulfures (Fe–Ni–Cu) – graphite des massifs lherzolitiques de la Serrania de Ronda et de Beni Bousera. Dans ce modèle, nous proposons que la chromite cristallise précocement en piégeant Os–Ir–Ru (alliages, sulfures); l'or et les éléments du groupe du platine (EGP) restant sont préférentiellement incorporés dans la phase arseniée liquide qui s'individualise dans le bain silicaté; il en résulte que la phase sulfurée liquide présente dans le bain silicaté reste pauvre en or et en EGP. Ceci explique pourquoi les minerais à chromite et arséniures de nickel sont riches en EGP (0.9–5 ppm) et or (3–18 ppm), alors que ceux à sulfures (Fe–Ni–Cu) – graphite sont pauvres en EGP (0.18–0.42 ppm) et en or (0.03–0.07 ppm). Les minerais de sulfures contenant des globules d'arséniures, à composition proche de celle de la mauchérite, montrent des teneurs intermédiaires en métaux précieux (0.6–1.07 ppm d'EGP et 0.07–0.45 ppm d'Au). Ces données font penser que les éléments du groupe du platine et l'or ont une plus forte affinité pour les liquides arseniés que pour les liquides sulfurés; elles soulignent le rôle de collecteurs de métaux précieux que peuvent jouer dans la nature les liquides arseniés.

Mots-clés: liquide à arseniure de nickel, liquide sulfuré, immiscibilité, éléments du groupe du platine, mécanisme de concentration, péridotite de Ronda, Espagne, péridotite de Beni Bousera,

INTRODUCTION

Sulfide ores of Fe, Ni and Cu in mafic–ultramafic complexes have long been interpreted as the consequence of segregation of an immiscible sulfide melt from a sulfur-saturated silicate melt (*e.g.*, Naldrett 1989). This mechanism also is considered to be the most efficient process for the collection and concentration of platinum-group elements (*e.g.*, Naldrett 1989). Recently, increasing evidence has appeared for the role of arsenic in the concentration of PGE in both magmatic and hydrothermal environments (Cabri & Laflamme 1984, Johan *et al.* 1989, 1990, Edwards 1990, Gervilla & Leblanc 1990, Leblanc *et al.* 1990, Merkle 1992, Ohnenstetter *et al.* 1992, Watkinson & Ohnenstetter 1992, Chen *et al.* 1993, Ripley & Chryssoulis 1994, among others), along with advances in experimental work on As- and PGE-containing systems (Cabri *et al.* 1975, Skinner *et al.* 1976, Makovicky *et al.* 1990, 1991, 1992, Fleet *et al.* 1993, Gervilla *et al.* 1994).

Although arsenic is generally concentrated by late hydrothermal processes, it can also be concentrated at the magmatic stage. An example of the latter situation has been described in spessartite at Laucane (Montagne Noire, southern France) by Béziat *et al.* (1993, 1996) and in lherzolite massifs at Serranía de Ronda (southern Spain) and Beni Bousera (northern Morocco), where two types of genetically related magmatic mineralization are known: 1) *Chromite – Ni arsenide ores (Cr–Ni ores)* are composed of chromite and nickel arsenides (mainly nickeline with some nickeliferous löllingite, maucherite and westerveldite), with orthopyroxene or cordierite or both (Oen 1973, Oen *et al.* 1979, Gervilla & Leblanc 1990). These ores show high gold contents (between 3 to 35 ppm) and up to 2 ppm PGE (Leblanc *et al.* 1990, Torres-Ruiz *et al.* 1991). 2) *Sulfide – graphite ores (S–G ores)* consist of pyrrhotite, pentlandite and chalcopyrite, with minor chromite, variable amounts of graphite, with plagioclase and phlogopite (Gervilla & Leblanc 1990). These ores are depleted in precious metals by a factor of ten with respect to the Cr–Ni ores (Leblanc *et al.* 1990).

Gervilla & Leblanc (1990) have proposed that these types of ore result from the early crystallization of chromite, followed by the segregation of an immiscible As-, S-rich melt. They also proposed that the segregation of an arsenide melt then led to the high-temperature crystallization of the Ni arsenides (Oen *et al.* 1971, Gervilla & Rønsbo 1992) among the chromite grains and the formation of a S-rich residual liquid. During this process, noble metals were proposed largely to collect in the arsenide melt and to concentrate in Cr–Ni ores, which led to the formation of an Au- and PGE-depleted sulfide melt.

The above metallogenic context provided us with a good opportunity to study the behavior of both arsenide and sulfide melts and their role in the segregation and fractionation of gold and PGE. For that purpose, we have studied selected samples collected from the Amasined occurrence in northern Morocco and from the Los Jarales mining district in southern Spain. In both localities, magmatic arsenides and sulfides coexist. In the present paper, we describe the textural relationships between arsenides and sulfides that are considered a consequence of immiscibility of a minor (Ni,As) melt in the host (Fe,Ni,Cu) sulfide melt. We stress the potential importance of this process for the concentration of noble metals in an As-bearing melt.

GEOLOGICAL SETTING AND OCCURRENCE

The Amasined occurrence and the Los Jarales mining district are located, respectively, in the Beni Bousera and Carratraca lherzolite massifs in northern Morocco and Serranía de Ronda, southern Spain, respectively. Both belong to a distinct set of Alpine-type peridotite massifs scattered in the westernmost part of the Betico-Rifean Alpine belt (Fig. 1). These massifs represent portions of lithospheric mantle emplaced at high temperature in the continental crust. From radiometric dating, the crustal emplacement of the massifs took place at around 21 m.y. (Priem *et al.* 1979, Zindler *et al.* 1983).

The Beni Bousera and Carratraca lherzolite massifs occur within high-grade metamorphic rocks (Loomis

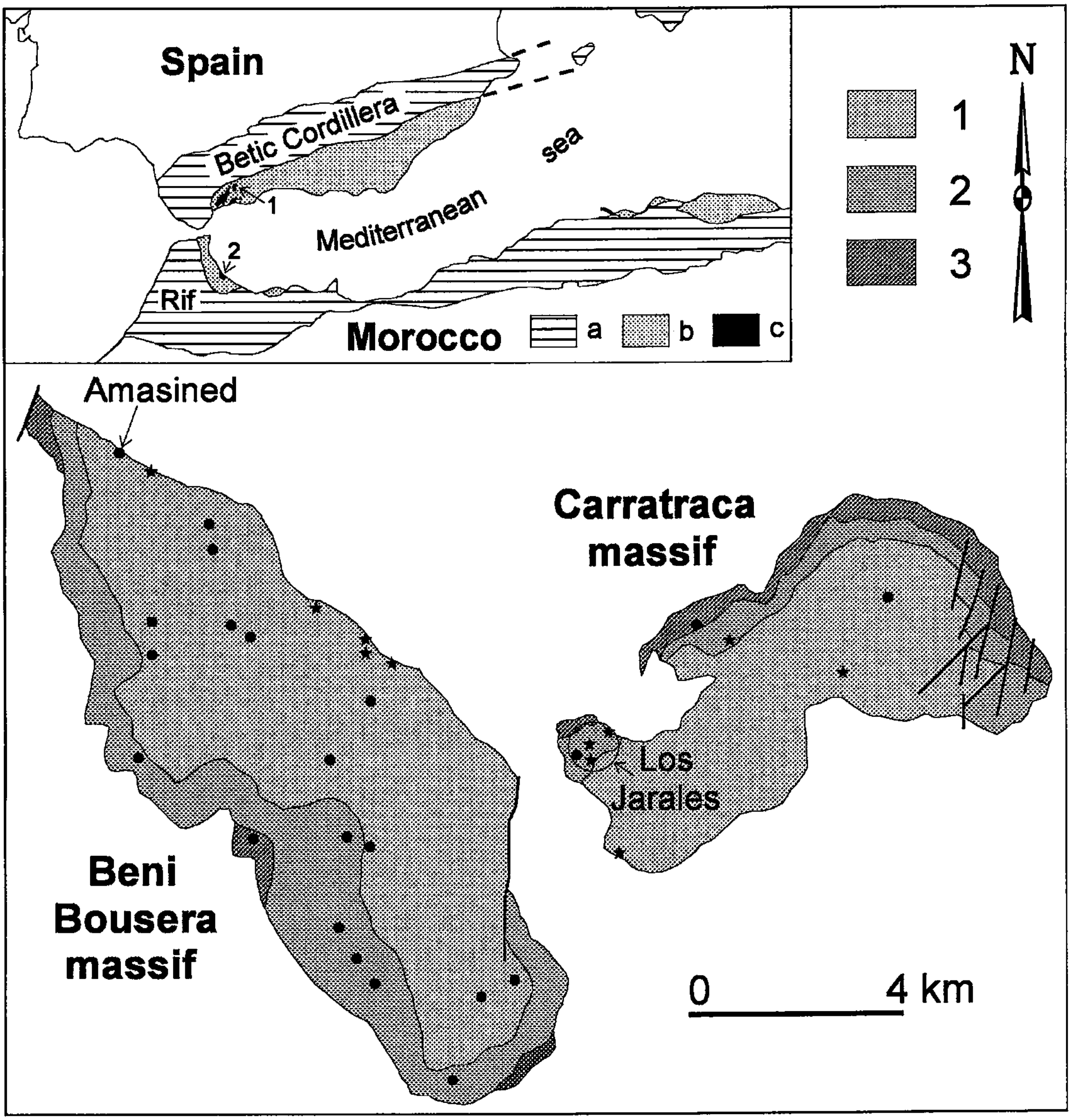

FIG. 1. Location of the Betico-Rifean lherzolite massifs in the Western Mediterranean alpine belt. a: External Zones, b: Internal Zones, c: ultramafic massifs, 1: Carratraca massif, and 2: Beni Bousera massif. The distribution of ore occurrences related to the mineral-facies zonation of the Carratraca (from Soto & Gervilla 1991) and Beni Bousera (from Reuber *et al.* 1982) lherzolite massifs also are shown. Black stars: occurrences of Cr–Ni ore, black circles: occurrences of S–G ore. Zoning of the lherzolite massifs: 1: Seiland subfacies of the spinel lherzolite facies, 2: Ariegite subfacies of the spinel lherzolite facies, 3: garnet lherzolite facies. This zoning is based on the work of Obata (1980), who defined the garnet lherzolite facies in the Ronda peridotite from the equilibrium between forsterite and pyrope in lherzolite, and the spinel lherzolite facies from the equilibrium between forsterite and spinel in lherzolite. The two subfacies of the spinel lherzolite facies were differentiated by the paragenetic assemblage in the pyroxenite layers present within spinel lherzolite. In the Ariegite subfacies, pyrope + diopside + enstatite coexist, and in the Seiland subfacies, spinel + diopside + enstatite coexist.

1972, Torres-Roldán 1981, Tubía 1985), and are made up of lherzolite and harzburgite with various types of pyroxenite layers. They show an incomplete zoning of mineral facies from the garnet lherzolite facies to the Ariegite subfacies of the spinel lherzolite facies, and then to the Seiland subfacies of the spinel lherzolite facies (Kornprobst 1969, Reuber *et al.* 1982, Soto & Gervilla 1991, Targuisti 1994). The existence of true garnet lherzolite facies rocks in Beni Bousera remains controversial, because Kornprobst (1969) ascribed the presence of garnet in the external zone of the peridotite body to an extreme boudinage of garnet pyroxenite layers, and Reuber *et al.* (1982) identified only small areas consisting of pyroxene-poor garnet lherzolite (garnet dunite) (Fig. 1).

The zonation of the Betico-Rifean lherzolite massifs was interpreted as the result of dynamic cooling of a portion of the mantle during its ascent from approximately 100 km to the base of the crust (Obata 1980, Kornprobst & Vielzeuf 1984). However, recent studies in the Ronda peridotite massif have shown that its present petrological and geochemical features are the consequence of the superimposition of a large-scale system of magma percolation onto an old, metamorphosed lithospheric protolith during the later stages of its mantle evolution in a suprasubduction environment (Remaïdi 1993, Gervilla & Remaïdi 1993, Garrido 1995, Van der Wal & Bodinier 1996), just before its tectonic emplacement in the crust. Samples of garnet lherzolite from the ancient lithosphere (not affected by the late percolation event) contains anomalously high levels of As [up to 4.8 ppm in sample OJ–223 of Torres-Ruiz *et al.* (1991), from the Ojén Massif], whereas some samples of non-percolated garnet pyroxenite contain graphitized diamond (Pearson *et al.* 1989, Davies *et al.* 1993) and primary nickel arsenides (Lorand 1987), and they show geochemical features compatible with an origin as high-pressure crystal segregation in magma conduits, the batches of magma being derived from a subducted oceanic lithosphere (Pearson *et al.* 1993, Garrido 1995). Pearson *et al.* (1993) also considered this oceanic lithosphere hydrothermally altered and sediment-bearing. During the late percolation of melt, the infiltrated melt reacted with the host rocks, giving rise to depleted peridotite (or pyroxenite equilibrated with the percolating melt: Garrido *et al.* 1993, Garrido 1995) and differentiated melts (Kelemen 1990). Incompatible elements (including S, As, C and noble metals), and other more compatible elements like Cr, were transported preferentially downstream, toward the percolation or reaction front (Navon & Stolper 1987, Godard *et al.* 1995), thus producing Cr-bearing, S- and As-enriched melts capable of forming the peculiar ores present in these massifs. Note that the most As-enriched ores in the Ronda peridotite all occur downstream from the percolation or reaction front defined by Van der Wal & Bodinier (1996).

The Amasined occurrence

This occurrence is located in the lowermost part of a cliff on the northern exposure of the Beni Bousera lherzolite massif (Fig. 1). It consist of a lens, 20–30 meters long and up to one meter thick, of massive sulfides oriented more or less parallel to the foliation of the enclosing spinel lherzolite, which trends NW–SE and dips SW. In detail, the sulfide lens is clearly discordant with the foliation of the peridotite. The mineralization occurs along a main fault-zone oriented NW–SE, then is cut by late faults that trend N160°E. Disseminated mineralization also occurs in the brecciated peridotite.

The ore association in the main sulfide lens consists of hexagonal pyrrhotite, pentlandite, violarite, chalcopyrite, talnakhite, nickeline, maucherite, westerveldite, cobaltite, chromite, graphite and minor molybdenite and melonite, with partly chloritized phlogopite as a silicate component. Secondary amphiboles, chlorite and magnetite are locally present along the N160°E faults.

Sulfides represent more than 80 vol.% of the ore minerals. This fraction consists of pyrrhotite crystals with scarce flame-like exsolution lamellae of pentlandite, and with intergranular violarite and aggregates of chalcopyrite – talnakhite. The other ore minerals are distributed through the sulfide lens with a remarkable upward transition: 1) arsenides are restricted to the lower 5 cm along the footwall of the orebody; above this arsenide-bearing zone, there are only minor sulfarsenides; 2) chromite crystals are scattered mainly in the lower and middle part, and 3) graphite, molybdenite and phlogopite are more abundant toward the top of the orebody.

Although arsenides are localized in a narrow basal zone, they display important textural and mineralogical variability. Along the lower contact, arsenides occur as round to lobate globules within the sulfide mass or along the border of the chromite crystals (Figs. 2A, B). These globules either show a core of nickeline rimmed by radially fractured maucherite, with westerveldite along the cracks (Figs. 2A, B, 3C), or consist of fractured maucherite only. Locally, these globules include scarce crystals of a PGE-free, Bi-rich Ni telluride, probably melonite. Above this lower zone, the arsenide globules tend to be more spheroidal, and they are composed of highly fractured maucherite (Fig. 2C). In the upper part of the arsenide zone, maucherite globules are surrounded by subidiomorphic crystals of nickeliferous cobaltite (Fig. 2D). These maucherite – cobaltite globules grade upward to aggregates of arsenides with an increasing ratio of cobaltite to maucherite.

Chromite occurs as disseminated grains or as chromite-rich sigmoidal lenses showing flow textures, essentially in the lower half part of the mineralized zone. The relatively large (>0.5 mm) crystals of chromite contain abundant polyphase inclusions (up to 50% of the grain) dominated by the association phlogopite – albite – quartz – (sulfides) (Leblanc & Gervilla 1994). The chemical composition of chromite (51–42 wt% Cr_2O_3, 23–15 wt% Al_2O_3, 5–2 wt% MgO, 31–25 wt% FeO, 1.5–0.9 wt% V_2O_3, 0.95–0.35 wt% ZnO and 0.71–0.23 wt% TiO_2) is within the range of

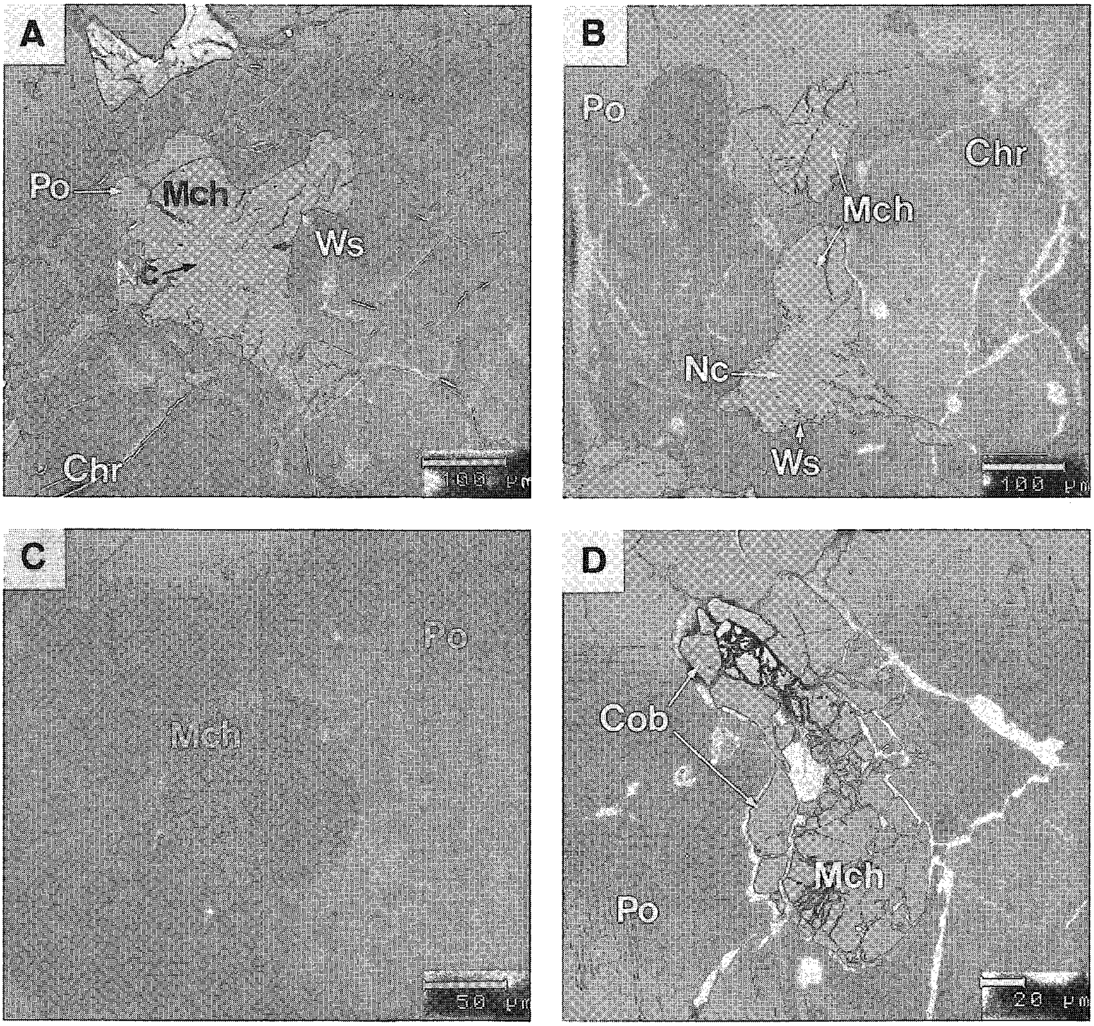

FIG. 2. Morphology of different arsenide globules from Amasined. Abreviations: Mch: maucherite; Nc: nickeline; Ws: westerveldite; Cob: cobaltite; Po: pyrrhotite and Chr: chromite.

values reported for chromite in the S–G ores by Gervilla & Leblanc (1990). The presence of some Zn in the chromite rather than as Zn sulfides is consistent with an orthomagmatic origin of the ore (Naldrett 1979).

Phlogopite (more or less transformed to chlorite), and minor graphite and molybdenite are slightly more abundant toward the hanging wall of the orebody, although they are also found as tabular crystals (rarely forming clusters of crystals) disseminated throughout the sulfide lens.

Secondary hydrothermal alteration occurred along the N160°E faults, resulting in: a) the corrosion of chromite and the development of a magnetite rim and of magnetite crystals around the chromite grains, b) the leaching of sulfides, and c) the crystallization of a complex association of amphibole and chlorite (± berthierine).

Los Jarales mining district

Los Jarales is a small mining district located in the southwestern part of the Carratraca massif. Several deposits of chromite – Ni arsenide ore (San Juan, El Inglés, and Pozo Moreno) and sulfide veins (Los Pobres) occur there (Fig. 1). Although the mineral association of Cr–Ni ores is well preserved, the S–G ores are strongly weathered to graphite-rich ores

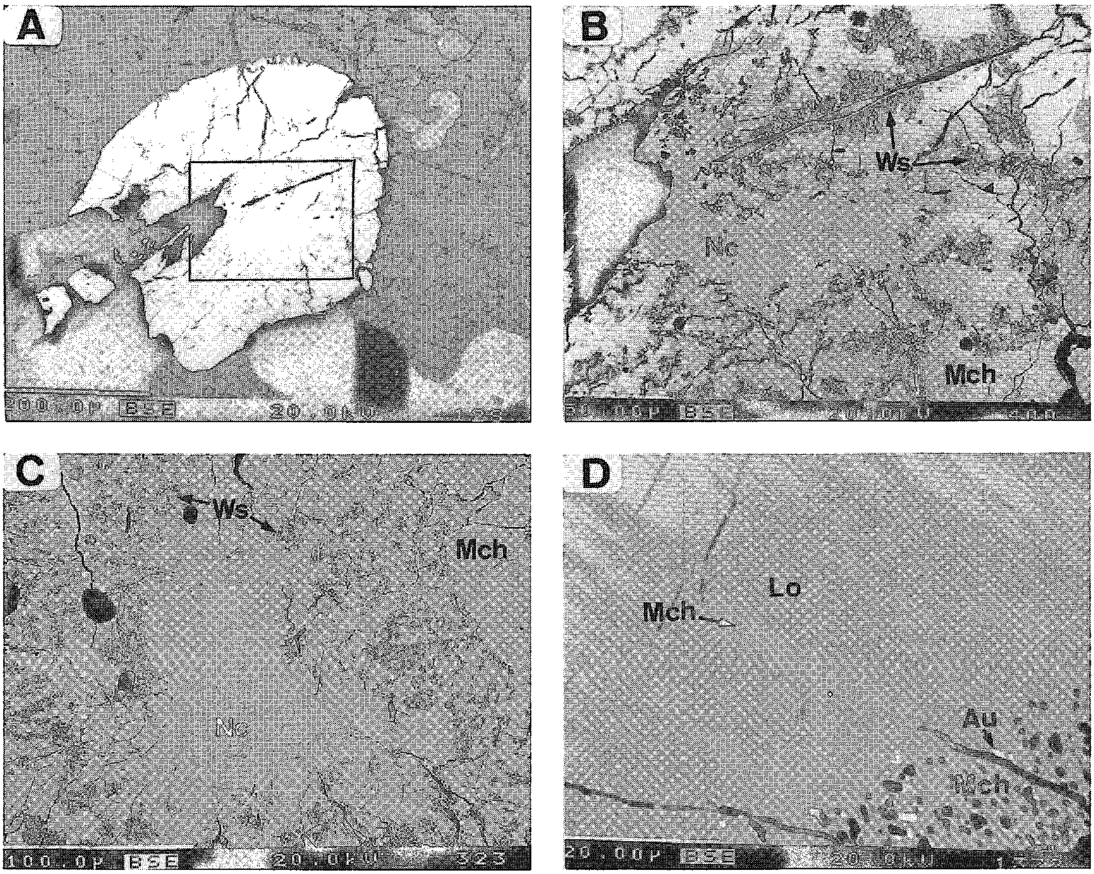

FIG. 3. A. Morphology of a maucherite – nickeline – westerveldite globule from Los Jarales (white) included in pyrrhotite (dark gray); the square marks the area shown in B. B. Texture of the core of the globule from A, showing the relationships among nickeline (Nc), maucherite (Mch) and westerveldite (Ws). C. Texture of the core of another globule from Amasined. D. Detail of a löllingite-bearing globule, showing the löllingite – maucherite intergrowths and the contact between these intergrowths and the late maucherite. The latter shows abundant minute inclusions of gold (white).

containing disseminated, corroded crystals of chromite and traces of Fe–Ni–Cu sulfides and Ni arsenides (Gervilla 1990). The only fresh sample (a polished section) in which we have found coexisting arsenides and sulfides comes from the Rewald collection from Heidelberg and was given to us by Professor L. Fontboté. This sample (Re–6190) contains a complex association of minerals, including chromite, pyrrhotite, nickeline, maucherite, westerveldite, nickeliferous löllingite, Co- and Fe-rich gersdorffite, chalcopyrite, cubanite, native gold and scarce molybdenite. Note that there is no Ni-sulfide (pentlandite) in this As-rich sulfide ore.

Nickel arsenides occur as round to lobate globules (Fig. 3A). Their composition is very variable; the following types occur: 1) globules of maucherite, 2) globules of nickeline, and 3) composite globules including a nickeline core rimmed by maucherite, containing westerveldite along radial fractures or with a thin and discontinuous corona of Co- and Fe-rich gersdorffite (Figs. 3A, B). In the latter type of globules, nickeline shows exsolution lamellae of pyrrhotite; inclusions of gold may be present also, especially where the ratio nickeline:maucherite is very high. All these globules coexist with globules rich in nickeliferous löllingite and aggregates consisting of nickeliferous löllingite, maucherite, nickeline, pyrrhotite and native gold. In spite of textural variations, the presence of lamellar intergrowths of nickeliferous löllingite and maucherite, surrounded by late maucherite, is noteworthy (Fig. 3D). Abundant minute grains of gold are present along the contacts between the löllingite – maucherite intergrowths and the late maucherite (Fig. 3D); gold also occurs at the contacts between nickeline and löllingite, and within maucherite.

CHEMISTRY

Analytical methods

Selected arsenides and sulfarsenides were analyzed with a CAMECA SX50 electron microprobe at the Technical Services of the University of Granada. The analyses were performed at 20 kV and with a beam current of 20 nA, using $CuFeS_2$, GaAs, NiS and Co metal as standards. Wavelengths employed were $SK\alpha$, $AsL\beta$, $FeK\alpha$, $NiK\alpha$ and $CoK\alpha$. Our analytical results are in good agreement with previous data reported from the same ores, performed with a different microprobe and different analytical conditions (Oen *et al.* 1971, Gervilla & Rønsbo 1992).

Whole-rock ore samples were analyzed by X-Ray Assay Laboratories Ltd., Don Mills, Ontario. The procedure involves a fire-assay preconcentration, followed by neutron activation. The detection limits are 1 ppb for Au, Pd, Pt, Ru, Rh and Ir, and 3 ppb for Os. The latter is the most volatile PGE and was probably partly lost during preconcentration processes, resulting in lower values. Detection limits increase for samples with high arsenic contents, which require a more elaborate procedure, including a second nickel sulfide fire assay after disolution of the first NiS button, and then concentration in resin. Precision and accuracy are stronly dependent on the "nugget effect" and on the small size of some samples.

Modal proportion of the different globules were calculated using an image analyzer from scanned photographs because the fineness of the maucherite – westerveldite and maucherite – löllingite intergrowths did not allow for mineral separation.

TABLE 1. CHEMICAL COMPOSITION OF THE VARIOUS PHASES IN GLOBULES FROM AMASINED (AM) AND SAMPLE Re-6180 (RE)

			weight percent						atomic proportions					
Sample	mineral	n	S	As	Fe	Ni	Co	Total	S	As	Fe	Ni	Co	Me/(As+S)
AM-1	Nc	3	0,19	54,66	0,07	43,98	0,50	99,39	0,01	0,98	0,00	1,00	0,01	1,03
	Mch	2	0,19	47,04	0,54	51,47	0,41	99,65	0,07	7,81	0,12	10,91	0,09	1,41
	Ws	1	0,42	54,61	34,11	8,34	0,54	98,02	0,02	0,97	0,81	0,19	0,01	1,03
AM-2	Mch	8	0,33	46,85	0,48	51,20	0,37	99,22	0,13	7,80	0,11	10,89	0,08	1,40
	Cob	8	19,21	44,50	4,33	10,55	21,13	99,73	0,99	0,99	0,13	0,30	0,59	0,52
AM-3	Nc	3	0,27	54,76	0,09	43,95	0,51	99,59	0,01	0,98	0,00	1,00	0,01	1,03
	Mch	4	0,24	47,60	0,15	51,67	0,44	100,09	0,09	7,87	0,03	10,91	0,09	1,39
AM-4	Mch	9	0,32	46,94	0,28	51,89	0,37	99,80	0,12	7,77	0,06	10,97	0,08	1,41
	Cob	3	19,25	44,54	4,70	10,86	20,35	99,70	1,00	0,99	0,14	0,31	0,57	0,51
AM-5	Nc	5	0,21	54,59	0,08	43,97	0,50	99,35	0,01	0,98	0,00	1,00	0,01	1,03
	Mch	3	0,17	47,08	0,17	51,29	0,43	99,15	0,07	7,86	0,04	10,94	0,09	1,40
	Ws	3	0,73	53,92	34,14	8,86	0,55	98,21	0,03	0,95	0,81	0,20	0,01	1,04
RE-1.1	Mch	4	0,04	47,64	0,55	52,07	0,51	100,81	0,02	7,83	0,12	10,93	0,11	1,42
	Ws	2	0,09	55,93	28,99	15,29	0,92	101,22	0,00	0,97	0,67	0,34	0,02	1,06
	Gd	7	18,37	46,18	9,50	17,97	8,38	100,40	0,95	1,02	0,28	0,51	0,24	0,52
RE-1.2	Mch	6	0,35	47,17	1,66	48,99	2,47	100,64	0,13	7,73	0,37	10,25	0,51	1,42
	Po	1	39,64	0,00	59,15	0,27	0,20	99,25	1,07	0,00	0,92	0,00	0,00	0,86
	Lo	6	0,48	70,62	15,23	8,89	4,40	99,62	0,03	1,94	0,56	0,31	0,15	0,52
RE-2.2	Nc	3	0,10	55,17	0,57	44,35	0,40	100,59	0,00	0,97	0,01	1,00	0,01	1,04
	Mch1	1	0,10	47,63	1,14	51,71	0,40	100,98	0,04	7,81	0,25	10,82	0,08	1,42
	Mch2	6	0,33	47,36	1,62	48,56	2,63	100,49	0,13	7,78	0,36	10,19	0,55	1,40
	Po	1	39,56	0,00	59,11	0,84	0,16	99,66	1,07	0,00	0,92	0,01	0,00	0,87
	Lo	8	0,47	70,24	14,76	9,11	5,23	99,80	0,03	1,93	0,54	0,32	0,18	0,53
RE-3.1	Nc	2	0,06	55,27	0,46	44,17	0,41	100,36	0,00	0,98	0,01	1,00	0,01	1,04
	Mch	2	0,03	47,72	0,44	52,23	0,42	100,85	0,01	7,84	0,10	10,96	0,09	1,42
	Gd	2	17,25	46,48	8,75	19,11	7,75	99,34	0,91	1,05	0,27	0,55	0,22	0,53
RE-3.3	Nc	2	0,06	55,22	0,56	43,87	0,54	100,25	0,00	0,98	0,01	0,99	0,01	1,04
	Mch	2	0,06	47,55	0,82	51,55	0,39	100,37	0,02	7,85	0,18	10,86	0,08	1,41

Symbols: Nc nickeline, Mch maucherite, Ws westerveldite, Cob cobaltite, Gd gersdorffite, Po pyrrhotite, Lo löllingite. The compositions quoted are the result of n analyses. The entries listed in the Sample column are all globules.

The arsenide globules

The chemical composition of arsenides and sulfarsenides in different globules from Amasined and sample Re–6190 (Los Jarales) are listed in Table 1. *Nickeline* displays distinct compositions: S-bearing and Fe-free in that from Amasined, and S-free and Fe-bearing in that from Los Jarales, where the nickeline contains small lamellar inclusions of pyrrhotite [probably exsolution lamellae along the (0001) planes of the host nickeline] and shows a slightly high ratio of metal to non-metal.

Maucherite associated with nickeline, westerveldite, cobaltite and gersdorffite shows a nearly homogeneous chemical composition, with minor amounts of sulfur, iron and cobalt, ranging between 0.03 and 0.33 wt% S, 0.15 and 0.82 wt% Fe, and 0.37 and 0.51 wt% Co. In löllingite-bearing globules and aggregates, the two texturally different varieties of maucherite also show distinct chemical compositions in terms of Fe and Co contents. The thin lamellae intergrown with the nickeliferous löllingite correspond to $(Ni_{10.82}Fe_{0.25}Co_{0.08})_{\Sigma 11.15}As_{7.81}S_{0.04}$, whereas maucherite enveloping the nickeliferous löllingite – maucherite intergrowths contain more Fe (up to 2.16 wt%) and Co (up to 3.12 wt%). The average formulae of the two aggregates of this type analyzed are $(Ni_{10.25}Fe_{0.37}Co_{0.51})_{\Sigma 11.13}As_{7.73}S_{0.13}$ and $(Ni_{10.19}Fe_{0.36}Co_{0.55})_{\Sigma 11.10}As_{7.78}S_{0.13}$.

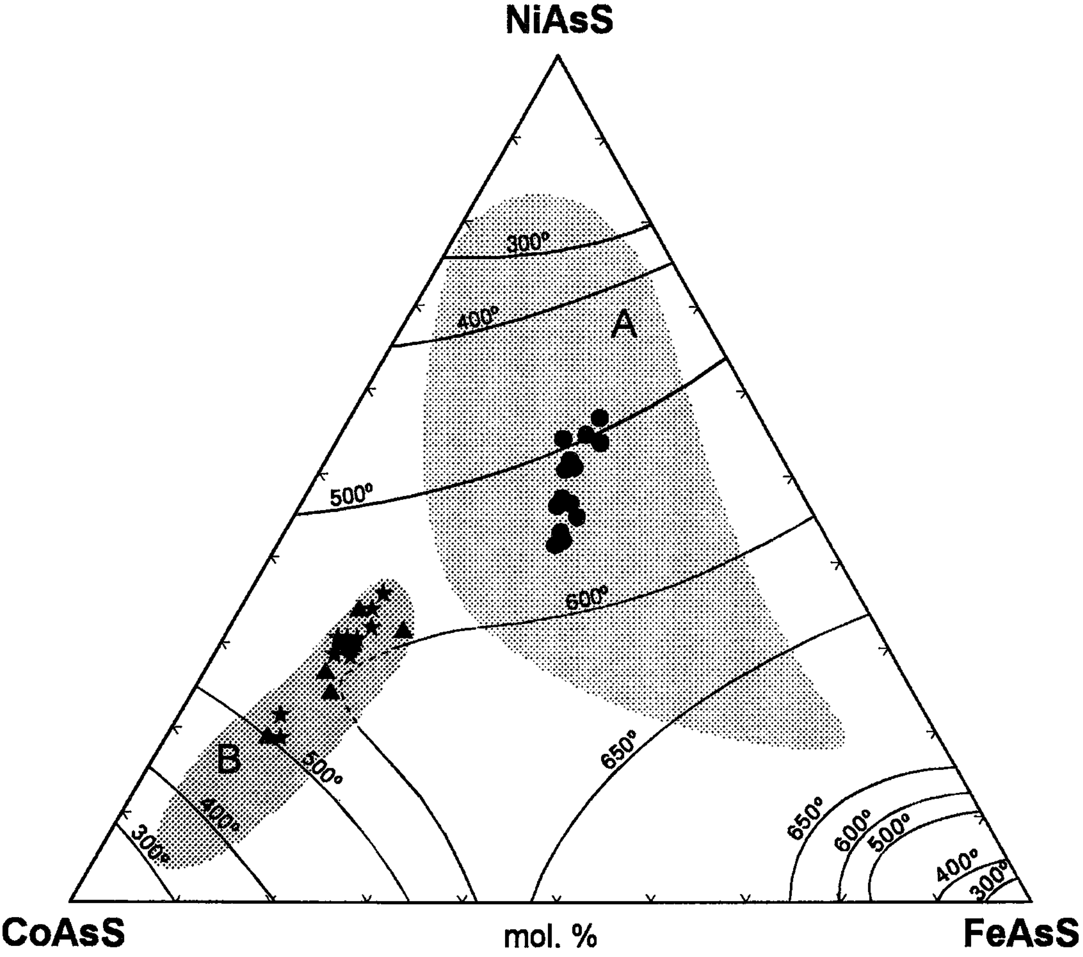

FIG. 4. Plot of the analyzed sulfarsenides with reference to the solvus in the condensed system CoAsS–NiAsS–FeAsS at 300°, 400°, 500°, 600° and 650°C (Klemm 1965). Black circles: gersdorffite from sample Re–6190, black stars: cobaltite from the lower arsenide-rich zone at Amasined, black triangles: cobaltite from a maucherite – cobaltite aggregate above the lower arsenide-rich zone at Amasined. For comparison, we have also shaded the compositional fields of Ni–Co–Fe sulfarsenides in Cr–Ni ores (A) (Gervilla & Rønsbo 1992) and S–G ores (B) (Gervilla, unpubl. data).

Westerveldite from sample Re–6190 is much richer in Ni and poorer in Fe [$(Fe_{0.67}Ni_{0.34}Co_{0.02})_{\Sigma 1.03}As_{0.97}$] than that from Amasined [$(Fe_{0.81}Ni_{0.20}Co_{0.01})_{\Sigma 1.02}As_{0.96}S_{0.02}$]; it resembles the composition of westerveldite from La Gallega (Cr–Ni ores), for which Oen *et al.* (1972) gave the average formula $(Fe_{0.635}Ni_{0.400}Co_{0.015})_{\Sigma 1.05}As_{1.00}$. The composition of westerveldite from Amasined is much closer to that described by Sizgoric & Duesing (1973), from a locality near the Birchtree mine, Thompson, Manitoba. These authors gave as its average formula $(Fe_{0.73}Ni_{0.32}Co_{0.01})_{\Sigma 1.06}As_{1.00}$.

The chemical composition of *sulfarsenides* plots in two clearly distinctive fields within the 500°C region of immiscibility in the system CoAsS – NiAsS – FeAsS (Fig. 4). Gersdorffite from sample Re–6190 is rich in Fe and Co, with a composition ranging between 41 and 58 mol.% NiAsS, 23 and 30 mol.% FeAsS, and 17 and 30 mol.% CoAsS. This composition falls within the compositional field of sulfarsenides from Cr–Ni ores (Oen *et al.* 1971, Gervilla & Rønsbo 1992). Cobaltite from Amasined is mainly rich in Ni with some Fe, having a composition between 50 and 72 mol.% CoAsS, 20 and 36 mol.% NiAsS, and 11 and 18 mol.% FeAsS. This compositional range overlaps the field of sulfarsenides from S–G ores. In both localities, sulfarsenides are zoned, with their ratio Co/(Co + Ni + Fe) increasing toward the contact with

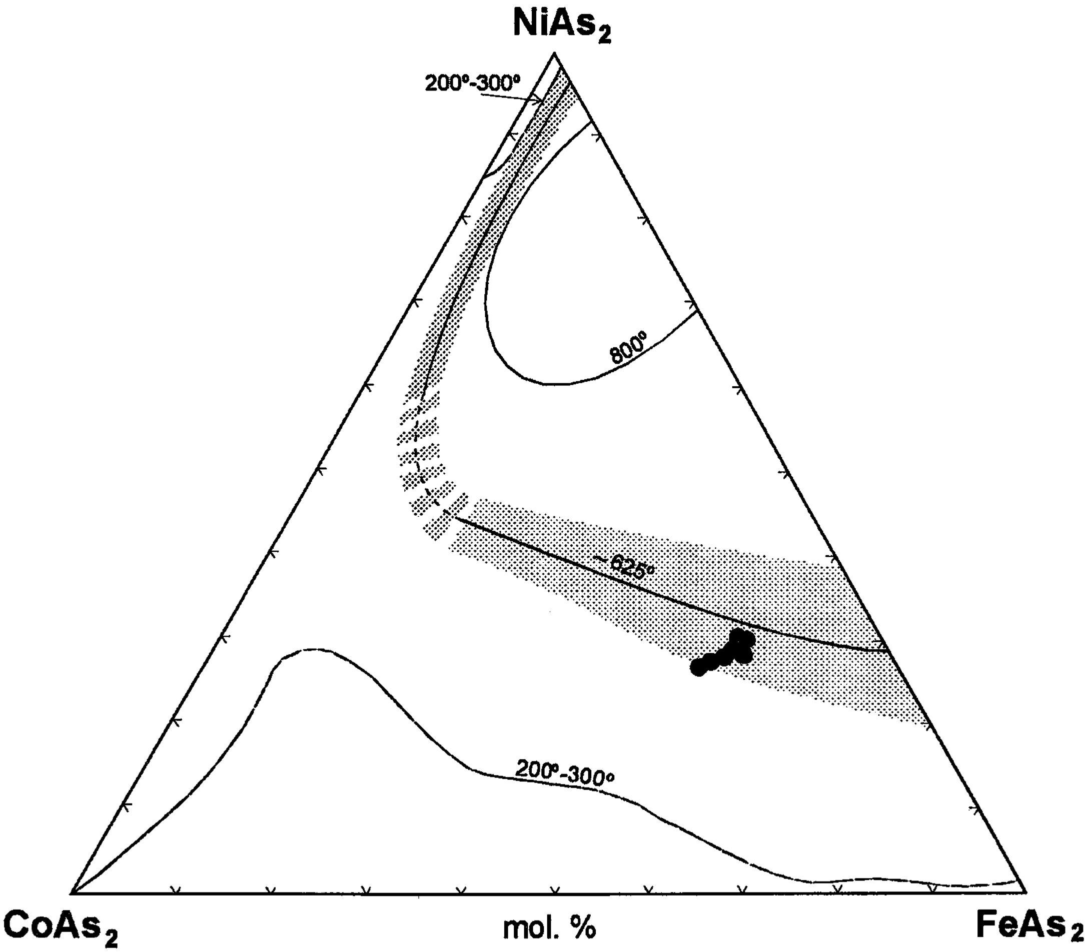

FIG. 5. Chemical composition of the analyzed diarsenides in the system $CoAs_2$–$NiAs_2$–$FeAs_2$. We have also represented the estimated solvus at 200°–300°C (Radcliffe & Berry 1968), at 625°C (Gervilla & Rønsbo 1992), and the experimentally determined extent of the immiscibility region at 800°C (Roseboom 1963). The shaded area shows the extent of the compositional field of Ni–Co–Fe diarsenides in Cr–Ni ores from the Betico-Rifean ultramafic massifs (Gervilla & Rønsbo 1992).

TABLE 2. BULK CHEMICAL COMPOSITION OF THE SULFARSENIDE-FREE GLOBULES LISTED IN TABLE 1

Sample	S	As	Fe	Ni	Co	Total
AM-1	0,24	49,07	7,67	41,47	0,44	98,89
AM-3	0,29	50,14	9,29	39,33	0,48	99,53
AM-5	0,16	48,58	4,05	46,13	0,50	99,42
AM-6	0,28	47,02	0,30	51,90	0,37	99,87
Re-1.2	1,02	48,82	4,86	43,19	2,61	100,50
Re-2.2	1,49	59,77	10,39	24,84	3,73	100,22
Re-3.1	0,14	51,28	3,87	44,63	0,51	100,43
Re-3.3	0,14	50,86	6,41	42,58	0,53	100,52
Re-4.1	0,09	55,11	0,64	44,15	0,43	100,42

In this table, we have included the globules AM-6 and Re-4.1, which contain, respectively, only maucherite and nickeline, and the globule Re-3.1, which shows only a small crystal of gersdorffite attached to its boundary. Data are quoted in wt%.

TABLE 3. CONCENTRATION OF NOBLE METALS AND ARSENIC IN WHOLE-ROCK SAMPLES

Sample	Os	Ir	Ru	Rh	Pt	Pd	Au	As
K5 (*)	400	620	1000	240	1500	1400	18000	37,10
O6811 (*)	16	150	490	65	460	610	8000	16,20
O6613 (*)	18	190	420	62	430	550	9200	15,60
O6643 (*)	68	210	390	91	410	540	15000	12,80
RO9 (*)	110	170	270	49	310	330	3700	10,10
LG50 (*)	51	133	420	59	320	370	9500	12,00
LG33 (*)	38	118	300	36	270	310	7900	9,20
RO14 (*)	56	120	210	35	250	260	3400	5,80
RO25	82	130	140	38	190	220	230	2,35
RO26	35	110	290	29	87	73	450	1,52
AM2b	50	135	147	44	183	512	94	0,19
AM2c	32	92	140	45	182	437	78	0,18
EG2 (#)	9	13	23	10	25	116	52	0,04
EG6 (#)	11	18	30	12	62	54	40	0,03
I4 (#)	11	20	36	16	77	267	68	0,02
I5 (#)	8	16	26	8	3	140	32	0,01

Two samples listed are from Amasined (AM2b, AM2c), and two samples are from Los Pobres, Los Jarales (RO25, RO26). Eight samples from Cr-Ni ores (*) and from S-G ores (#) (Leblanc et al. 1990, Torres-Ruiz et al. 1991) have been listed for comparison. The samples are listed in order of decreasing As content (quoted in wt%). The concentrations of the noble metals are quoted in ppb.

the enclosing pyrrhotite. This zonation is especially marked in the globule AM–2 (Fig. 2D, Table 1), where this ratio varies from 0.56 to 0.70 in a single crystal.

Nickeliferous löllingite from sample Re–6190 is relatively homogeneous: 51–55 mol.% $FeAs_2$, 27–31 mol.% $NiAs_2$ and 14–21 mol.% $CoAs_2$. This composition overlaps the field of the diarsenides from Cr–Ni ores in the system $CoAs_2$–$NiAs_2$–$FeAs_2$; the field of diarsenides may represent, according to Gervilla & Rønsbo (1992), the approximate position of the solvus at around 625°C (Fig. 5).

Whole-globule compositions have been calculated for ten different globules by taking into account the modal proportions of the different arsenides and their mineral chemistry. The results are listed in Table 2. There are no important compositional variations among the investigated globules. The composition of most of the arsenide globules is in the interval between 48 and 52 wt% As, and between 39 and 46 wt% Ni, with minor Fe (between 3 and 6 wt%). The löllingite-

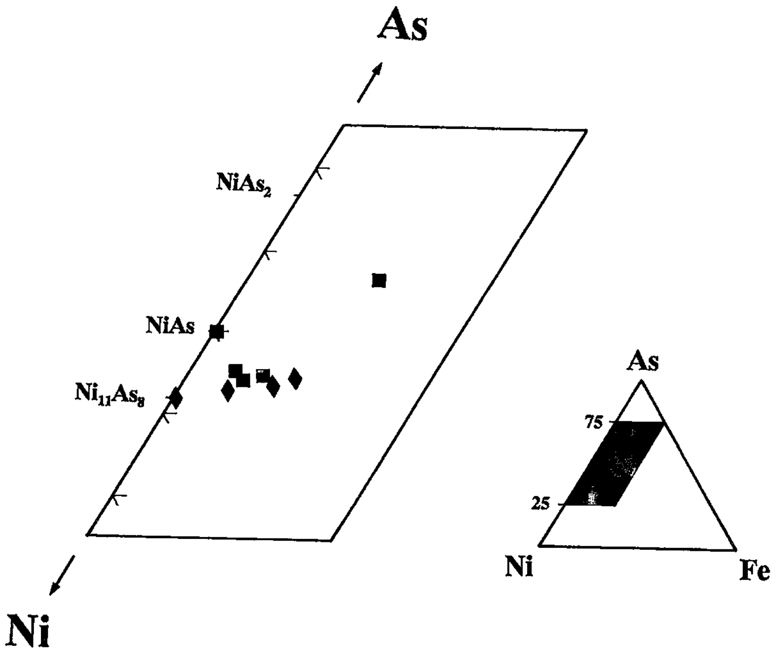

FIG. 6. Bulk composition of the arsenide globules listed in Table 2, with reference to the system Ni–As–Fe. Black diamonds: Amasined; black squares: sample Re–6190.

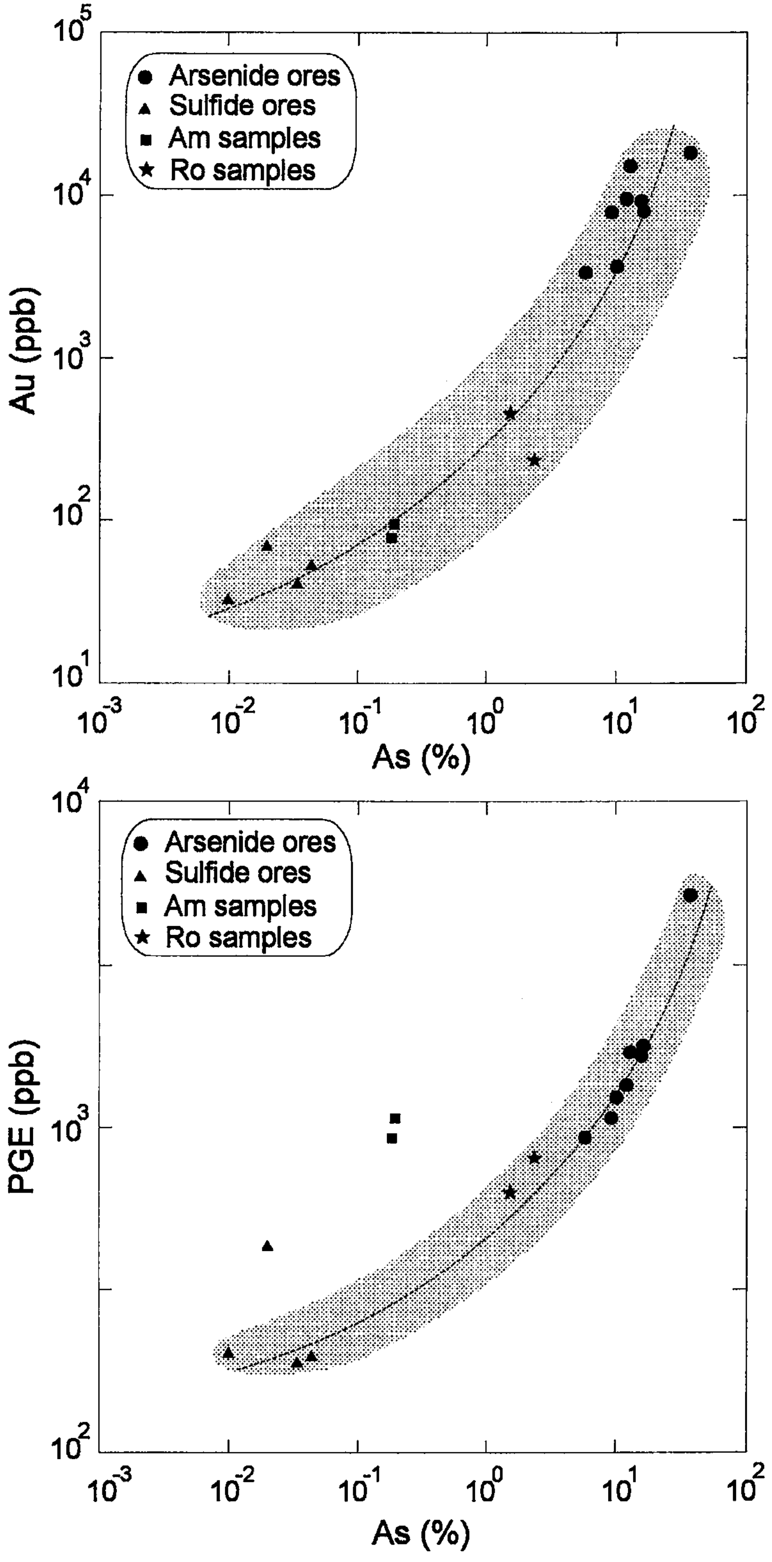

FIG. 7. Plot of concentrations of Au and PGE (total) *versus* As from Cr–Ni ores and S–G ores (Leblanc *et al.* 1990, Torres-Ruiz *et al.* 1991) from Los Pobres (Los Jarales) and Amasined (Table 3).

containing aggregates show higher As and Fe contents. In Figure 6, we have plotted the calculated compositions in the system Ni–As–Fe. This diagram shows that where the ratio As/Ni of the arsenide globules is high, these tend to contain more iron. Arsenic also is correlated with sulfur, which varies from 0 to 1.5 wt %.

Whole-rock noble-metal contents

The noble metal and As contents of two arsenide-bearing samples from Amasined and two samples from Los Pobres (an altered arsenide-bearing S–G mineralized sample from Los Jarales), together with

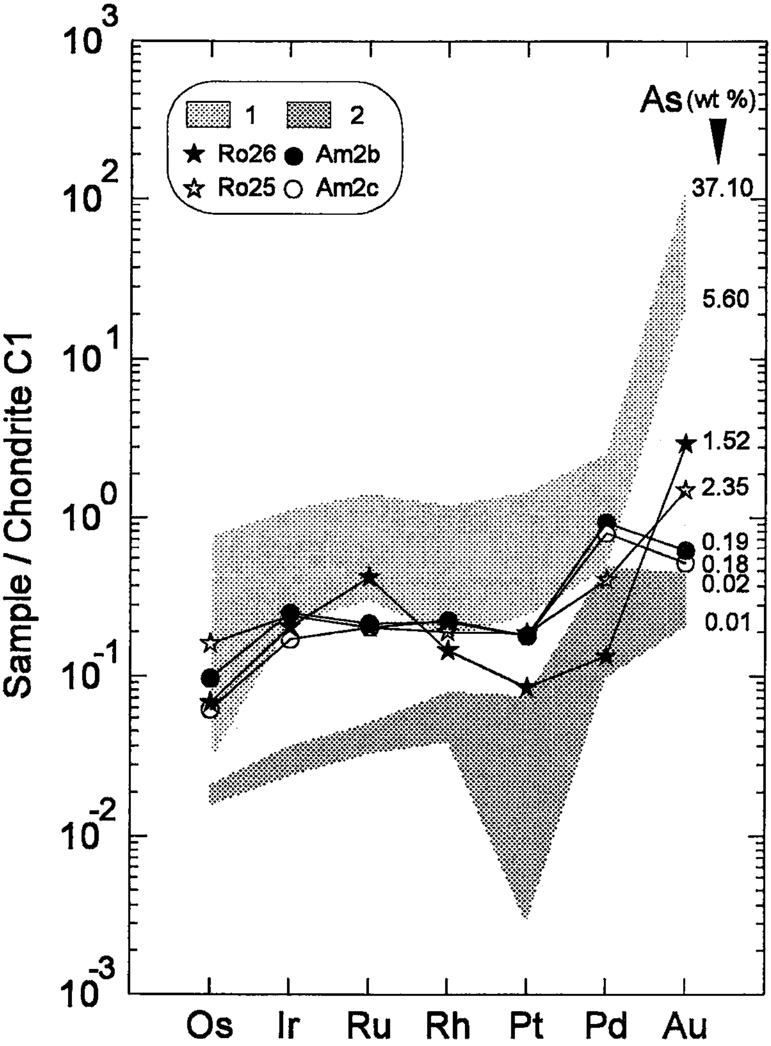

FIG. 8. Chondrite-normalized patterns of platinum-group elements for the analyzed samples from Amasined (Am2b and Am2c) and Los Pobres (Los Jarales) (samples Ro25 and Ro–26). The shaded areas represent: 1) Cr–Ni ores and 2) S–G ores from the Betico-Rifean lhezolite massifs. At the right side of the figure, we have also represented the As content (wt%) of the samples and the minimum and maximum As contents of the analyzed Cr–Ni and S–G ores (data from Leblanc *et al.* 1990 and Torres-Ruiz *et al.* 1991, Table 3).

eight samples from Cr–Ni ores and four from S–G ores (Leblanc *et al.* 1990, Torres-Ruiz *et al.* 1991) are listed in Table 3. Samples from Amasined and Los Pobres have noble-metal contents between those of the Cr–Ni ores (0.9–5 ppm PGE, 3–18 ppm Au) and S–G ores (0.18–0.42 ppm PGE, 0.03–0.07 ppm Au, on average) from the various Betico-Rifean lherzolite massifs (Fig. 7). This figure also shows a striking positive correlation between concentrations of noble metals and of As in the different types of ores. It is interesting to note that grains of gold are present only in the arsenic-rich globules.

The chondrite-normalized patterns of the two samples from Amasined (Am2b and Am2c in Fig. 8) partly overlap the lower part of the field of Cr–Ni ores and show a positive slope from Os to Pd, with two slight negative anomalies in Pt and Au, resembling the shape of the field of S–G ores. The sample RO–25 (containing small amount of maucherite) shows the same pattern, but with a positive anomaly in Au similar to that in the patterns of Cr–Ni ores. The pattern of sample RO–26 (more altered than RO–25) shows a slight positive anomaly in Ru and negative anomalies in Pd and Pt; it contains more Au and less As than RO–25. This variation may result from alteration.

INTERPRETATION OF ORE TEXTURES AS THE CONSEQUENCE OF IMMISCIBILITY BETWEEN ARSENIDE AND SULFIDE MELTS

The mineral association and chemistry of the ores described above confirm the genetic link between Cr–Ni ores and S–G ores. The magmatic origin of these ores was discussed in detail in a previous contribution (Gervilla & Leblanc 1990); consequently, the peculiar textures reported here should be interpreted in the context of the magmatic evolution of arsenide and sulfide melts. However, a similar association of Ni arsenides, Ni sulfarsenides and Ni sulfides has been described recently in the Thompson mine (Thompson Nickel Belt, Manitoba) by Chen *et al.* (1993), who considered this association formed from hydrothermal reworking of previous Ni sulfide ores. In their model, the noble metal- and As-rich ores were attributed to a late event of low-temperature (250°–300°C) hydrothermal alteration. The authors stressed the role of Cl-rich fluids in the concentration of the noble metals.

Comparing the mineralogical and chemical data reported in this paper with those for the Thompson mine, many differences can be observed, pointing to an orthomagmatic rather than a hydrothermal origin of the arsenide-bearing sulfide ores at Amasined and Los Jarales:

1. The sulfide lens at Amasined is hosted by relatively fresh peridotite, which shows extensive alteration only along late faults, whereas at the Thompson mine, the ores occur in metapelite and granitic pegmatite associated with alteration assemblages. At Los Jarales, the host peridotite is more serpentinized than at Amasined, although this alteration event corresponds to late regional serpentinization.
2. The morphology of most arsenide globules described in this paper can be compared with that of the sulfide globules reported in basalts (*cf.* Czamanske & Moore 1977), which was considered a case of immiscibility of a sulfide melt in a basaltic melt. On the contrary, Ni arsenides and sulfarsenides from Thompson mine occur as late, cross-cutting veins.
3. Cobaltite and gersdorffite reported here exhibit chemical compositions that fall within the 500°C immiscibility region in the system CoAsS–NiAsS–FeAsS, showing that these sulfarsenides crystallized at higher temperatures and equilibrated on cooling broadly between 600° and 500°C. This is in agreement with the composition of nickeliferous löllingite from sample Re–6190 and in contrast to the composition of gersdorffite from the Thompson mine. The latter is consistent with a lower temperature (250°–300°C) estimated by Chen *et al.* (1993) for the formation of the As-rich ores.
4. If the extreme fractionation of Pd from Pt at Thompson mine ores is considered as evidence for fluid involvement in the concentration of PGE (Chen *et al.* 1993), then the low Pd/Pt ratio of the samples analyzed in this study (ranging between 0.84 and 2.80) further corroborates the orthomagmatic concentration of the PGE. It is also interesting to note that processes of low-temperature alteration at Los Jarales (samples from Los Pobres) produce impoverishment of both Pt and Pd.

In addition to the above lines of evidence, preliminary sulfur isotope data, obtained by mean of an ion microprobe at Nancy (France), show that two samples from the central part of the Amasined orebody exhibit δ^{34}S values of 1.4 and 0.7‰, and exsolution lamellae of sulfides in nickeline from Los Jarales show δ^{34}S values of –1.0‰. These isotopic compositions clearly indicate a magmatic origin of sulfur from a mantle source, in both deposits.

The observed ore textures at Amasined and in sample Re–6190 can therefore be interpreted by referring to the model of segregation of droplets of immiscible sulfide liquids from silicate melts. At Amasined, the mineralogical and textural variations of the ore could be explained by considering a dynamic model based on several influxes of chromite-bearing sulfide magma, the first one being rich in As. The following influxes of sulfide melt were progressively impoverished in As. Thus, the segregation of an immiscible arsenide melt from the sulfide melt took place only in the earlier batches of magma, whereas in the later batches, As remains dissolved in the sulfide melt (Fleet *et al.* 1993), then forming sulfarsenides on cooling. According to Fleet *et al.* (1993), small amounts of As, Te and Bi lower the freezing point of the sulfide melt. Hence, high As contents may prevent

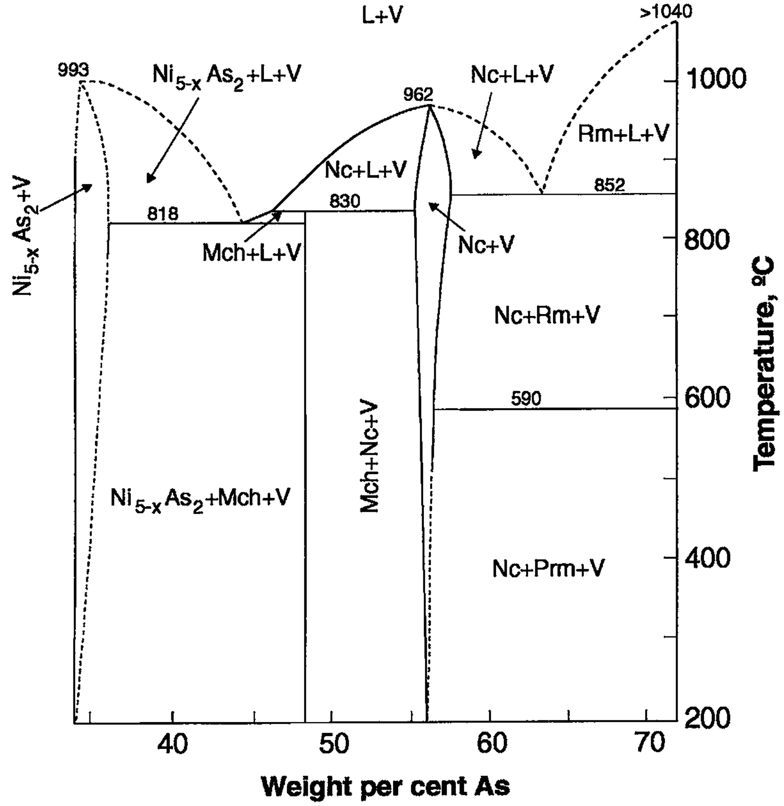

FIG. 9. Central portion of the system Ni–As (from Yund 1961). Mch: maucherite, Nc: nickeline, Rm: rammelsbergite, Prm: pararammelsbergite, L: liquid, V: vapor.

the crystallization of a monosulfide solid-solution, promoting liquid immiscibility at relatively low temperatures (tentatively, around 1000°C). The flow texture of the chromite-rich sigmoidal lenses present within the sulfide ore is consistent with such a dynamic model. In sample Re–6190, As concentration was high enough to the formation of diarsenide-bearing globules, and the abundant arsenide melt collected most of the nickel, inhibiting the formation of a Ni-rich monosulfide solid-solution. This model explains the absence of pentlandite in the ore association.

Arsenide droplets behave as close systems, crystallizing according to the phase relations in the system Ni–As (Yund 1961) (Fig. 9). Thus from the composition of the arsenide melt (Fig. 6), the Ni–As phase diagram predicts that nickeline would crystallize at around 900°C, associated with liquid and vapor. Below 830°C, a peritectic reaction takes place, and maucherite replaces nickeline. Iron and the corresponding portion of arsenic should be used to form westerveldite during this peritectic reaction. The starting composition of the arsenide droplets determines the presence or absence of nickeline and westerveldite in the mineral association of the globules. Arsenide globules with As contents slightly lower than that of stoichiometic maucherite crystallize below 850°C to form nickeline + liquid + vapor, then transform below 830°C to maucherite + liquid + vapor, or they directly yield this association, which is transformed below 818°C to $Ni_{5-x}As_2$ + maucherite + vapor (Fig. 9). After the crystallization of maucherite at 830–818°C, the residual Co-rich As-depleted liquid concentrated at the borders of the globule, dissolving important amounts of sulfur, thus forming a corona of cobaltite (gersdorffite in sample Re–6190).

The mineralogy and texture of the löllingite-bearing globules do not correspond to what would be expected from the phase relations in the system Ni–As (Yund 1961) and in the system Ni–Fe–As at 800°C (Maes & de Strycker 1967, Buseck 1963). In our globules, nickeliferous löllingite is in equilibrium with maucherite (forming lamellar intergrowths) instead of with nickeline, suggesting later re-equilibration at lower temperatures. In fact, Oen *et al.* (1977) described westerveldite (formed by replacement of nickeline) including fine exsolution blades of löllingite. These authors explained the löllingite – westerveldite – maucherite association from its crystallization at 450°C under partial pressures of arsenic, below that necessary to stabilize nickeline. On the other hand, the presence of a Co- and Fe-rich maucherite rim around the löllingite – maucherite aggregates further supports the idea that after the crystallization of the more stable arsenide phases at high temperature, a Co- and Fe-rich residual Ni–As melt is concentrated along the border of the globules, crystallizing either as maucherite or forming sulfarsenides. This residual arsenide melt also concentrates gold, which crystallizes as minute grains within the Co- and Fe-rich maucherite (Fig. 3D). Note that the melt of maucherite composition does not dissolve sulfur (and does not form sulfarsenides), as does the residual arsenide melt of $Ni_{5-x}As_2$ composition obtained after the formation of maucherite globules, from which the cobaltite – gersdorffite corona formed. These observations suggest that liquid immiscibility in the system Ni–Fe–As–S can take place in Ni arsenide melts of a restricted composition, near that of maucherite and nickeline (in the range 48–58 wt% As, Fig. 9).

Although this is the first description of a possible immiscibility relationship between arsenide and sulfide melts in nature, there exist Ni arsenide ores rich in noble metals that are associated with magmatic Ni sulfides with the same texture as that described here. They have been recognized in the offset of the quartz diorite "sublayer" at the Frood–Stobie mine at Sudbury, Ontario (W.V Peredery, pers. comm., 1994) and at the base of the olivine-rich Kabanga intrusion in Tanzania (D.M. Evans, pers. comm., 1994). The latter shows a basal zone enriched in Ni arsenides consisting of nickeline globules included in pyrrhotite – pentlandite ores.

In addition to the above lines of evidence, experimental data suggest that most arsenide and sulfide melts are essentially immiscible at high temperatures. Thus, in the system Pt–Pd–As–S at 850°C, Makovicky *et al.* (1991) found three different melts: 1) a barren As–S melt; 2) a Pt–Pd–As melt interconnected with a Pd–As melt that dissolved, respectively, 0.3 to 6.7 at.% sulfur and 1.5 to 9 at.% sulfur, and 3) a quaternary Pd–Pt–As–S melt with 20 to 40 at.% sulfur and up to 19 at.% arsenic. Similarly, in the system Pt–Fe–As–S at 850°C, Makovicky *et al.* (1992) also found three different melts: 1) a barren As–S melt; 2) a platinum-bearing Fe–As melt that can dissolve only 2.6 at.% sulfur, and 3) a sulfur-free Pt–As melt. The latter shows very limited solubility of sulfur, 3.5 at.% S as a maximum, even at 1,000°C (Skinner *et al.* 1976). These results indicate a limited capacity of arsenide melts to dissolve sulfur and show the restricted composition of the only arsenic-bearing sulfide melt found.

ROLE OF ARSENIDE MELTS AS COLLECTORS OF NOBLE METALS

The existence of droplets of an immiscible Ni–As melt in the sulfide melt during the formation of the Amasined and Los Jarales ores further supports the genetic relationship between chromite – Ni arsenide ores and sulfide – graphite ores in the Betico-Rifean lherzolite massifs. In particular, these examples show how an immiscible Ni–As melt could be segregated from the former As-, S-rich melt. However, an important question arises if the geochemical behavior of platinum-group elements is considered: Why are the S–G ores depleted in PGE by a factor of ten with respect to the Cr–Ni ores (Table 3, Fig. 7)? If the earlier immiscible Ni–As melt segregated from the former As-, S-rich ore-magma was able to collect most Rh, Pt, Pd and Au (Os, Ir and Ru were previously concentrated in the chromite as sulfide, arsenide and sulfarsenide inclusions: Leblanc & Gervilla 1988, Torres-Ruiz *et al.* 1996, Garuti *et al.* 1995), then we must assume that these noble metals have a higher affinity for arsenide melts than for sulfide melts. Nevertheless, this assumption must be considered as a general tendency for the platinum-group elements as a whole. Discrepancies could arise for individual PGE if we take into account their own partition coefficients between arsenide and sulfide melts (new experimental data are needed). For example, although the As-rich ores show the higher Pd values and a good correlation between both elements exists within the Cr–Ni ores (Table 3), consistent with the high capacity of Ni arsenides to dissolve Pd at different temperatures (Gervilla *et al.* 1994), for low As concentrations in S–G ores, Pd does not follow As, in agreement with the experimental results of Fleet *et al.* (1993).

Similar magmatic associations of PGE-rich arsenides and PGE-poor sulfides described in the literature further corroborate this conclusion: (1) in the Lewis Hills massif, Bay of Island Ophiolite Complex, Newfoundland, Edwards (1990) showed that during the fractional crystallization of probable boninitic-type melts, Os, Ru and, possibly, Ir sulfides were removed from the silicate melt and concentrated in chromite, then As saturation led to the crystallization of Pt and Pd arsenides (occurring as inclusions in both pyroxenes), and finally, barren base-meltal sulfides crystallized; (2) the PGE in the offset of the quartz diorite "sublayer" at the Frood–Stobie mine, Sudbury, Ontario, display a similar distribution, with PGE-rich Ni arsenide ores (ranging between 10–150 ppm PGE), associated with massive sulfides relatively poor in PGE (ranging between 2 to 5 ppm) and with still further impoverished brecciated Ni sulfides (ranging between 0.5–1 ppm PGE) (W.V. Peredery, pers. comm., 1994). Furthermore Merkle (1992) explained the distribution of platinum-group minerals in a section of the Middle Group in the Bushveld Complex by the crystallization of PGE- and As-rich phases before the formation of an immiscible sulfide melt, followed by resorption of these As-rich phases into the sulfide melt.

The above evidence suggests that arsenide melts can be formed by the As saturation in the silicate melt (prior to its saturation in S; Merkle 1992) or as immiscible droplets segregated from a sulfide melt. In either case, this arsenide melt could act as an efficient collector of PGE, giving rise to mineral associations containing PGE arsenides and PGE-bearing arsenides.

The good correlation between As and Au shown in Figure 7 indicates the capacity of arsenide melts to collect this noble metal. However, the textural relations that we described in the arsenide globules suggest that although gold can be collected by an arsenide melt, it tends to be concentrated in late associations in the rim of Co- and Fe-rich maucherite present around löllingite-bearing globules. Preliminary data in the system Ni–As–Au at 950°C (Gervilla & Makovicky, work in progress) support this conclusion.

CONCLUSIONS

Textural relationships between arsenides and sulfides in the Amasined and Los Jarales mineralized occurrences, as well as their mineral and bulk chemistry, allow us to conclude that:

1) These ores were formed by the segregation of an immiscible Ni-arsenide melt with a composition close to that of maucherite and nickeline, from a sulfide melt. This is the first description of an immiscibility relationship between arsenide and sulfide melts in nature, although it is in agreement with experimental results of Makovicky *et al.* (1991, 1992) and Skinner *et al.* (1976) in different As- and S-containing systems. These authors have demonstrated the limited capacity of an arsenide melt to dissolve sulfur at temperatures as high as 1000°C.

2) The distribution of PGE and gold in the mineralized samples and in other arsenide and sulfide ores from the Betico-Rifean lherzolite massifs is consistent with the higher affinity of these noble metals for an arsenide melt than for a sulfide melt. In other words, arsenic likely plays an important role in the distribution of platinum-group elements and gold in many magmatic Ni–Cu sulfide deposits. If, as suggested by Merkle (1992), the solubility of arsenic in mafic melts is more restricted than that of sulfur, the earlier formation of an immiscible arsenide melt could collect most noble metals; if any immiscible sulfide melt is formed later, it should be, therefore, depleted in these elements. The effectiveness of this process will depend on the As/S ratio of the parental magma.

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