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Trace platinum group elements in arsenides and sulfarsenides from magmatic ores: An electron microprobe and proton microprobe (micro-pixe technique) study

Elementos traza del grupo del platino en arseniatos y sulfoarseniatos de menas magmáticas: estudio a la Microsonda electrónica y a la Microsonda de protones (técnica micro-pixe)

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The usefulness of micro-PIXE technique to determine ppm quantities of platinum-group elements in sulfide minerals has been widely demonstrated in the past twenty years (e.g., Cabri et al., 1984; Czamanske et al., 1992), although only few data are published on the distribution of such elements in arsenides and sulfarsenides (e.g. Ryan et al., 1990). On the other hand, the development of the CSIRO-trace analysis package at CSIRO, Perth, Western Australia (Robinson and Graham, 1992) has also made possible the determination of noble metals (at ppm levels) in ore minerals by means of electron microprobe (e.g., Gervilla et al., 1998; Kojonen and Johanson, 1999). In this note we present the results obtained by these two techniques on arsenides and sulfarsenides from the following localities: i) chromite-Ni arsenide ores (Cr-Ni ores) and arsenide-bearing sulfide-graphite ores (S-G ores) of the betico-rifean ultramafic massifs in Spain and Morocco (Gervilla and Leblanc, 1990), ii) arsenide-rich sulfide ores of the Vammala Ni-Cu mine and iii) arsenide-sulfide and arsenide ore types from the Kylmäkoski Ni-Cu mine in the Vammala Nickel Belt, Finland (Gervilla et al., 1998).

Though the analyses were not made on the same points, a comparison of both sets of results provides an opportunity to make some observations.

The micro-PIXE analyses were done at CSIRO Exploration and Mining Laboratories, North Ryde, Australia. The measurements were carried out with 10 x15 µm beam spots. Typical measurement time for a 6 micro-Coulomb (µC) integrated charge was 25 to 30 minutes. Count rate was kept below 3000 counts per second. Under these conditions the detection limit for Pd is of the order of 20 to 30 ppm. Detection limits for Ru and Rh are slightly lower, of the order of 10 to 15 ppm. Two additional runs were made at 32 and 58 µC for about 3 and 5 hours, respectively, on one grain of nickeline and one grain of nickeliferous löllingite from betico-rifean ores, to reduce the detection limit down to ≈ 2 ppm for Ru and Rh and 2.5 ppm for Pd. These two analyses will be called here LDLA (low detection limit analysis). The detection limit for Pt is very high (≈ 400 ppm) because of strong interferences with Bi for the relatively weak PtLα line.

The EMP analyses were performed with a CAMECA SX50 instrument at the Geological Survey of Finland, Espoo, by means of the CSIRO-trace analysis package. The calculated detection limit for Pt (30-34 ppm) in the analyzed minerals is higher than that for Rh (24-28 ppm), Ir (20-22 ppm) and Pd (18-20 ppm).

With the micro-PIXE technique Ru was detected in nickeline (4-23 ppm) and nickeliferous löllingite (9-19 ppm); Rh was found in single LDLA in nickeliferous löllingite (6 ppm) and in cobaltite (14 ppm); Pt was not found above the detection limit except for one analysis of nickeliferous löllingite (756 ppm) and two of cobaltite (717 and 1031 ppm); Pd was measured in nickeline (7-149 ppm), in nickeliferous löllingite (8-30 ppm), and principally in maucherite (18-265 ppm). Pd partitioning between coexisting nickeline and maucherite varies from primary ores crystallized at high temperature (≈ 800ºC) to ore assemblages formed by remobilization at lower temperatures (≈ 500ºC). Thus, in the arsenide globules occurring in S-G ores (Gervilla et al., 1996) nickeline contains 70 ppm Pd and maucherite 58 ppm Pd. In the late magmatic, arsenide-rich Ni-Cu sulfide ores of Vammala, nickeline contains 44-149 ppm Pd and maucherite 92-117 ppm Pd. In contrast, the Pd content in nickeline is close to or below the detection limit and ranges between 83 and 265 ppm in maucherite in the remobilized sulfide-arsenide and arsenide ores from Kylmäkoski

By means of EMP only Pt and Pd were both found to be above the detection limit. Pt was detected in nickeliferous löllingite (52-162 ppm) and cobaltite (122-650 ppm). Pd was found in nickeline and maucherite from the arsenide-rich Ni-Cu sulfide ores of Vammala (28-63 ppm and 67-84 ppm, respectively) and maucherite from arsenide ores of Kylmäkoski (76-120 ppm). Pd values close to the detection limit were measured too in nickeline (20-38 ppm), maucherite (21-38 ppm), nickeliferous löllingite (22-38 ppm) and cobaltite (22-27 ppm). As in the above set of results Pd distribution between coexisting nickeline and maucherite indicate a higher affinity of Pd for maucherite at relatively low temperatures (≈ 500ºC).

Conclusions:

i) The two techniques used give rise to comparable analytical results for PGE abundances well above their respective detection limits.

ii) In ore assemblages crystallized at high temperature (≈ 800ºC) nickeline and maucherite contain comparable amounts of Pd whereas at ≈ 500ºC maucherite is the principal Pd carrier. This is in agreement with the experimental results in the system Pd-Ni-As at 790º and 450ºC (Gervilla et al., 1994).

iii) In spite of the high detection limits for Pt by micro-PIXE, comparison of data obtained with those from EMP suggest that the principal carriers of Pt are nickeliferous löllingite and cobaltite. These minerals also carry some Ru and Rh.

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