Petrology and geochemistry of eclogitic sulfides: a new insight on the origin of mantle eclogites?

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The alternative hypotheses that mantle eclogites are either rocks produced by mantle processes or fragments of subducted oceanic slabs have been intensively debated for 30 years, and the origin of these rocks is still not well constrained.

In the last decade sulfide assemblages were extensively used to constrain mantle processes. These minerals are the main carrier of the platinum group elements (PGEs) in the mantle. PGEs are useful petrological indicators due to their specific behaviour. The Ir-group PGEs (IPGE- Os, Ir and Ru) are compatible elements while the Pd-group PGEs (PPGEs- Rh, Pt and Pd) are more incompatible (Barnes et al., 1985), in consequence they are useful to trace melting events.

In this study we use the mineralogical and geochemical features of base metal sulfides (BMS) to obtain new information on the history and the origin of mantle eclogites.

Samples

We studied 19 eclogite xenoliths recently sampled at the Roberts Victor mine (South Africa), and 7 samples already within the GEMOC collection. The new suite includes 4 kyanite-bearing eclogites and all the samples except one belong to Type I as defined by McCandless and Gurney (1989) using Na_2O content of garnet and K_2O in clinopyroxene.

The samples are mainly bimineralic eclogites with modal proportions garnet/omphacite varying from 80:20 to 40:60. They are usually coarse grained and show a wide range of microstructures (e.g. layering, patchy accumulation of garnets). Several samples show a microstructural garnet/cpx disequilibrium defined by high-energy surfaces. Most of the rocks also show a destabilisation of the primary omphacite into a spongy inhomogeneous secondary cpx, which is Na-depleted. Garnets are usually fresher than the cpx and are in general chemically homogeneous at the thin section scale. However some specimens (e.g. layered or ky-bearing xenoliths) show variations of the garnet composition within a single thin section. Several accessory minerals such as phlogopite, rutile, amphibole, sulfide, feldspar, spinel, calcite or barite are also commonly present.

Sulfide mineralogy

In the Roberts Victor xenoliths, sulfides occur as veins, as interstitial phases or as inclusions hosted by omphacite and/or garnet. The modal abundance of sulfides varies from 0 to 5%; among 29 thin sections studied only 6 do not contain sulfide phases. Sulfide inclusions are mostly spheres or subhedral polygons 30 to 350 μm long. Intergranular sulfides are generally anhedral with curved or elongate shapes, and grainsizes from < 20 μm to 3 mm. Reflected-light microscopy and backscattered-electron images show that most of the sulfides have been re-equilibrated at low temperature and are polyphase grains composed of pyrite (or Ni-rich pyrite) ± pyrrhotite ± pentlandite ± mono-sulfide solid solution (mss) ± chalcopyrite (Fig.1). The most typical occurrence is a grain of Ni-rich pyrite or pyrrhotite displaying pentlandite flames and euhedral pyrite crystals, with the whole assemblage surrounded by a chalcopyrite corona (Fig 2.).
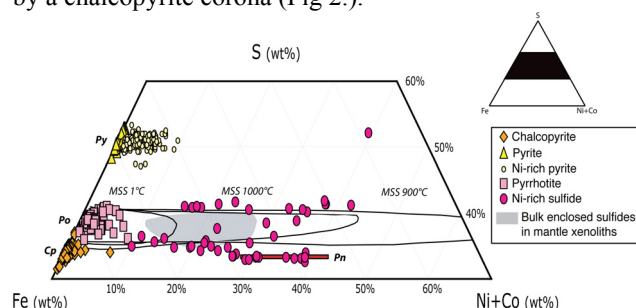

Fig.1 Point analyses of the different sulfide phases plotted in the Fe-Ni-S system. MSS stabilty field from Kullerud et al., 1969. Grey field, bulk compositions of enclosed sulfides in mantle xenoliths (Lorand & Conquéré, 1983; Szabó & Bodnar, 1995). Red bar, compositional range of pentlandite (Lorand, 1989). End-member phases: Cp, chalcopyrite; Po, pyrrhotite; Py, pyrite; Pn, pentlandite.

Sulfide chemistry

Bulk sulfur contents of 21 xenoliths have been analysed by High-Temperature Iodo-Titration (HTIT) and the results range from 0 to 1600 ppm; most are between 200 and 400 ppm with an average of 313 ppm,

similar to accepted values of 200-300 ppm for the subcontinental mantle (O'Neill, 1991). A correlation between sulfide modal abundances and whole-rock S-content confirms that sulfides are controlling the S budget of the eclogites.
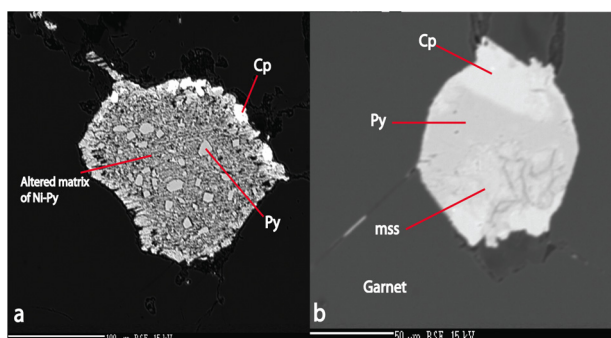

Fig. 2 Back-scattered electron images of polyphased sulfides. a, Typical sulfide with euhedral pyrite crystals within an altered matrix of Ni-rich pyrite and a chalcopyrite corona. b, eclogitic sulfide enclosed within a garnet and showing a pyrite and mss core with a chalcopyrite corona.

LAM-ICP-MS analyses of sulfides from the Roberts Victor samples reveal important variability in the PGE patterns (Fig.3). However it seems that such a feature is mainly due to the low-T subsolidus re-equilibration of the sulfide assemblages. Basically, PGE patterns can be sorted into 4 main groups, 3 of which are related to a specific mineralogy of the ablated phase.

The first kind of occurrence is associated with Ni-rich pyrite with a potential minor component of chalcopyrite. These analyses show enrichment of light PGEs (Ru, Rh and Pd), Os and Ir relative to Pt. The IPGEs show flattened patterns that are essentially chondritic (0.1-2 x CI) and are positively correlated with the nickel concentration (2-6 wt%) of the analysed area. An enrichment in Rh relative to the light PGEs (Rh/Ir_N=6.28± 1.34) is visible on analyses with a chalcopyrite contribution, while the analysis RV07-17S3-1, which has a low Cu content (<1500 ppm), shows Rh/Ir_N=1.40. This positive correlation between the Cu-content and Rh is characteristic of the four groups described here.

The second group is also associated with Ni-rich pyrite but is characterized by a pattern different to those detailed above. In this case, Ru (0.53±0.16 ppm) and Rh (0.048±0.03 ppm) are enriched relative to Os (0.019±0.001 ppm), Ir (0.011 ppm), Pt (0.026±0.011 ppm) and Pd (0.055±0.027 ppm), and Ru/Rh_N >1.

The third type of PGE pattern is related to analyses with a high Cu-content, consisting principally of chalcopyrite and mixtures of chalcopyrite and mss. As previously seen for the second group, there is an enrichment in Ru and Rh relative to the other PGEs, but due the high Cu contents Rh is enriched relative to Ru (Ru/Rh_N =0.03±0.01). In the chalcopyrite-mss mixture where Cu/Ni<1 the depletion in Pt is less important (Rh/Pt_N =21.5±11.8) than in the almost pure chalcopyrite (Rh/Pt_N =955±73). Chalcopyrite patterns are then

similar to those observed for magmatic chalcopyrite described from abyssal peridotite (Luguet et al., 2001,
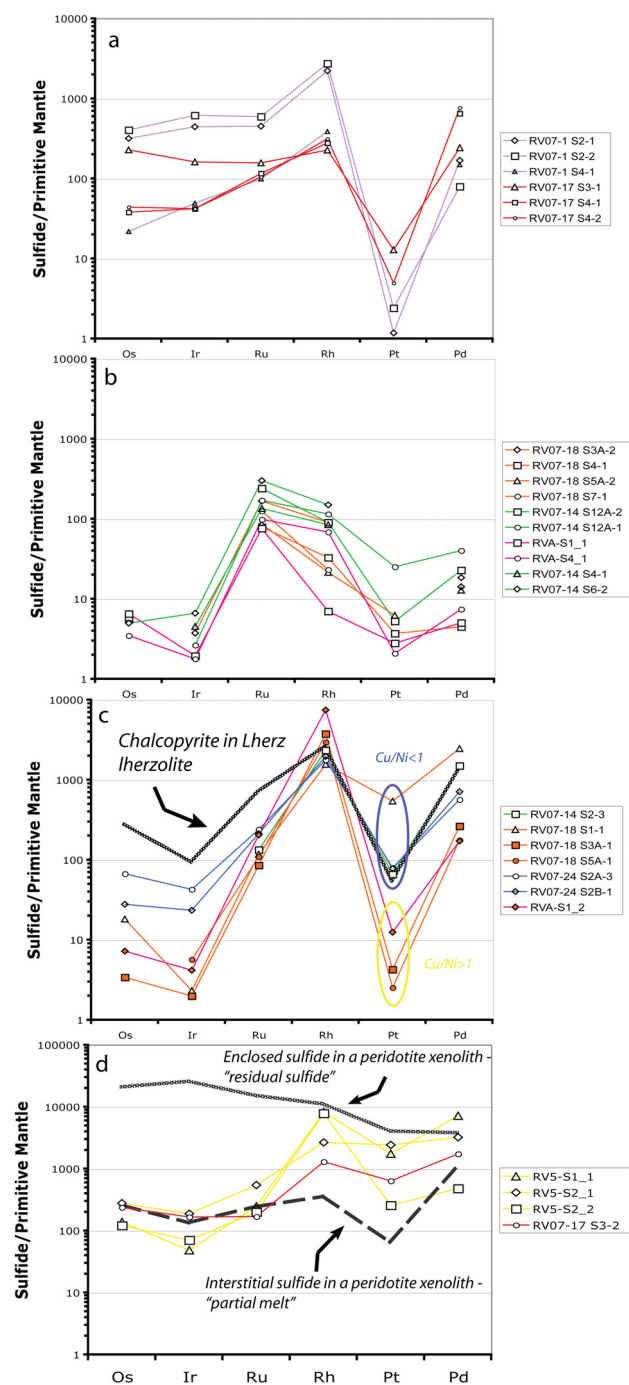

Fig. 3 Primitive mantle normalized PGE abundances of sulfides. a, Ni-rich pyrites (type I) with a minor chalcopyrite component. b, Ni-rich pyrites (type II). c, Chalcopyrites and chalcopyrite/mss mixtures; solid symbols, pure chalcopyrites; black thick line, chalcopyrite in FON B 93 lherzolite (Lherz, France). d, Sulfides with PPGE enrichment relative to IPGEs; black thick line, enclosed sulfides in a peridotite xenolith in alkali basalt (Mt Gambier, Australia); thick dashed line, interstitial sulfides in a peridotite xenolith (Mt Gambier, Australia)

2004) and from peridotite from Lherz (Lorand et al., 2008). There is also a transitional subgroup in which all

the steps between the second group (Ni-rich pyrite) and pure chalcopyrite are observable, basically with an increase in Rh and Pd-contents with the addition of chalcopyrite to the mixture.

The fourth type of PGE pattern shows an enrichment in PPGEs relative to IPGEs. IPGEs are generally chondritic while PPGEs show a negative anomaly in Pt. These patterns are similar to those of interstitial sulphide observed in mantle peridotite xenoliths from Australian alkali basalts and interpreted as partial melts of a chondritic sulfide (Alard et al., 2000).

LAM-ICP-MS has been also used to quantify the siderophile and chalcophile element budget of the interstitial sulfides found in crosscutting veinlets. While Se-contents are mostly between 50-90 ppm for the sulfides described above the Se is very low in the veinlet sulfides and do not exceed 4 ppm, and all the PGE are below the minimum detection limit of the instrument. This kind of mineralisation is clearly of secondary origin and can be probably related to the hostkimberlite, whereas the bulk of the observed sulfides must be related to the eclogite formation or later mantle metasomatism.

Preliminary investigations of the sulfur isotopic compositions were carried out using in situ ion-probe techniques (CAMECA IMS-5F, Universite de Montpellier). The results obtained on 3 samples show that the $\delta^{34}S$ of the sulfides varies from –4.93‰ to +2.73‰ with an average of –0.95‰. Considering that the primitive mantle value is defined at 0±2‰ (Thode et al., 1961) and sulfide inclusions in mantle xenoliths are 1.3±3.8‰, these first results seem to be consistent with a mantle origin of the sulfides in Roberts Victor eclogites.

Conclusion

Although this study does not provide clear evidence to decide between one hypothesis and the other, the different aspects of the sulfide assemblages in the Roberts Victor eclogites tend to suggest a mantle origin for these minerals. Therefore, it becomes crucial to define whether the BMS origin is related to a late metasomatism or to the origin of the eclogites.

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