

SULPHIDE MINERALOGY AND CHALCOPHILE/SIDEROPHILE ELEMENT GEOCHEMISTRY OF ABYSSAL PERIDOTITES FROM THE MARK AREA (20-24°N MID-ATLANTIC RIDGE, SOUTH OF THE KANE TRANSFORM)

Ambre Luguet*, Jean Pierre Lorand* and Monique Seyler**

* *Laboratoire de Minéralogie ESA CNRS 7058, Muséum National d'Histoire Naturelle, 61 rue Buffon, 75005 Paris, France.*

** *UFR Sciences de la Terre, SN 5, ESA CNRS 7058, Université de Lille 1, 59655 Villeneuve d'Ascq cedex, France.*

ABSTRACT

A coupled study of sulphide mineralogy and chalcophile/siderophile elements geochemistry (i.e., S, Se, Cu, As, V, Cd, Co, Zn, platinum-group elements and Au) has been undertaken in abyssal peridotites from the MARK area. The 28 samples analysed were mostly collected by submarine along the southern wall of the Kane transform fault. Compared to the peridotites drilled in the same area, our samples show a wide range of modal compositions (lherzolites, cpx-poor lherzolites and harzburgites) and of bulk-rock chemistry ($1.5 < \text{Al}_2\text{O}_3 < 3.2$ wt%). However, half of the samples experienced sea-floor weathering by cold seawater in addition to serpentinization. Our study provides the opportunity to see whether abyssal peridotites collected directly on the ocean floor may provide reliable information on the oceanic mantle as regards chalcophile/siderophile element geochemistry.

Most of the studied samples have mineral and whole-rock compositions characteristic of mantle residues having experienced 10 to 20% adiabatic partial melting (Ghose et al., 1996). However, four samples show geochemical evidence of refertilization by evolved MORB-type magmas (i.e. TiO_2 -enriched chromiferous spinel ($0.2 < \text{TiO}_2 < 0.5$ wt%); LREE-enriched chondrite normalized REE patterns ($\text{Ce}_N/\text{Sm}_N > 1.85$; Sm_N/Yb_N up to 1.4, N= chondrite normalized). Lherzolites and cpx-poor lherzolites show coarser-grained isolated cpx crystals in addition to the smaller cpx forming cpx+opx±sp clusters. These coarse-grained cpx are ascribed to in-situ precipitation of clinopyroxene from partial melts (Seyler et al., in prep.).

Sulphides of indisputable magmatic origin have been observed in all of the peridotites. In spite of sea-water alteration and serpentinization, the number of magmatic sulphide grains positively correlates with fertility in the residual samples, decreasing from 1.2-3.7 grains/cm² in the lherzolites to less than 0.5 grain/cm² in the most refractory harzburgites. These latter still contain residual sulphides which provides further hypothesis of immiscible sulphide persisting in the mantle source of MORB-melts. Magmatic sulphides are closely associated with the small clusters-forming cpx crystals, being either enclosed or forming discrete grains adjacent to this silicate. In the weathered samples, magmatic sulphides are totally replaced by hydrous iron hydroxides (limonites) whereas the samples free from weathered products preserved sulfide assemblages typical of the reducing conditions generated by low T-serpentinization (i.e. Fe-rich pentlandite + magnetite ± mackinawite ± digenite ± troilite ± awaruite). Nevertheless, the peridotites refertilized by exotic MORB-type magmas display systematic sulphide enrichments (up to 5 grain/cm²) with respect to the sulphide vs. fertility correlation documented in the residual samples. Sulphides preferentially occur along or within the grain

boundaries of the coarse-grained cpx. Similar sulphide enrichments have been observed in a few residual cpx-poor lherzolites devoid of melt/rock reaction evidence; however sulphides are disseminated within the serpentinized matrix at distance from the cpx. Clearly, several sulphide precipitation mechanisms operated in the oceanic mantle sampled by the Kane transform fault.

The contents of moderately chalcophile elements (Cu, Zn, V, Co, Cd) and chalcogenides (S, Se, As) have been variably upgraded by sea-floor alterations. Weathered samples are systematically enriched compared to typical mantle compositions (up to 265 ppb Se; 200-400 ppm S with 2 occasional peaks at 2,000 ppm; up to 60 ppm As; up to 120 ppm Cu). None of the moderately chalcophiles positively correlates with the number of sulphide grains per polished thin sections and correlations with fertility indices are poor. By contrast, positive correlations such as Cu vs. Se, As vs. Se; Cu vs. As; Cd vs. Se and Zn vs. Cu suggest that these elements were contaminated by fluids from hydrothermal vents. However, apart from the weathered samples, S, Se as well as numerous moderately chalcophiles still show concentration ranges plotting on mantle melting trends. Some lherzolites display sub-chondritic S/Se ratios (~2,800) and Se and S contents that fit the range of oceanic mantle compositions recomputed from primitive MORBs (~200 ppm S; ~80 ppb Se).

Gold contents (0.8-5 ppb) are almost systematically higher than mantle abundances, probably because of contaminations from hydrothermal vents. This element poorly correlates with indicators of melt depletion or magmatic sulphide precipitation. On the contrary, platinum-group elements were mostly insensitive to hydrothermal alterations, whether serpentinization or sea-floor weathering. Weathered and unweathered peridotites display PGE concentration ranges typical of mantle rocks (2-4 ppb Os, 2-4 ppb Ir; 4-8 ppb Ru; 0.7-1.4 ppb Rh; 3-9 ppb Pt; 0.2-8 ppb Pd). These concentration range are not affected by the alteration of magmatic sulphides into iron hydroxides. Strongly serpentinized harzburgites are the poorest in PGEs, perhaps because of the well-known diluting effect of serpentinization on trace elements. CI-chondrites normalized PGE patterns are similar to those reported for on-land unserpentinized mantle rocks, ranging from nearly flat to slightly fractionated. Compatible PGEs (Os, Ir, Ru and Rh) were not affected by partial melting or melt/rock reactions as their concentration ranges are uncorrelated with petrogenetic indicators of these processes. Os/Ir ratio is within the range of chondrites (0.9-1.2) whereas Ru/Ir and Rh/Ir are slightly higher than chondritic (1.7-2.3 and 0.3-0.4, respectively). Our sample provide further evidence that compatible PGEs are not extracted from the mantle as long as

residual sulphides survive in partial melting residues. Pt/Pd systematics are more variable. The most refractory harzburgites preserve negatively-trending chondrite normalized PGE patterns ($0.7 < \text{Pt}_N/\text{Ir}_N < 1.1$; $0.3 < \text{Pd}_N/\text{Ir}_N < 0.5$). Even in S-saturated conditions, the most incompatible PGEs are more readily extracted than compatible PGEs from the oceanic mantle; however, Pt was less systematically fractionated than Pd. The lherzolites and cpx-poor lherzolites show Pt/Ir and Pd/Ir varying in a rather complex way, especially the cpx-poor lherzolites that show the largest scatter of Pd_N/Ir_N (0.2-2.2). The samples refertilized by exotic MORB-type melts have been enriched in all the PGE by sulphide precipitation. However, their PGE patterns are typical of residual mantle rocks (i.e. lower-than-chondritic Pd_N/Ir_N (0.2-1). Where sulphides precipitated during in-situ fractional crystallization of partial melts, the samples show suprachondritic Pd_N/Ir_N (1.6-2.0) and Pt_N/Ir_N (1-1.2). Their PGE patterns is complementary to those of the refractory harzburgites and their PGE contents do not correlate with sulphide modal abundance or in-situ precipitated coarse cpx crystals. As documented in other abyssal peridotites (Hess Deep (Leg 895), Kane fracture zone (Leg 920), i.e. Rehkämper et al., 1998), PGE systematics of abyssal peridotites are not fully explained by considering these rocks as

simple mantle melting residues. Complex melt/rock reaction processes and coupled sulphide precipitation are to be considered to explain the large scatter of Pd/Ir and Pt/Ir. Preliminary *in situ* LA-ICPMS data on sulphides suggest the same variability between each sulphide grain. However, segregation of immiscible sulphide liquids does not necessarily yield supra-chondritic Pd/Ir and Pt/Ir ratios. Incomplete sulphide-silicate equilibration as well as mechanical transport of sulphides by silicate melts have to be taken into account to interpret these ratios.

REFERENCES

- Ghose I, Cannat M. and Seyler M., 1996. Transform fault effect on mantle melting in the MARK area (Mid-Atlantic Ridge south of the Kane transform). *Geology*, 24: 1139-1142.
- Rehkämper M., Halliday A.N., Alt J., Fitton J.G., Zipfel J. and Takazawa E., 1998. Non-chondritic platinum group element ratios in abyssal peridotites: petrogenetic signature or evidence of core-mantle interaction?. *EOS transactions* 79, AGU Fall Meeting, p. 1012.
- Seyler M., Luguët A. and Lorand J.P., (in prep.). Petrological and geochemical heterogeneity of the upper mantle in the MARK area (Atlantic ocean).