Se contents and S/Se ratios of spinel peridotite xenoliths from the Massif Central (France)

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Selenium and sulphur are volatile chalcophile elements in meteorites (S/Se = 2560 ± 200; Dreibus *et al.*, 1995). In mantle peridotites, these two elements are concentrated into low-melting sulphide microphases belonging to the Fe-Ni-S system and their abundances are relevant to core-mantle segregation models and the late accretionary history of the Earth (e.g. O'Neill, 1991). Nevertheless, the behaviour of S and Se is far from being fully understood. Interpretations of S data are strongly debated because of the poor stability of host sulphides with respect to supergene weathering and late-stage oxidations which preferentially affect mantle xenoliths uplifted by within-plate alkali lavas (Lorand, 1990). Compared to S, reliable Se data are almost lacking. We have analysed 43 spinel lherzolite xenoliths from the Massif Central Cenozoïc volcanism by hydride generation-flameless AAS. Selenium is considerably more stable than S during low temperature alterations. It thus provides a means to overcome late-stage perturbations of chalcogenide abundances.

The Massif Central and neighbouring areas of recent volcanic activity (Bas-Languedoc-Causses) offer a complete section across a thinned, mainly Middle to Upper Proterozoïc SCLM reactivated by the mantle plume that triggered the alkali volcanism. The samples analysed for Se come from 19 volcanic vents either older (e.g. Languedoc-Causses-Livradois; 9–25 Ma) or contemporaneous to the impigement of the mantle plume beneath the Massif Central (e.g. Sioule, Devès, Velay; Vivarais; 5–0.1 Ma). Their modal compositions range from fertile lherzolites (3.75 wt.% CaO) to harzburgites (0.3 wt.% CaO; Fig. 1). Three groups can be defined from textures, equilibration temperatures and incompatible trace element patterns. Group I samples are low-*T* (<1000°C) protogranular to porphyroclastic peridotites from the Causse-Languedoc area. Group II peridotites come from volcanic vents less than 5 Ma old; these are medium *T* (1000–1100°C) protogranular to granular/granuloblastic peridotites. Group III peridotites, all from Quaternary volcanic vents, display high-temperature (1200°C) poikiloblastic textures. Incompatible trace element patterns of group I and group II peridotites range from DMM-like to *LREE* and/or LILE enriched. Some samples display strong LILE enrichments and HFSE negative anomalies, some of them in group II have also U-shaped *REE* patterns. Such trace element features are ascribed either to percolation of volatile-enriched small volume melts or to chromatographic effects coupled with melt-rock reactions. Textures and trace element patterns of group III peridotites (regular enrichment from the less incompatible to the most incompatible trace elements) are considered to be due to extensive re-equilibration with large volumes of magmas at the base of a thinned (<60 km) SCLM above the mantle plume (Alard *et al*, 1996).

The Se concentration range (0.2 to 67 ppb) conforms with the few results previously reported for similar mantle xenoliths (Morgan, 1986). However, distinctions can be established between the three groups. Group I lherzolites have broadly similar Se contents (17–67 ppb) as the highly fertile mantle xenoliths analysed by Morgan (1986). In the Montferrier neck (Languedoc) fertile lherzolites displaying ITE patterns of the volatile-enriched small-volume metasomatic melts are slightly higher in Se than the other samples which show LILE-depleted ITE patterns (40–67 pb *vs.* 17–48 ppb). Group 2 protogranular and granular/granuloblastic xenoliths are on average Se-poorer than Group I samples, although some overlaps are observed in Fig. 1. Most group II Se contents span the range 5–22 ppb irrespective of ITE patterns; fertile lherzolites with up to 5 wt.% Ti pargasite and high Ba, Rb and Sr contents and lherzolites with DMM-like *REE* patterns may show similar Se contents. Group III

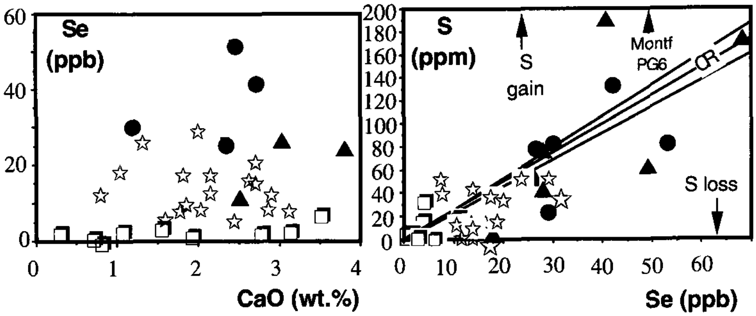

FIG. 1. Se *vs.* CaO and S *vs* Se diagrams (closed symbols = Group I (closed triangles = Montferrier); open stars = group II; open squares = group III). S data from Lorand (1990 and this study); CR = Chondritic Ratio.

poikiloblastic xenoliths are markedly depleted in Se (<5 ppb) compared to the other two groups, with Se contents as low as 0.2 ppb.

Although usually believed to be moderately incompatible, Se does not correlate with lithophile elements of similar incompatibility (e.g. Al_2O_3; CaO, used as Fertility Indexes). Lherzolites display the largest scatter (Fig. 1). However, poikiloblastic Group III peridotites preserve almost constant Se abundances in spite of large variation of CaO (0.3–3 wt.%). A broadly positive correlation is observed between S and Se ($r = 0.75$). Very few xenoliths have preserved chondritic S/Se ratios (Fig. 1). These are either small chips encasted in massive basaltic lava flows or group III peridotite xenoliths which contain only fully enclosed sulphides in olivine and pyroxenes. There, sulphides display no petrographic evidence of weathering. Some samples that have been metasomatized by volatile-rich small volume melts (e.g. Montferrier; Montboissier) and an amphibole-rich lherzolite display higher than chondritic S/Se (up to 10^4 in Montferrier sample PG6) typical of hydrothermal sulphide ores. Half of the analysed samples display lower than chondritic S/Se. These are xenoliths from scoria cones and oxidized magmatic breccias where petrographic evidence of wheathering of host sulphides are widespread (Lorand, 1990).

There is indisputable evidence of modification of S-Se systematics relative to chondrites. Volatile-rich metasomatic melts produced S gains relative to Se whereas S-losses resulted from supergene weathering. Assuming chondritic S/Se in the unmetasomatized mantle, the amount of S lost, probably as sulphates, through weathering of sulphides can reach 100%. According to Fig. 2 about half of the sulphur data measured in MCF xenoliths are not reliable and care must also be exercised in recomputing pre-entrapment S contents assuming a chondritic S/Se ratio because this ratio may have been modified by mantle metasomatism prior to supergene weathering. Nevertheless, Se data seriously question the conclusion that supergene weathering was responsible for the low and uniform S contents of continental mantle xenoliths (c.f. Lorand, 1990). The relationships between Se abundances and petrographic characteristics of the investigated xenoliths argue for large scale variations of chalcogenides abundances in the SCLM beneath the Massif Central, unrelated to post-entrapment alteration processes.

As it was only marginally affected by the plume, group I peridotites could have preserved the Se contents of the SCLM before reactivation by the plume. Assuming chondritic S/Se ratios, the Se data (20–50 ppb) suggest primary S of about 50–130 ppm. These latter are at the lower bound of the MORB-source Mantle sampled by orogenic lherzolites, although significantly depleted (see also Alard *et al*, this volume). The uniformly low Se (and S) contents of poikiloblastic peridotites can be explained by an almost complete removal of molten sulphides by the melt infiltrated from the plume. The fact that both harzburgites and lherzolites are similarly Se-depleted suggests that such high-T percolation processes involving large melt fractions could generate sulphide-depleted haloes at the base of thinned SCLM. The significance of Group II Se data is more controversial. The lack of positive correlation between Se and fertility indexes indicates that Se has been mobile at some stages postdating the ancient melting event(s). However, the Group II S contents (30–60 ppm) that can be recomputed from Se contents fit well the range reported for xenolith suites from worldwide provenances (c.f. Lorand, 1990; Ionov *et al.*, 1992). In short, the S/Se systematics of MCF peridotite xenoliths highlight the difficulty of ascribing a unique S and Se concentration range for the SCLM.