

# Trace element characteristics of the lower mantle: an ion probe study of inclusions in diamonds from São Luiz, Brazil

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## Introduction

The São Luiz alluvial deposit of Mato Grosso State, Brazil, has yielded diamonds with syngenetic inclusions (50–400  $\mu\text{m}$  diameter) indicating parageneses stable at pressures corresponding to the transition zone and lower mantle. One suite of these inclusions shows majorite garnet coexisting with calcic pyroxene (Harte, 1992). Another, which is the subject of this paper, shows periclase-wustite, (Mg,Fe)O inclusions (referred to as *fPer*), probably coexisting with  $\text{CaSiO}_3$  and (Mg,Fe) $\text{SiO}_3$ ; the latter two are assumed to have been Ca-silicate with a perovskite structure (*CaSiPvk*) and Mg-silicate with a perovskite structure (*MgSiPvk*). These mineral suites have also been observed in very high pressure experimental work on pyrolite, tholeiite and harzburgite (e.g. Ringwood, 1982; Irifune and Ringwood, 1993). The lower mantle mineral suite from São Luiz, of *MgSiPvk* + *fPer* + *CaSiPvk*, also appears to include normal-Si garnets (Harris and Harte, 1994; Harte and Harris, this volume). In this suite there is considerable regularity in host diamond composition with  $\delta^{13}\text{C}$  values of *c.* –5 (per mil) and nitrogen contents of under 50ppm. The inclusions themselves, however, show some wide variations in composition such as a range of 0.85 to 0.36 in atomic Mg/(Mg + Fe) of *fPer* grains (Harte and Harris, this volume).

## Methodology

Ion microprobe analyses for nineteen trace elements (*REE*, HFSE and LILE) were made on the perovskite (*MgSiPvk* and *CaSiPvk*), periclase-wustite (*fPer*) and garnet (*Gnt*) phases, using the Cameca ims-4f secondary ion mass spectrometer of the University of Edinburgh/NERC. Measurements were made using an 8–10 nA  $\text{O}^-$  primary beam with spot size of 20–30  $\mu\text{m}$ , and were calibrated against NBS glass and natural garnet and pyroxene standards. The positions of

analysis pits were checked after analysis to make sure of ion beam positioning on small inclusions. Low concentrations in the *fPer* and *MgSiPvk* inclusions meant that separation of peak from background, especially for odd atomic number rare-earth elements, was often indistinct.  $^{134}\text{BaO}$  was measured to improve quantification of Eu. Weight concentrations were calculated with reference to Si for silicates and Mg for *fPer*.

## Results

Averaged analyses are plotted in Fig. 1 along with N-MORB and OIB data. The most striking feature of the chondrite normalised patterns, is the very high concentration of rare earths in *CaSiPvk*. The trend exhibits a negative slope towards the *HREE* and a small positive Eu anomaly of a factor of two. There is also a relatively high Y to Zr ratio. The other three phases contain roughly three orders of magnitude less of *REE* and other trace elements than the *CaSiPvk*. Garnet exhibits a level *MREE* and *HREE* trend close to chondrite but with a two order of magnitude deficiency of Y by comparison with Ho. The disjointed and staggered nature of the *fPer* and *MgSiPvk* trends is due to the low concentrations ( $0.01\text{--}0.1 \times$  chondrite), and so, low peak to background ratio for these analyses, but, a Y deficiency is again indicated. The relatively high Zr and Nb values in *MgSiPvk* compared with *Gnt* have been observed in experimental studies (Kato *et al.*, 1988).

## Discussion

The data support the evidence of experimental work (Kato *et al.*, 1988) that the perovskite structure of  $\text{CaSiO}_3$  is most suitable for accommodating *REE* and other traces. The Eu anomaly shown by the *CaSiPvk* is particularly interesting. It may be a product of the distinctive features of the *CaSiPvk* structure and the redox state; but an

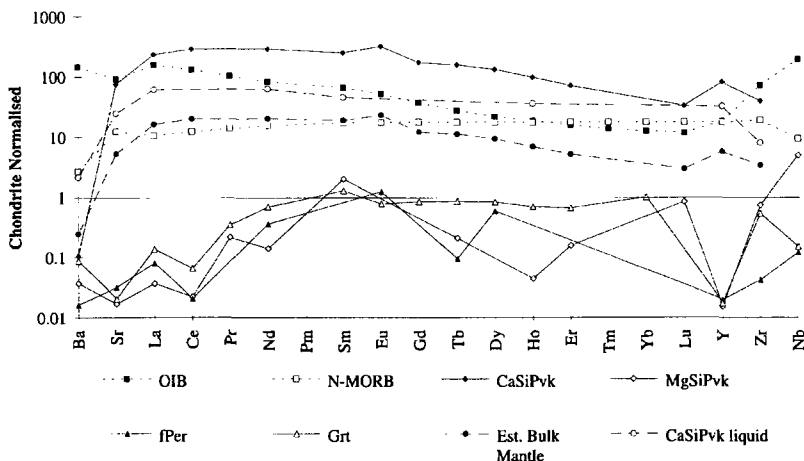


FIG. 1 Provisional trace element compositions of average *MgSiPvk*, *fPer*, *CaSiPvk* and *Grt* inclusions from São Luiz diamonds are plotted with N-MORB and OIB data (Sun and McDonough, 1989). For notes on calculation of estimated bulk lower mantle composition (Est. Bulk Mantle) and melt co-existing with *CaSiPvk* (*CaSiPvk* liquid) see text.

important alternative is that the inclusions were derived from material whose protolith had been feldspar-bearing and, therefore, probably represented subducted crust. Unfortunately the low abundance of REE in the other phases makes it difficult to assess these possibilities further at present. Clearly an Eu anomaly of crustal origin would support theories of the 670 km zone being one of entrainment of subducted material (Ringwood, 1982; Ringwood and Irifune, 1988). However, the uniform diamond  $\delta^{13}\text{C}$  values of *c.* -5 (per mil) provide no evidence of a crustal signature.

A composition has been calculated for a melt (*CaSiPvk* liquid in Fig. 1) coexisting with *CaSiPvk* using partition coefficients from experimental work (Kato *et al.*, 1988). This shows values close to those for OIB but with a trend of N-MORB; and suggests that melts of both these types may be possible for a source along or below the 670 km mantle transition. Assuming a lower mantle origin for the inclusions, an estimated bulk trace composition for the lower mantle may be calculated if the proportions of the phases are known. Using ratios of the four phases *MgSiPvk*, *fPer*, *CaSiPvk* and *Grt*, which would yield a solar mantle composition for major elements (see Harte and Harris, this volume), the resultant estimated bulk lower mantle composition is shown in Fig. 1, and is again close to N-MORB for all except the HREE.

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