

Lower mantle mineral associations preserved in diamonds

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Introduction

The composition of the Earth's mantle inferred from carbonaceous chondrites and also from solar energetic particles and spectroscopy, is hugely dominated by SiO₂ and MgO, with subordinate but significant contents of FeO, CaO and Al₂O₃ (Anderson, 1989). This evidence coupled with geophysical data on mechanical properties and density, and ultra-high pressure experimental work has led to the consensus that the 670 km seismic discontinuity is associated with the stabilisation of a mineral assemblage of dominantly MgSiO₃ (in the perovskite structure) together with MgO (in the rock salt or periclase structure). The FeO component of the lower mantle is expected to be in solid solution in these phases, whilst the CaO is expected to form CaSiO₃ in perovskite structure. Whether Al₂O₃ is present as oxide or located in some silicate phase has been a matter of uncertainty.

To what extent the lower mantle mirrors the upper mantle in details of composition - for example, to what extent it is like the upper mantle lithosphere represented by various peridotite xenoliths from basalts and kimberlites (e.g. Harte and Hawkesworth, 1989) or Ringwood's pyrolites (e.g. Ringwood, 1982) - is uncertain; but

it is of considerable importance with respect to whether convection systems are unified or separated for the upper and lower mantle and has important implications for the detailed distributions of many elements and isotopes (e.g. O'Nions, 1987).

Minerals with the (Mg,Fe)O composition are not expected to form part of stable mantle mineral assemblages at depths shallower than 670kms, and the occurrence of a small number of such minerals as inclusions in natural diamonds led Scott-Smith *et al.* (1984) and Moore *et al.* (1986) to suggest that these inclusions came from the lower mantle. Association of such inclusions with ones of (Mg,Fe)SiO₃ composition strengthened this likelihood. Since these inclusions are usually Mg-rich, as expected, we refer to them as ferro-periclase (*fPer*) and MgSi-perovskite (*MgSiPvk*) on the basis of the expected crystal structure as well as composition.

Lower mantle minerals from São Luiz

Mineral assemblages. The São Luiz source of diamonds we have been studying considerably enlarges the number of potential lower mantle minerals found within diamonds, and is further notable for the occurrence of (Mg,Fe)O and silicate inclusions together in the same diamond. Table 1 shows the number of such inclusions found so far, and is based upon identifications by electron microprobe analysis. These data show the expected associations of *MgSiPvk* and *CaSiPvk* with *fPer*, that SiO₂ (stishovite) may occur, and that the coexisting Al-phase is a garnet (*Gnt*) of pyrope-almandine composition. Note that in recording these mineral associations we refer simply to the occurrence of inclusions in one diamond; in only one case did the mineral inclusions actually touch one another (specimen BZ207 with *MgSiPvk* and *Gnt* in contact). Inclusions of only one phase [e.g. (Mg,Fe)SiO₃] within a diamond are not recorded in Table 1 when there is no clear basis for deciding if the inclusion is of lower mantle or upper mantle derivation.

TABLE 1. Mineral associations involving (Mg,Fe)O phase, found as inclusions in diamonds from São Luiz, Brazil

Mineral assemblage	Frequency of occurrence	atomic M/FM of <i>fPer</i> (%)
<i>fPer</i>	17	36→85
<i>CaSiPvk</i>	3	-
<i>fPer</i> + SiO ₂	1	69
<i>fPer</i> + <i>CaSiPvk</i>	1	81
<i>fPer</i> + <i>MgSiPvk</i>	2	69→82
<i>fPer</i> + <i>Mg-Fe Gnt</i>	2	69→82
<i>fPer</i> + <i>MgSiPvk</i> + <i>Mg-Fe Gnt</i>	1	69

Mineral compositions. All the minerals listed in Table 1 have been analysed by electron microprobe. The following features are particularly noteworthy.

1) There is an exceptionally wide range of atomic Mg/(Mg+Fe) or M/FM. The São Luiz (Mg,Fe)O inclusions range from 0.36 to 0.85, whilst the range for other localities is 0.85 to 0.88 with one exception (Moore *et al.*, 1986). The M/FM range for *fPer* occurring in the same diamond as silicates is 0.69 to 0.82 (discounting one inclusion for which there is evidence of disequilibrium).

2) Fe is partitioned preferentially into the *fPer* phase by comparison with the silicates; the $D_{\text{Fe/Mg}}$ for *MgSiPvk/fPer* is 0.40, within the range of Kesson and Fitz Gerald (1991); $D_{\text{Fe/Mg}}$ for *Gnt/fPer* is 0.48.

3) The garnet compositions show normal compliments of approximately 3Si, 2Al (+Cr and Ti), and 3 divalent cations, per 12 oxygen formula unit. Thus there is no evidence of majorite solid solution compositions. This conflicts with the experimental evidence of Kato *et al.* (1988) indicating that majorite garnet might be stable with perovskite-structured silicates, but accords with aspects of Irifune and Ringwood's (1993) experimental data.

4) The garnets have extremely low Ca contents, which are much lower than those of garnets from upper mantle assemblages (either peridotitic or eclogitic).

5) The *CaSiPvk* inclusions are virtually pure CaSiO_3 with respect to their major-minor element composition. [See Harte *et al.*, this volume, for trace element data].

6) Of the elements Cr, Mn and Ni, only Ni shows marked preferential partitioning between the oxide and silicate phases, and is more enriched in *fPer* than associated *MgSiPvk* or *Gnt*. These natural data are broadly in line with the experimental data of Kesson and Fitz Gerald (1991), though the *fPer/MgSiPvk* D_{Ni} for the São Luiz inclusions are in the range 33 to 70, which is higher than that recorded by Kesson and Fitz Gerald (1991).

7) A positive correlation exists between the abundance of Ni and the M/FM of the *fPer* inclusions.

Diamond characteristics. Five of the diamonds showing the lower mantle suite inclusions have been analysed for carbon isotope composition and for nitrogen content and aggregation state. The $\delta^{13}\text{C}$ group tightly around 5‰ and therefore have typical mantle (rather than crustal) signatures. Uniformly low N contents (max 50 ppm) have been determined, and the diamonds are of Type II or Type IaB.

Discussion

The geochemical coherence of the (Mg,Fe)O oxides, the silicate inclusions associated with them and the diamonds containing them, together with the mineral association *MgSiPvk* + *fPer* + *CaSiPvk*, all argue strongly in favour of the São Luiz inclusion assemblages coming from below the 670 km mantle discontinuity. They further suggest that the Al-rich phase in the uppermost lower mantle is a *Fe-Mg Gnt* (Ca-poor and 'non-majoritic'). Thus at lower mantle depths, with the stabilisation of *MgSiPvk* and *CaSiPvk*, *Gnt* ceases to show majorite-like (Si-rich) compositions (as found for the lower part of the upper mantle, op.cit.); and virtually all Ca becomes lodged in *CaSiPvk*.

Taking an assemblage of *MgSiPvk* + *fPer* + *CaSiPvk* + *Gnt* and the mineral compositions, one may calculate mineral proportions yielding particular bulk compositions. Using inclusion compositions from the low M/FM range of São Luiz silicate compositions (which are associated with a median *fPer* M/FM composition of 69%), a terrestrial bulk composition very close to that based on solar estimates is given by the following mineral proportions: *MgSiPvk* 68%, *fPer* 18%, *CaSiPvk* 7% and *Gnt* 7%. With high M/FM mineral compositions (for all phases), then pyrolite-chondrite model terrestrial compositions are approximately given using the mineral proportions: *MgSiPvk* 58%, *fPer* 20%, *CaSiPvk* 7% and *Gnt* 15%.

However, the wide range of M/FM values recorded for the inclusions suggest that they have been affected by differentiation processes, presumably involving melts, and this may well indicate that individual inclusions are unrepresentative of average lower mantle. From this viewpoint the material might form part of a zone of subducted crustal material entrained along the 670 kms discontinuity, as discussed by Ringwood (1982). However, the diamonds do not support this with their typical mantle $\delta^{13}\text{C}$ values.

If one considers the inclusion suite to be representative of the lower mantle, then it indicates average Earth compositions more similar to those of recent solar-based estimates (Anderson, 1989) and would imply a lower mantle distinctly more Fe-rich than the upper mantle; which in turn would favour a separation of upper and lower mantle convective systems.

References

See Harte, Hutchison and Harris, this volume.