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MINERAL ASSOCIATIONS IN DIAMONDS FROM THE LOWERMOST UPPER MANTLE AND UPPERMOST LOWER MANTLE

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INTRODUCTION

A small number of inclusions found in natural diamonds show chemical compositions essentially indicating the phase MgSi-perovskite. In ultrabasic and basic bulk rock compositions this phase is stable, under expected mantle P-T conditions, at depths around and greater than the Upper/Lower Mantle (UM/LM) seismic boundary at 660 kms. When inclusions of MgSi-perovskite are associated with inclusions of ferropericlase (dominantly MgO) in the same diamond they specifically indicate the dominant Lower Mantle mineral assemblage that replaces phases of $(\text{Mg,Fe})_2\text{SiO}_4$ composition which are characteristic of the Upper Mantle. The purpose of this paper will be to review the worldwide occurrence of sets of inclusions in diamonds which involve MgSi-perovskite (mPv), ferropericlase (fPer) and other phases suggestive of depths of origin around the UM/LM boundary and in the Lower Mantle. Emphasis will be placed upon cases with Si-bearing (silicate) minerals and where several minerals are associated together in the same diamond; thereby giving mineral assemblages that may be assigned to depth ranges on the basis of high P-T experimental studies.

The suite of diamonds and inclusions to be described is will be referred to as the MgSi-perovskite & ferropericlase suite or *mPv & fPer suite*. This suite occurs at localities in North and South America, Africa and Australia, and may be

accompanied by other suites of unusually deeply formed diamonds (Harte, 2010; Harte & Richardson, 2011). Thus diamonds with majoritic garnet inclusions, largely from the depth range 250-550 km have been found at several localities where *mPv & fPer suite inclusions occur*. In addition, particularly at Juina (Brazil), a wide range of Ca-rich and Al-rich inclusions with 'deep' Upper Mantle mineral compositions are also found. All these suites are clearly distinct from the common suites of inclusions with peridotitic and eclogitic minerals found in diamonds from the continental lithosphere (Stachel & Harris, 2008).

MGSI-PEROVSKITE & FERROPERICLASE SUITE

Table 1 lists associations of minerals which have been found together as separate inclusions within single diamonds. As well as MgSi-perovskite (mPv) and ferropericlase (fPer), the associations include other silicate minerals believed to indicate other ultra-high pressure phases. Diamonds with inclusions of ferropericlase alone or with $(\text{Mg,Fe})_2\text{SiO}_4$, spinel or other oxide phases are omitted, because of uncertainties over their depth of origin. Some associations involving an SiO_2 phase, especially with fPer, have been reported, but they are of uncertain origin (Hayman, 2005; Stachel et al., 2000) and are omitted.



It should be noted that the phases listed in Table 1 are predominantly those believed to have been stable at the time of incorporation in diamond. The mPv and cPv inclusions have been widely found to have inverted to lower pressure phases; and this is also true of the rare CF and NAL phases found. The inclusions listed as TAPP and 'NaAl-pyroxene/garnet' do not represent the original included phases but probably represent a Mg(Fe)Si-perovskite phase and/or ultra-high pressure garnet. However, there is some uncertainty over the precise original phase compositions represented by TAPP and 'NaAl-pyroxene/garnet' and it is for this reason that the retrograde phases are listed.

On the basis of experimentally determined phase equilibria, the associations in Table 1 are divided into the following groups.

(1) *UM/LM boundary associations marked by the occurrence of fPer, Mg₂SiO₄, and mPv: that is an assemblage of minerals which defines the UM/LM boundary with the breakdown of Mg₂SiO₄ to mPv+fPer. The three phases may occur as separate inclusions within the same diamond, or sometimes as composite inclusions, or sometimes as both single phase and composite inclusions. Some uncertainty exists in the case of some of the composite inclusions, because it is possible that the Mg₂SiO₄ phase has formed by retrograde reaction of touching fPer + mPv upon decompression (Stachel et al., 2000; Brey et al., 2004; Hayman et al., 2005); such composite inclusions have been ignored in discussion of mineral compositions.*

(2) *Lower Mantle associations involving mPv. These associations lack Mg₂SiO₄ and on the basis of MgSi-perovskite composition and experimental data they are divided into two groups:*

2a) with low-Al MgSi-perovskite (mPv in Table 1)

2b) with high-Al MgSi-perovskite (mPvAl in Table 1)

An exception to the listing of only multiple phase associations is made under this heading in Table 1. This is because the mPv(Al), CF, NAL and cPv(basic) inclusions noted provide the most clearcut evidence of basic, rather than ultrabasic, inclusion and bulk compositions in the Lower Mantle (Walter et al., 2011).

Table 1: MPv & fPer suite inclusion associations from the lower Upper Mantle(UM) and the Lower Mantle (LM)

Mineral Associations	No ^a	Localities ^b
(1) UM/LM boundary		
fPer + mPv ^c + Mg ₂ SiO ₄	2	J-RS, DO27
fPer + mPv + cPv + Mg ₂ SiO ₄	1	Ka
fPer + mPv + TAPP + Mg ₂ SiO ₄	1	J-RS
fPer + mPv + cPv + TAPP + Mg ₂ SiO ₄	1	J-RS
(2a) LM (low-Al mPv)		
fPer + mPv	4	Or, J-SL, Ko, Ka
fPer + mPv + TAPP	1	J-SL, Ka
fPer + mPv + cPv	2	Ka, DO27
fPer + mPv + cPv + Si-Mg phase	1	DO27
fPer + mPv + Ni	1	DO27
fPer + mPv + FeCO ₃	1	Ka
mPv + TAPP	2	J, J-SL
mPv + KAlSi ₃ O ₈	1	Ka
(2b) LM (high-Al mPv)		
fPer + mPv(Al)	1	J-SL
fPer + mPv(Al) + cm	1	J-SL
mPv(Al)	2	J-5
CF	1	J-5
NAL	2	J-5
cPv (basic)	1	J-5
(3) Uncertain UM/LM boundary region		
fPer + 'NaAl-pyroxene/garnet'	1	J-SL
fPer + TAPP	3	J-SL
fPer + TAPP + Mg ₂ SiO ₄	1	J-SL
fPer + cPv	9	J-SL, J-RS, Ka, Pa
TAPP + 'NaAl-pyroxene/garnet'	1	J-SL

Footnotes to Table 1.

^a No is the number of diamonds containing the given association of inclusions

^b Locality abbreviations as follows: J-Juina with RS (Rio Soriso), SL (São Luiz), 5 (Juina 5); Or-Orrorroo; DO27 in Slave craton; Ka-Kankan; Ko-Koffiefontein; Pa-Panda. Principal references for the localities are as follows. *São Luiz* – Harte et al., 1999; Hutchison et al., 2001. *Kankan* – Stachel et



al., 2000. *Juina* – Kaminsky et al., 2001; Bulanova et al., 2010. *Juina-5* – Walter et al., 2011; *Rio Soriso* – Hayman et al., 2005. *Koffiefontein* – Moore et al., 1986. *DO27* – Davies et al., 1999, 2004. *Panda* - Tappert et al., 2005b.

fPer – ferropericlasite; mPv – MgSi-perovskite; mPv(Al) – Al-rich MgSi-perovskite; cPv – CaSi-perovskite; TAPP – tetragonal almandine-pyrope phase. Mg₂SiO₄ assumed to have originally been ringwoodite. Further information on ‘NaAl-pyroxene/garnet’ and TAPP in text.

(3) *Uncertain UM/LM boundary region associations*. These associations commonly contain fPer, but not mPv, and so formation at the UM/LM boundary or within the Lower Mantle is uncertain. However, the TAPP and/or NaAl-pyroxene”/grt phases listed are believed to represent retrograde products from original mPv or ultra-high pressure garnet and thereby indicate an origin near the UM/LM boundary or in the LM. The fPer+cPv assemblage could form in the Transition Zone as well as the Lower Mantle. It is possible that this cPv association, and other associations of cPv alone or with Mg₂SiO₄ and SiO₂ (Harte, 2010) belong to the Ca-rich suite inclusions believed to have crystallized from carbonatitic melts in the Upper Mantle (Walter et al., 2008; Bulanova et al., 2010).

The mineral associations listed in Table 1 largely give the impression of ultrabasic bulk rock compositions because of the extensive involvement of fPer. However, basic rock compositions are clearly represented by the CF and NAL inclusions and the compositions of some mPv(Al) and cPv inclusions (see below). The assemblages of deepest origin, indicated by group 2b associations, do not necessarily indicate great depths in the Lower Mantle. Experimental data indicate that mPv(Al), CF and NAL become stable in basic rock compositions at ca 750 km (Irfune et al. 1996; Hirose et al., 2001, Perillat et al., 2006). The overall set of mineral assemblages

shown by Table 1 might form in the depth range 550 to 800 km.

MINERAL COMPOSITIONS IN THE MPV & FPER SUITE

Ferropericlasite (fPer)

Of all the phases of potential origin at the UM/LM boundary and in the Lower Mantle, ferropericlasite (fPer) is by far the most abundant. The wide involvement of ferropericlasite in associations with MgSi-perovskite is evident in Table 1, but there are also many diamonds in which ferropericlasite is the only included phase (ca 100 diamonds from the locations itemised in Table 1 are reported as containing ferropericlasite alone). Since fPer is stable in both crust and mantle, the single fPer inclusions *do not necessarily* indicate deep provenances (Brey et al., 2004), but all fPer inclusions are noted below.

The chemical compositions of fPer inclusions are typically close to stoichiometric (Mg,Fe)O and the principal chemical variation seen is in Mg/(Mg+Fe) ratio. Overall, considering inclusions of fPer alone as well as those associated with silicate phases, the Mg/(Mg+Fe) ratios are usually highly magnesian. In the Slave province (Canada), southern Africa and Australia fPer compositions are in the range 88.6 to 80.1 at % Mg/(Mg+Fe), with the exception of a very unusual value of 12.3 for a single Mg-wustite inclusion from Monastery (South Africa). At Kankan (west Africa) the range is 93.8 to 74.7 % (Mg/(Mg+Fe)), but at Juina the range is from 88.9 to 35.9 and therefore extends into the magnesiowustite field.

The minimum Mg/(Mg+Fe) found for fPer associated with mPv in the same diamond is 69.4.

Despite the wide range in Mg/(Mg+Fe), the (Mg,Fe)O inclusions show very limited variation in other chemical elements. Ti is usually less than 0.001 cats pfu and Al <0.002. Mn abundances are often <0.004 cations per formula unit, but occasionally approaches 0.010. The most

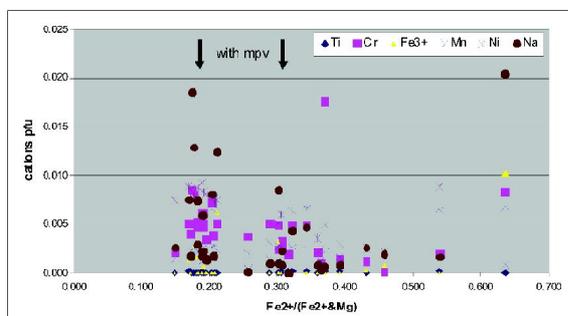


Fig. 1. Minor element compositions in ferropervicase inclusions from São Luiz diamonds, plotted against $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$. Single ferropervicase inclusions are plotted as well as ones co-existing with MgSi-perovskite and other phases. The black arrows show the range of $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ from 0.178 to 0.306 of ferropervicase inclusions co-existing with MgSi-perovskite (mPv). Ferrous/ferric ratios determined by stoichiometry

abundant additional elements are Cr, Ni and Na., but even these are typically <0.01 and only rarely reach 0.02 cats pfu. The compositions are illustrated in Fig. 1 for the São Luiz (Juina province) inclusions, which are the ones showing the widest range in $\text{Mg}/(\text{Mg}+\text{Fe})$, but similar ranges of composition of minor elements are seen at the other localities. The Na is probably charge balanced by Cr and Fe^{3+} (Stachel et al., 2000); and Fe^{3+} calculated stoichiometrically is also shown in Fig. 1. There is a suggestion of decreasing Ni and Cr with decreasing $\text{Mg}/(\text{Mg}+\text{Fe})$ in the main range of inclusions shown in Fig. 1. Kaminsky et al. (2001) and Davies et al. (2004a) also find Ni and $\text{Mg}/(\text{Mg}+\text{Fe})$ to be positively correlated for the Juina and Lac de Gras (Slave) localities. Davies et al. (2004) note that the compositions of all ferropervicase inclusions show a similar range of minor element compositions irrespective of whether they occur as single inclusions or are associated with other phases in the same diamond. This observation appears to be true for all localities, and in Fig. 1 it can be seen that ferropervicase inclusions associated with MgSi-perovskite in the same diamond do not have distinct compositions from those without MgSi-perovskite. Rarely Fe-rich

and Ni rich bodies are found within ferropervicase inclusions.

MgSi-perovskite (mPv)

MgSi-perovskite inclusions are dominantly of $(\text{Mg},\text{Fe})\text{SiO}_3$ composition, but show a clear distinction to upper mantle $(\text{Mg},\text{Fe})\text{SiO}_3$ (orthopyroxene) phases in that they show very low Ni contents (typically <0.03 wt%). This reflects the partitioning of Ni into ferropervicase in preference to MgSi-perovskite (Harte et al., 1999; Stachel et al., 2000). The range of $\text{Mg}/(\text{Mg}+\text{Fe})$ compositions found in mPv in the various Juina localities is reasonably similar with an overall range of 95.1 to 86.4. As with the fPer compositions, the mPv $\text{Mg}/(\text{Mg}+\text{Fe})$ ratios are limited to more magnesian values at other localities.

Al abundances in MgSi-perovskite inclusions show a bimodal distribution, with most inclusions showing a range of 0.55 to 3.37 wt %, but other inclusions (designated mPvAl in Table 1) showing >7.6 wt %. Within the mPv(Al) group there is further distinct separation between the inclusions associated with fPer and those without fPer. MgSi-perovskites associated with fPer have relatively low TiO_2 and FeO^i (below 0.22 and 9.0 wt % respectively), whilst those not associated with fPer have $\text{TiO}_2 >4.0$ and $\text{FeO}^i >20.3$ (wt%). The mPv(Al) with high Al, Ti and Fe are believed to be of basic rather than ultrabasic origin (Walter et al., 2011).

To document phase relations and test consistency in their mutual compositions, $\text{Mg}/(\text{Mg}+\text{Fe})$ partition coefficients have been calculated for the ferromagnesian phases. Fig. 2 illustrates the relationships for pairs of ferropervicase and low-Al-MgSi-perovskite occurring in the same diamond, and shows a considerable consistency despite the fact that the data is taken from several different localities. There is also a good correspondence of the maximum $\text{Fe}/(\text{Fe}+\text{Mg})$ in MgSi-perovskite with

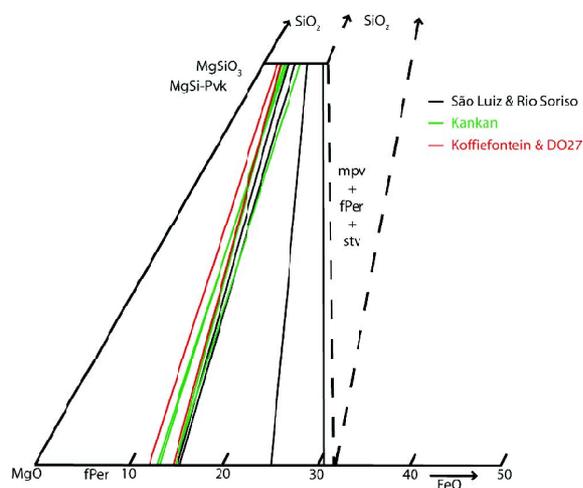


Fig. 2. Plot in MgO-FeO-SiO₂ of Mg/(Mg+Fe) ratios for ferropericlase and MgSi-perovskite. The tie-lines link single inclusions of each phase occurring in the same diamond, for the localities indicated (the source data may be found in the references given in Table 1). FeO compositions were calculated stoichiometrically from the total Fe of electron microprobe analyses. The dashed lines give the position of the 3-phase field for ferropericlase+MgSi-perovskite+stishovite based on the experimental data of Fei et al. (1996).

the experimental data of Fei et al. (1996) for the position of the fPer+mPv+stv 3-phase field.

Mg₂SiO₄

Twenty analyses have been recorded of Mg₂SiO₄ in association with other potentially 'deep' inclusion phases listed in Table 1. In its occurrence Mg₂SiO₄ is unique amongst inclusions in occurring more frequently in composite (polymineralic) inclusions than in single of single minerals; 12 of the 20 being composite. The overall range of Mg/(Mg+Fe) composition is similar for the two groups, being 96.5 to 87.4 for single inclusions and 96.5 to 89.1 for composite inclusions. Thus the Mg₂SiO₄ compositions in sublithospheric inclusions tend to be more Fe-rich than those found in lithospheric diamonds with a dominant range of 91 to 95 (Stachel and Harris, 2008). As with the ferropericlase and MgSi-perovskite data, the Mg₂SiO₄ inclusions of the

Juina province have lower Mg/(Mg+Fe) ratios than those from elsewhere.

Where the crystal structure of the Mg₂SiO₄ phase has been determined it has been found to be that of olivine, which is presumed to be a result of retrogression on decompression from ringwoodite. The possibility of distinguishing the Mg₂SiO₄ phases using geochemical criteria has been extensively considered, and the possibility of using minor concentrations of Al, Cr, Ni and Mn explored. However, no consistent relationships have been found (e.g. Davies et al., 2004, Tappert et al., 2005b; Hayman et al., 2005). The situation is further complicated if the composite inclusions of Mg₂SiO₄ accompanying ferropericlase and or MgSi-perovskite are considered. Brey et al. (2004) suggest that such Mg₂SiO₄ inclusions show distinctly low Ni and Cr values because the Mg₂SiO₄ formed by reaction between ferropericlase and MgSi-perovskite on decompression, with the low Ni and Cr contents of the initial MgSi-perovskite controlling the composition of the resultant Mg₂SiO₄.

Fig. 3 shows Mg₂SiO₄ compositions plotted in FeO-MgO-SiO₂ with tie-line connections to ferropericlase and MgSi-perovskite found in association in the same diamonds. Composite inclusions have been omitted from this plot, because of the possibility of retrograde olivine formation (see above). Many of the tie-lines in Fig. 3 show close consistency of orientation, indicating similar partition coefficients and equilibration conditions for sets of inclusions from different localities. But some distinctly crossing Mg₂SiO₄-ferropericlase tie-lines clearly indicate different conditions of equilibration or disequilibrium.

TAPP and 'NaAl-pyroxene/garnet'.

The phase listed as TAPP in Table 1 is a FeMg-silicate phase that until very recently has only been found as inclusions in diamonds. It has a tetragonal crystal structure, distinct to that of

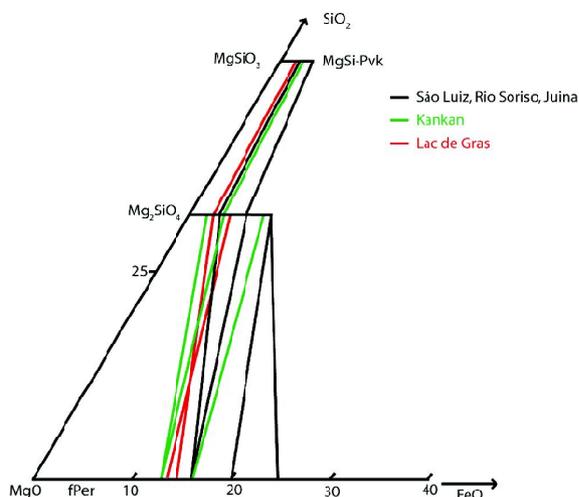


Fig. 3. Plot in MgO-FeO-SiO₂ of Mg/(Mg+Fe) ratios for Mg₂SiO₄ inclusions associated with ferropericlase and MgSi-perovskite. The tie-lines link single inclusions of each phase occurring in the same diamond, for the localities indicated (references given in Table 1) and does not include data from composite inclusions. FeO compositions were calculated stoichiometrically from the total Fe analyses.

garnet, but its compositions may be recast to conform with cation site occupancies found in garnets of pyrope-almandine composition – hence it acquired the name of Tetragonal Almandine-Pyrope Phase and the acronym TAPP (Harris et al., 1997). The place of TAPP in the UM/LM boundary assemblages has been enigmatic because its molar volume differs little from garnet and its Si is in [4]-fold coordination. Recently a phase with TAPP structure and composition has been synthesised at relatively low pressures (6 to 10 GPa), and it now appears that TAPP must be retrograde product formed by decompression of MgSi-perovskite and/or garnet (Armstrong & Walter, in press).

The “NaAl-pyroxene/grt” phase also listed in group 3 (Table 1) has a very limited occurrence, but is believed on experimental grounds (Gasparik and Hutchison, 2000; Hutchison et al., 2001) to represent a retrogressed Mg- and Na-rich majoritic garnet which would have co-existed with a carbonatitic melt in the lower Transition Zone.

This phase and TAPP may form in basic bulk compositions.

CaSi-perovskite

The CaSi-perovskite (cPv) inclusions listed in Table 1, and co-existing with ferropericlase and/or MgSi-perovskite, are characteristically extremely pure, consisting of ca 99% of the CaSiO₃ molecule. Minor impurities are Al, Fe, Mg, Na and Sr, each of which is usually < 0.2 wt %, though as much as 0.39 wt % Al₂O₃ and 0.85 wt % SrO are recorded by Stachel et al. (2000b). The cPv (basic) inclusion listed in Table 1 is also near pure CaSiO₃, but it is relatively Ti-rich (2.9 wt%), which is believed to indicate a basic rather than an ultrabasic composition (Walter et al., 2011).

NAL and CF phases

As found these inclusions consist of a composite of retrograde phases, but their bulk compositions fall in the range of experimentally synthesized phases in basic bulk compositions at upper Lower Mantle P-T conditions (Walter et al., 2011). They are Mg-Fe-Al-Si-O phases with very high Al content. The CF phase also carries substantial Na, whilst NAL has moderate Na and K contents, which may be around 4 wt %.

Diamond c isotope compositions and subduction

The mineral associations listed in Table 1 dominantly occur in diamonds with carbon isotope compositions ($\delta^{13}\text{C}$) in the host diamonds of -2.6 to -5.8 ‰, which are very close to the range expected for ‘normal’ mantle compositions. Prominent exceptions with $\delta^{13}\text{C}$ values of -15.4 to -24.1 ‰ have been found in the in the mPv(Al) and NAL phases believed to be derived from basic, rather than ultrabasic, compositions. Such extremely negative values suggest protoliths of crustal origin with organic carbon (Walter et al., 2011), and in this respect resemble $\delta^{13}\text{C}$ values in

