



Ferropericlase—a lower mantle phase in the upper mantle

Gerhard P. Brey^{a,*}, Vadim Bulatov^b, Andrei Girmis^c,
Jeff W. Harris^{a,d}, Thomas Stachel^{a,e}

^a*Johann Wolfgang Goethe-Universität Institut für Mineralogie, Fachbereich Geowissenschaften, Universität Frankfurt, Senckenberganlage 28, D-60054 Frankfurt, Germany,*

^b*Vernadsky Institute, Moscow, Russia*

^c*IGEM, Moscow, Russia*

^d*University of Glasgow, UK*

^e*University of Alberta, Edmonton, Canada*

Received 27 June 2003; accepted 22 January 2004

Available online 28 May 2004

Abstract

Experiments on compositions along the join $\text{MgO}-\text{NaA}^{3+}\text{Si}_2\text{O}_6$ ($A = \text{Al}, \text{Cr}, \text{Fe}^{3+}$) show that sodium can be incorporated into ferropericlase at upper mantle pressures in amounts commonly found in natural diamond inclusions. These results, combined with the observed mineral parageneses of several diamond inclusion suites, establish firmly that ferropericlase exists in the upper mantle in regions with low silica activity. Such regions may be carbonated dunite or stalled and degassed carbonatitic melts. Ferropericlase as an inclusion in diamond on its own is not indicative of a lower mantle origin or of a deep mantle plume. Coexisting phases have to be taken into consideration to decide on the depth of origin. The composition of olivine will indicate an origin from the upper mantle or border of the transition zone to the lower mantle and whether it coexisted with ferropericlase in the upper mantle or as ringwoodite. The narrow and flat three phase loop at the border transition zone—lower mantle together with hybrid peridotite plus eclogite/sediments provides an explanation for the varying and Fe-rich nature of the diamond inclusion suite from Sao Luiz, Brazil. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ferropericlase; Olivine; Diamond; Upper mantle; Lower mantle; Inclusions

1. Introduction

The Earth's mantle may be subdivided into a number of layers, that correspond to phase transitions of its constituent minerals. The 400-km discontinuity marks the top of the transition zone at the onset of the transformation of olivine into a spinel-like β -phase named wadsleyite (Ringwood and Major, 1966; Akaogi et al., 1989). The 650-km discontinuity, leading

into the lower mantle, is attributed to the decomposition of Mg_2SiO_4 spinel (γ -phase) or ringwoodite to $\text{Mg}-\text{Si}$ perovskite plus periclase (Liu, 1974, 1975). Ferropericlase is therefore a major constituent of the Earth's lower mantle. Minor amounts also occur in the Earth's crust, where it forms in high-temperature contact metamorphic processes. When ferropericlase was found as inclusion in diamonds from Orroroo and together with enstatite in diamonds from Koffiefontein, it was considered as an indicator of a lower mantle origin of the host diamond (Scott Smith et al., 1984). On this basis Wilding (1990), Harte and Harris (1994) and Hutchison

* Corresponding author. Fax: +49-69-798-28066.

E-mail address: brey@em.uni-frankfurt.de (G.P. Brey).

(1997) identified a number of lower mantle parageneses in diamonds from Sao Luiz (Brazil). A critical voice came when Gurney (1989) and later Stachel et al. (1998) pointed out, that some of these “lower mantle” parageneses could be explained in terms of disequilibrium between different inclusion generations within individual diamonds.

Stachel et al. (2000) reported further evidence that ferropericlase may form as inclusion in diamonds at upper mantle conditions, provided that the Si activity was low enough. In a sample collection from the Kankan district, Guinea, they found a diamond (KK84) with ferropericlase and olivine both as separate monomineralic inclusions and as a contacting pair. The olivine crystal structure was confirmed for both olivines by in situ single crystal X-ray measurements (see Stachel et al., 2000). They show sharp reflexes characteristic for untwinned crystals. Twinning might be expected if the olivines were the retrograde products of ringwoodite through an ex-

tremely rapid uprise of the diamond from 670 km. The single olivine inclusion is identical in composition to that in contact with ferropericlase and vice versa (Fig. 1). This demonstrates their entrapment in a single stage of diamond growth as a ferropericlase–olivine pair and excludes the possibility of the formation as an original ferropericlase–ringwoodite pair in the narrow divariant field at the 670-km discontinuity (where ferropericlase, ringwoodite and Mg–perovskite coexist). In the latter case, ringwoodite would have to transform to olivine which would necessitate Fe- and Mg-exchange of the touching pair. Thus, this diamond has grown in the upper mantle in a region with a particularly low Si activity. Disequilibrium between different inclusion generations is highly unlikely because the chemical similarity includes all measured trace elements (Stachel et al., 2000). Yet, the ferropericlases have elevated concentrations of Na and Cr, which was considered to be indicative of a lower mantle origin (Kesson and Gerald, 1992). The solubility of Na in periclase has been determined experimentally so far only at high pressures corresponding to the transition zone (Gasparik and Litvin, 1997; Gasparik, 2000, 2002) but not at upper mantle pressures. This led us to study the solubility of Na in periclase at upper mantle pressures in the presence of the trivalent cations Al, Fe³⁺ and Cr.

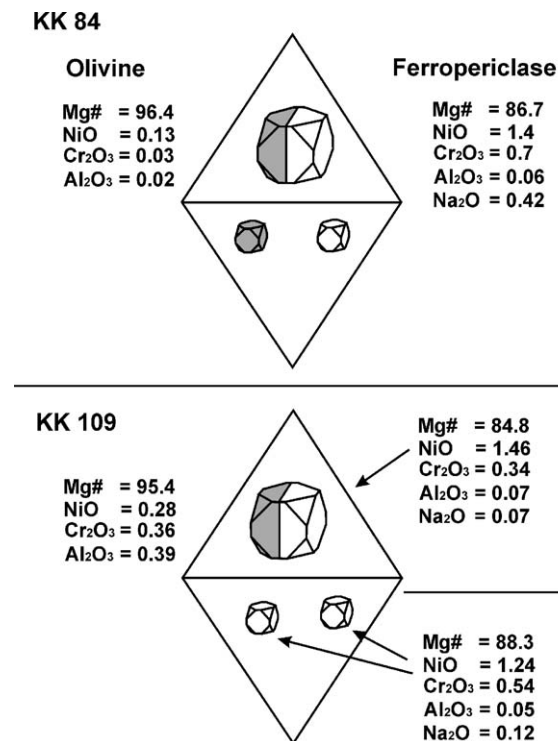


Fig. 1. Compositions two different kinds of coexisting olivine and ferropericlase inclusions in diamond.

2. Experiments

2.1. Starting materials and experimental procedures

Starting compositions along the joins MgO–NaAlSi₂O₆, –NaCrSi₂O₆, –NaFe³⁺Si₂O₆ were selected such that MgO was stable together with olivine, spinel (chromite, magnetite) and a Na-bearing phase, in our case melt (Fig. 2). In order to generate large amounts of periclase, the bulk MgO:–SiO₂ was chosen to be 2.5 in experiments at 1300–1400 °C and 4.0 at 1600 °C. The mixtures were prepared from crystalline jadeite and fired oxide mixtures of NaCrSi₂O₆ and NaFeSi₂O₆ composition added in appropriate amounts to crystalline MgO. The two latter mixtures were fired at ~900 °C in air, which provided a highly oxidized state. The starting materials were welded shut into Pt capsules. The

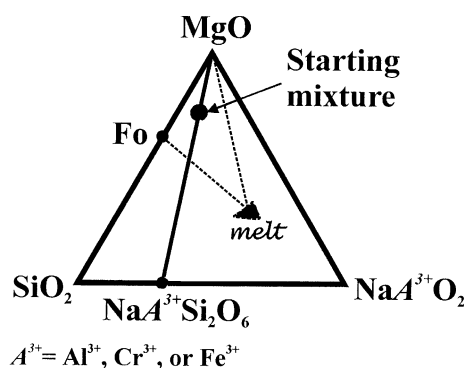


Fig. 2. Composition of the starting mixes in mol% and of the melts produced in the sandwich experiments plotted in a diagram MgO–SiO₂–NaA³⁺O₂.

experiments were carried out under dry conditions in a belt apparatus at 30 and 50 kbar and 1300, 1400 and 1600 °C. One experiment at 30 kbar in the Cr-bearing system was carried out in a Pt double capsule with hematite + H₂O in the outer capsule to ensure highly oxidizing conditions (denoted in Fig. 3 with fO_2). There is no difference in Cr₂O₃ content to the equivalent run without an outer buffer capsule. In order to determine the melt composition more accurately in the Al-bearing system, a sandwich technique was applied. A crude estimate of melt composition was made from earlier runs and a fired oxide mix of that composition sandwiched between two layers of a jadeite–MgO mixture in a Pt capsule.

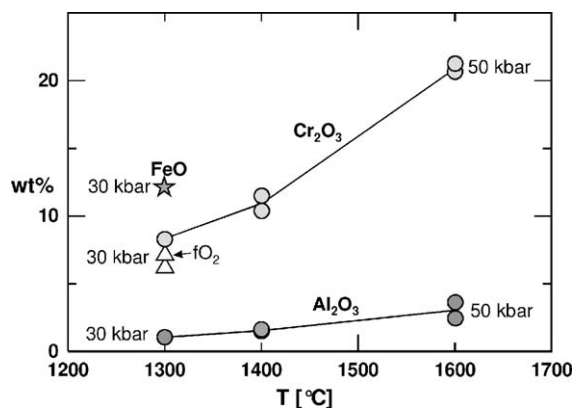


Fig. 3. FeO, Al₂O₃ and Cr₂O₃ contents in periclase vs. experimental temperature at 30 and 50 kbar. “ fO_2 ” indicates a run carried out in a double capsule with hematite as a buffer.

2.2. Analytical methods

All runs were analysed by EPMA with a JEOL 8900 Superprobe with 15 kV acceleration voltage and 20 nA. For the analysis of solid phases the beam was focussed to 250 nm. It was widened to 30 μ m for the quenched melt analysis.

2.3. Experimental results

Experimental run conditions, results and the composition of the synthesized periclases are given in Table 1. The structural formula of periclases calculated with different oxidation states of Fe and Cr are given in Table 2. In all but one run, the experimental products were always periclase, olivine, spinel (chromite, magnetite) and interstitial, quench-modified liquid. A hitherto unknown Na- and Cr-rich phase grew in the subsolidus experiment run at 50 kbar and 1300 °C in the Cr-bearing system. Significant amounts of

Table 1
Run conditions and experimental run products

P	T	Run no.	Phases	Remarks	Computed (wt.%) of periclase		
					MgO–NaAlSi ₂ O ₆	Al ₂ O ₃	MgO
30	1300	295/2	P, ol, sp, L		0.98	96.92	0.59
30	1300	299	P, ol, sp, L	held at 1450	0.87	96.87	0.38
50	1300	1214/2	P, ol, sp, L		1.06	96.05	0.50
50	1400	1209/1	P, ol, sp, L		1.49	94.90	0.73
50	1600	1218/1	P, ol, sp, L	MgO-richer	3.64	94.86	0.78
50	1600	1221/1	P, ol, sp, L	MgO-richer	2.56	94.53	0.67
30	1300	300	P, ol, sp, L	Sandwich	0.84	98.39	0.33
50	1400	1216	P, ol, sp, L	Sandwich	1.63	97.32	0.64
					MgO–NaCrSi ₂ O ₆		
30	1300	295/1	P, ol, chr, L		6.18	89.30	0.78
30	1300	296	P, ol, chr, L	high fO_2	7.10	89.60	0.65
50	1300	1214/1	P, ?, L		8.32	87.34	1.80
50	1400	1209/2	P, ol, chr, L		11.49	84.78	1.58
50	1400	1215/2	P, ol, chr, L	synthesis	10.38	89.15	0.57
50	1600	1218/2	P, ol, chr, L	MgO-richer	20.66	77.17	0.77
50	1600	1221/2	P, ol, chr, L	MgO-richer	21.19	76.99	1.21
					MgO–NaFe ³⁺ Si ₂ O ₆		
30	1300	292	P, ol, mt, L		11.88	87.75	0.27

Table 2

Structural formula of periclase based on one oxygen and calculated for Al^{3+} , Cr^{3+} , Cr^{2+} , Fe^{3+} and Fe^{2+}

Run no.	Al^{3+}	Mg	Na	Sum
295/2	0.008	0.984	0.008	1.000
299	0.007	0.989	0.005	0.999
1214/2	0.009	0.984	0.007	0.999
1209/1	0.121	0.977	0.010	0.999
1218/1	0.029	0.952	0.010	0.991
1221/1	0.021	0.965	0.009	0.994
300	0.007	0.988	0.004	0.999
1216	0.013	0.976	0.084	0.998

Run no.	Cr^{3+}	Mg	Na	Sum	Cr^{2+}	Mg	Na	Sum
295/1	0.035	0.943	0.011	0.988	0.035	0.959	0.011	1.001
296	0.039	0.937	0.009	0.985	0.040	0.955	0.009	1.005
1214/1	0.046	0.918	0.025	0.989	0.048	0.940	0.025	1.013
1209/2	0.064	0.893	0.022	0.979	0.066	0.922	0.022	1.011
1215/2	0.056	0.912	0.008	0.976	0.058	0.938	0.008	1.004
1218/2	0.117	0.820	0.011	0.947	0.124	0.871	0.011	1.006
1221/2	0.119	0.814	0.017	0.949	0.126	0.865	0.018	1.009

Run no.	Fe^{3+}	Mg	Na	Sum	Fe^{2+}	Mg	Na	Sum
292	0.068	0.896	0.004	0.968	0.071	0.928	0.003	1.002

Na_2O were present in the synthetic periclases at all run conditions (Table 1 and Fig. 4). Their compositions duplicate the range of values observed in natural ferropericlases.

The sodium content of periclase is lowest in the one Fe-bearing run, is higher at the same conditions when Al is present, and is the highest in the Cr-bearing system. In the Al-bearing system Na solubility

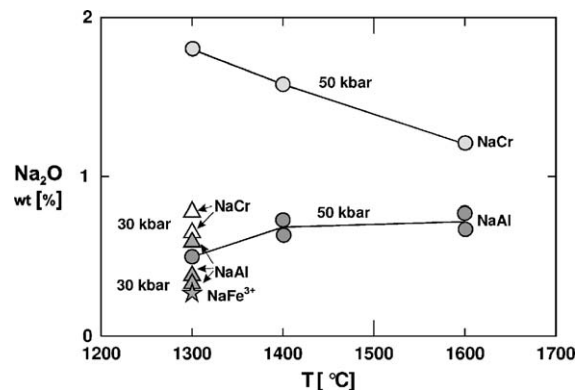


Fig. 4. Na_2O in periclase vs. experimental temperature at 30 and 50 kbar. Sodium solubility lowest in the Fe-bearing system, increases with Al and is highest in the Cr-bearing system.

Table 3

Composition (wt.%) of melts from sandwich experiments

Run no.	SiO_2	Al_2O_3	MgO	Na_2O
300	38.4 ± 7	14.1 ± 6	15.0 ± 1.8	29.7 ± 1.8
1216	42.0 ± 6	11.4 ± 3	18.1 ± 7	30.1 ± 1.0

in periclase seemingly increases with temperature. It decreases in the Cr system with temperature yet is favoured by pressure. These results cannot be applied directly to natural ferropericlases because no other Na-bearing phase is present and the melt coexisting in the experimental charges presumably varies in amount and composition. The melts from the two sandwich runs are very rich in sodium and are highly silica undersaturated (Table 3). Partition coefficients $D_{\text{Na}}^{\text{Fe-Per/melt}}$ are 0.011 at 30 kbar, 1300 °C and 0.021 at 50 kbar, 1400 °C.

Al and Cr in periclase show a positive dependency on pressure and very pronounced dependence on temperature, with Cr_2O_3 reaching more than 20 wt.% at 50 kbar and 1600 °C (Fig. 3). These elements (especially Cr) are incorporated into periclase in amounts far in excess of what is needed for charge balancing Na (Fig. 5). Al is present at 1300 and 1400 °C in just the correct amounts, but at 1600 °C it is double the amount of sodium and the ferropericlases must be nonstoichiometric. This is much more so the case for Cr which, however, may also partly be incorporated in the divalent state. Fe is also far above the amount necessary for charge balance,

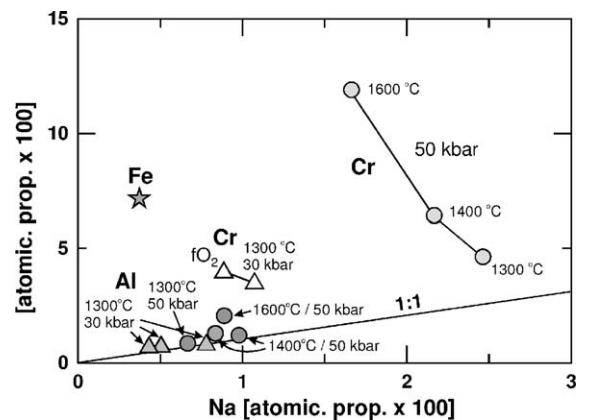


Fig. 5. Atomic proportions of Fe, Al and Cr vs. the atomic proportion of Na in periclase at the various experimental conditions. The 1:1 line is the reference line for charge balance.

but much of it will be Fe^{2+} . The effects of non-stoichiometry and varying oxidation states may be judged from the structural formula calculations given in Table 2.

The new and unknown crystalline phase produced at 50 kbar and 1300 °C in the Cr-bearing system forms large poikilitic grains with abundant periclase and chromite inclusions. It is pleochroic in blue and green shades. It is extremely low in silica and Cr-rich. An idealized formula would be $\text{Na}_2\text{Mg}_3\text{Si}_2\text{O}_8$ with significant $2\text{Cr} \rightarrow \text{MgSi}$ and $\text{NaCr} \rightarrow 2\text{Mg}$ isomorphism to yield $(\text{Na},\text{Mg})_2(\text{Mg},\text{Cr})_3(\text{Si},\text{Cr})_2\text{O}_8$.

3. Ferropericlase–olivine relations in diamonds

3.1.1. Ferropericlase–olivine pairs

Ferropericlases occurring together with olivine in a single diamond are reported from Guinea, Brazil and Canada. They are compared with the worldwide data set of inclusions in Fig. 6 and individually discussed in the following.

The olivines (structure confirmed by in situ X-ray diffraction) in diamond KK84 are distinct from other olivine inclusions in diamonds worldwide (Fig. 6, see also Fig. 1) in their extremely high Mg-numbers (96.5) and very low NiO (0.13 wt.%) and low Cr_2O_3 (0.03 wt.%) contents, an expression of the bulk composition of the source rock and of equilibrium with ferropericlase at upper mantle pressures. The ferropericlases have high Mg-numbers and Ni, Cr and Na and fall within the range of the worldwide database; that is, they do not occupy a separate compositional field.

A second diamond (KK109) from Guinea (Fig. 6, see also Fig. 1) has a ferropericlase/olivine contacting pair and two separate ferropericlases with a common composition which is different to that of the ferropericlase in contact with olivine (Stachel et al., 2000). Because of micron to submicron spinel exsolutions and generally higher Cr and Al contents in the olivine than found in the worldwide database, a case could be made that this diamond inclusion had grown near the lower mantle boundary, that the touching pair was originally ferropericlase + Mg-perovskite and that it reacted on uprise to form ferropericlase + ringwoodite

(a spinel structure, which, in comparison to the olivine structure, takes in trivalent cations and whose partitioning behaviour with ferropericlase is such that it takes more Mg, Ni and Co compared to olivine). The final adjustment, but not to completion, to coexisting ferropericlase + olivine occurred in the upper mantle before the kimberlite eruption. The chemical composition of the ferropericlases falls within the spread of the worldwide database.

Diamond KK 44 from Guinea seems unusual since it contained the three major lower mantle phases and, in addition, a touching pair of former Mg-perovskite (now orthopyroxene) and olivine with very low nickel (Fig. 6). This pair must have originally formed as an intergrowth of small amounts of ferropericlase and abundant perovskite which kept the bulk Ni abundance of the inclusion at a very low level. Thus, after upward transport and on final adjustment to ambient conditions in the upper mantle, the olivine was left with only little nickel.

Two examples of joint occurrences of olivine and ferropericlase in a single diamond are described from the Juina district in Brazil (Kaminsky et al., 2000; Hutchison, 1997; Hutchison et al., 2000). In both cases, the ferropericlases are indistinguishable from the world database (except for the relatively Fe-rich nature of the whole Brazilian suite), while the “olivines” show very high Ni, Co and Cr (Fig. 6). In both cases, the authors used this as an indication for the origin of these diamonds from the boundary to the lower mantle. A further olivine with similar high Ni, Co and Cr coexists with CaSiO_3 , fortifying the conclusions about a very high-pressure origin of this suite.

The diamond suite from Panda, Canada (unpublished) also yields olivine–ferropericlase pairs (PA 39 and PA 54), but with much lower Ni and also Cr contents in the olivines relative to the worldwide database, but similar to olivine–ferropericlase pairs thought to be of upper mantle origin. Diamond DO 27–300 (Davies et al., pers. comm. and submitted to *Lithos*) has olivine and MgSiO_3 as separate inclusions with the olivine being far too low in Ni and Cr (Fig. 6) to have originated as ringwoodite. It may, however, be a former coupled pair of Mg-perovskite in excess and ferropericlase which reacted to olivine and some leftover MgSiO_3 not observed during the study.

From the above discussion, it appears that the composition of the ferropericlases does not allow

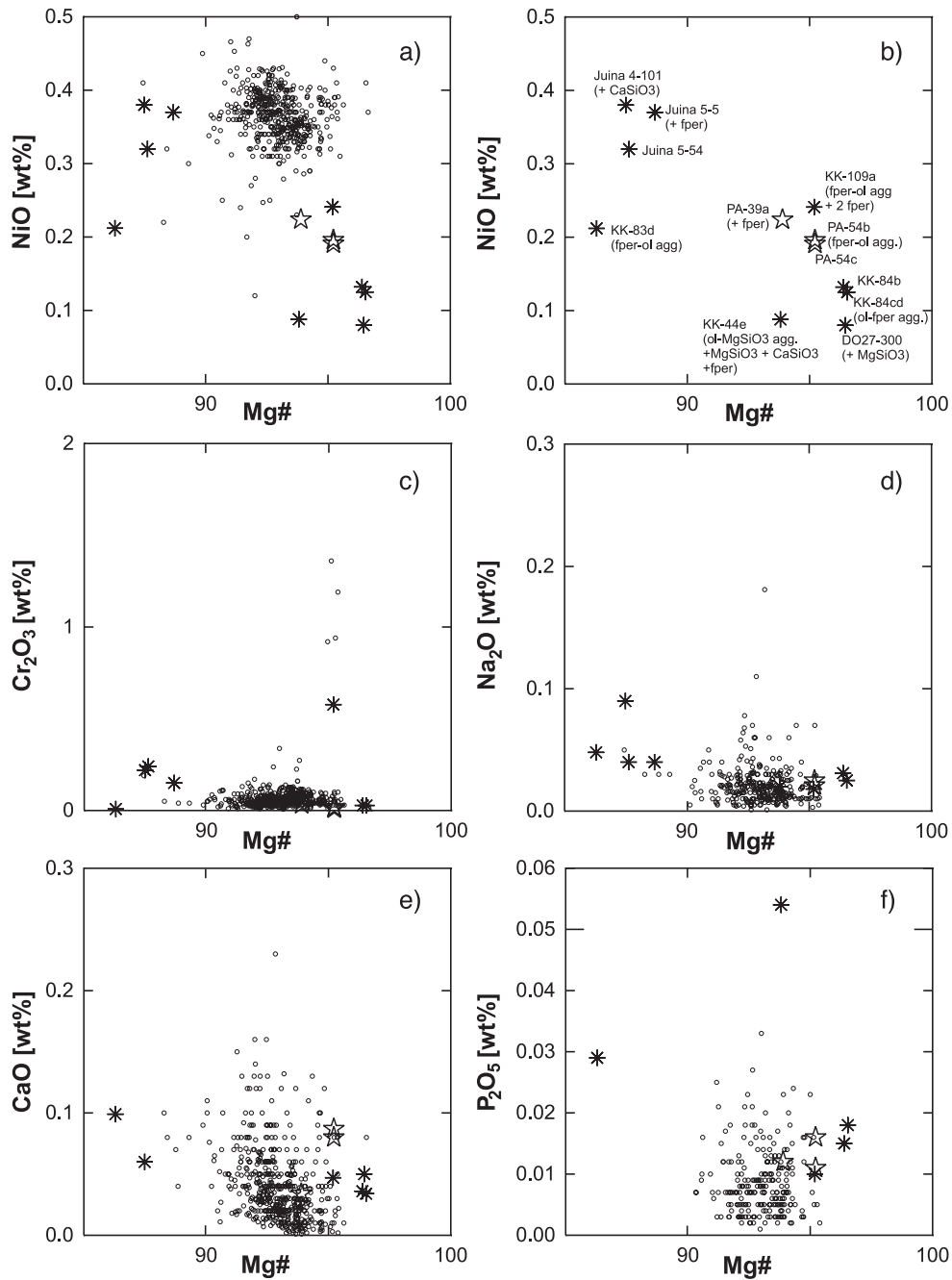


Fig. 6. Composition of olivine inclusions from the worldwide database. Olivines coexisting with ferropericase (stars and double crosses) plot away from the field of peridotitic olivines of upper mantle origin (small circles), both to low and high Ni and Cr contents. A number of olivines from the worldwide database plot in the vicinity of these uncommon types. They indicate a similar origin as those described in this paper but detailed descriptions are lacking in the literature. (a) All available data are compiled. (b) Only olivines with coexisting ferropericase are shown and their sample numbers are given. (c) Shows the Cr content which is analogous to Ni low in olivines considered to have an origin in the upper mantle and high in those considered to have originated at or within the perovskite–ferropericase–ringwoodite loop. Sodium (d), calcium (e) and phosphorous (f) do not differ significantly from the worldwide database.

distinction between an origin in the upper mantle, the transition zone or the lower mantle, but that olivines could carry this information.

3.2. Single ferropericlases, single olivines

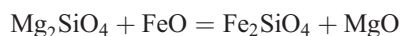
Single ferropericlases and their chemical compositions are not indicative of a lower or an upper mantle origin. Because there is no structural change occurring in this pressure range, its uptake of suitable elements does not change drastically with pressure. Olivine, however, undergoes two phase transitions with concomitant changes in partition coefficients of divalent cations and the enhanced intake of trivalent cations. Olivines with low Ni, Co and Cr contents at high Mg-values are indicative of an upper mantle origin, and equilibrium with ferropericlase, whereas olivines with high Cr (and Al) and Ni and Co at “normal” mantle values indicate an origin in the transition zone or the boundary to the lower mantle.

4. Discussion and conclusions

We have shown that sodium can be incorporated into ferropericlase at upper mantle pressures in amounts commonly found in natural diamond inclusions. Our experiments and the diamond inclusions establish firmly that ferropericlase exists in the upper mantle in regions with low silica activity. Such regions could be a magnesite bearing dunite in which ferropericlase may form by reduction of magnesite during diamond growth by the following reactions:



concomitant with the Fe–Mg exchange reaction



The difficulty is how to generate a magnesite-bearing dunite free of orthopyroxene in the first place. This can only be via the introduction of a carbonatite melt into dunite, since carbonation reactions in peridotite generally increase the activity of silica by converting olivine to orthopyroxene. Another scenario to be imagined is that ferropericlase crystallizes from a melt containing 8–10 wt.% Na₂O (this number is

deduced from our sandwich experiments). Carbonated peridotite may generate Na-rich carbonatite melts near the mantle solidus (Wallace and Green, 1988) in equilibrium with orthopyroxene and olivine. CO₂-degassing of the carbonatite melt at decreasing pressures may produce a silicate melt with very low Si content, which crystallizes olivine and periclase. Experimental evidence for this is presented by Brey and Ryabchikov (1994) who found a vastly expanded field of crystallisation of ferropericlase in carbonated, highly Si-undersaturated magmas with decreasing pressure. This and the above model are similar except that instead of a solid carbonate we have carbonate liquid, which can easily move and produce mantle lithologies with very low Si/Mg ratios.

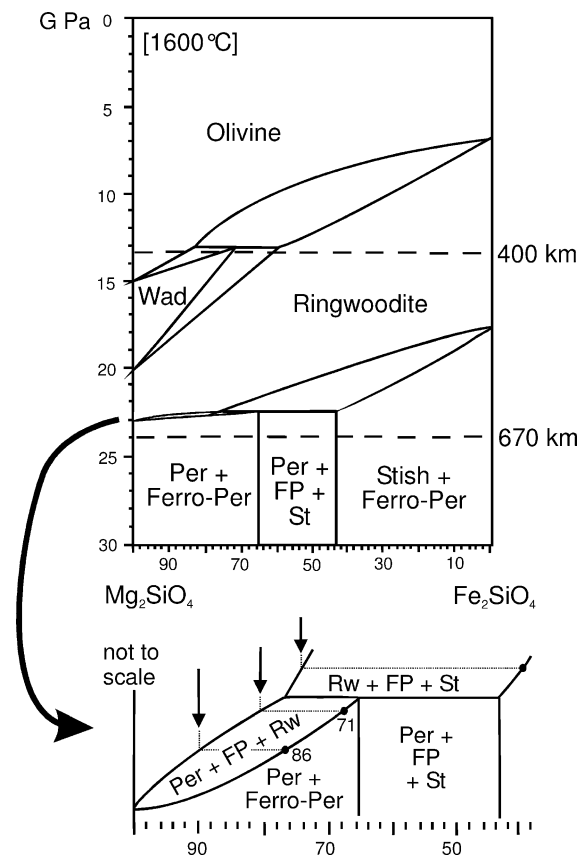


Fig. 7. Largely schematic phase relationships for olivine with increasing pressure. The numbers written on the loop for coexisting ringwoodite, ferropericlase and perovskite correspond to the Mg-value of ferropericlase.

In summary, ferropericlase as an inclusion in diamond on its own is not indicative of a lower mantle origin, let alone of a mantle plume. The composition of coexisting phases has to be taken into account to decide on an upper mantle, transition zone or lower mantle origin.

From the presently known diamond inclusion inventory we have clear indications that diamonds come from the upper mantle, the transition zone, from the boundary to the lower mantle and from its uppermost part. Ferropericlase with very variable Fe/Mg-ratios in diamond inclusions from Juina, Brazil has been inferred to originate in the D'' layer (Harte et al., 1999; Kaminsky et al., 2000). We argue here that they also stem from the border zone of the lower mantle from the loop with coexisting Mg-perovskite, ferropericlase and ringwoodite (Fig. 7). Their protoliths were hybrid rocks of peridotite plus subducted eclogite or sediments to increase bulk Fe/Mg. The partitioning behaviour of Fe and Mg (e.g., Frost and Langenhorst, 2002) between coexisting Mg-perovskite and ferropericlase, between ringwoodite and ferropericlase (Frost et al., 2001) and the very narrow and flat loop readily explain the observed variation in Fe/Mg ratios in both phases. From their work, a ringwoodite with an Mg-value of 90 would coexist with ferropericlase with Mg# \approx 86 and Mg-perovskite with Mg# \approx 95, ringwoodite with Mg# \approx 80 with ferropericlase₇₁ and perovskite₈₅ and ringwoodite with Mg# \approx 75 with a ferropericlase with Mg# \approx 40 (schematically shown in Fig. 7) which coincides with the range observed in Sao Luis.

Acknowledgements

We would like to thank D.H. Green for helpful discussions and Kai Klama, Marina Lazarov and Iris Sonntag for help with the final preparation of the manuscript. We thank the reviewers Kathy McCammon, Tibor Gasparik and Reidar Tronnes for helpful and interesting suggestions and Herman Grütter for careful editorial handling.

References

- Akaogi, M., Ito, E., Navrotsky, A., 1989. Olivine-modified spinel–spinel transition in the system Mg_2SiO_4 – Fe_2SiO_4 : calorimetric measurements, thermochemical calculation, and geophysical application. *J. Geophys. Res.* 94, 15671–15685.
- Brey, G.P., Ryabchikov, I.D., 1994. Carbon dioxide in strongly undersaturated melts and origin of kimberlitic magmas. *Neues Jahrb. Mineral., Monatsh. H.* 10, 449–463.
- Frost, D.J., Langenhorst, F., van Aken, P.A., 2001. Fe–Mg partitioning between ringwoodite and magnesiowüstite and the effect of pressure, temperature and oxygen fugacity. *Phys. Chem. Miner.* 28, 455–470.
- Frost, D.J., Langenhorst, F., 2002. The effect of Al_2O_3 on Fe–Mg partitioning between magnesiowüstite and magnesium silicate perovskite. *Earth Planet. Sci. Lett.* 199, 227–241.
- Gasparik, T., 2000. Evidence for the transition zone origin of some [Mg,Fe]O inclusions in diamonds. *Earth Planet. Sci. Lett.* 183 (1–2), 1–5.
- Gasparik, T., 2002. Experimental investigation of the origin of majoritic garnet inclusions in diamonds. *Phys. Chem. Miner.* 29 (3), 170–180.
- Gasparik, T., Litvin, Y.A., 1997. Stability of $Na_2Mg_2Si_2O_7$ and melting relations on the forsterite–jadeite join at pressures up to 22 GPa. *Eur. J. Mineral.* 9 (2), 311–326.
- Gurney, J.J., 1989. Diamonds. In: Ross, J., et al., (Eds.), *Kimberlites and Related Rocks. Spec. Publ.-Geol. Soc. Aust.* 14, vol. 2. Blackwell, Carlton, pp. 935–965.
- Harte, B., Harris, J.W., 1994. Lower mantle mineral associations preserved in diamonds. *Min. Mag.* 58, 384–385.
- Harte, B., Harris, J.W., Hutchison, M.T., Watt, G.R., Wilding, M.C., 1999. Lower mantle mineral associations in diamonds from Sao Luis, Brazil. In: Fei, Y., Bertka, C., Mysen, B.O. (Eds.), *Mantle Petrology: Field Observations and High Pressure Experimentation: A Tribute to Francis R. (Joe) Boyd*. Publication-The Geochemical Society, Houston, vol. 6, pp. 125–153.
- Hutchison, M.T., 1997. Constitution of the deep transition zone and lower mantle shown by diamonds and their inclusions. PhD thesis. University of Edinburgh, UK, vol. 1, 340 pp. vol 2 (Tables and Appendices), 306 pp.
- Hutchison, M.T., Hursthouse, M.B., Light, M.E., 2000. Mineral inclusions in diamonds: associations and chemical distinctions around the 670-km discontinuity. *Contrib. Mineral. Petrol.* 142, 119–126.
- Kaminsky, R.V., Zakharchenko, O.D., Davies, R., Griffin, W.L., Khachatryan-Blinova, G.K., Shiryaev, A.A., 2000. Superdeep diamonds from the Juina area, Mato Grosso State, Brazil. *Contrib. Mineral. Petrol.* 140, 734–743.
- Kesson, S.E., Gerald, J.D.F., 1992. Partitioning of MgO , FeO , NiO , MnO and Cr_2O_3 between magnesian silicate perovskite and magnesiowüstite—implications for the origin of inclusions in diamond and the composition of the lower mantle. *Earth Planet. Sci. Lett.* 111, 229–240.
- Liu, L.-G., 1974. Silica perovskite from phase transformations of pyrope–garnet at high pressure and temperature. *Geophys. Res. Lett.* 1, 277–280.
- Liu, L.-G., 1975. Post-oxide phases of forsterite and enstatite. *Geophys. Res. Lett.* 2, 417–419.
- Ringwood, A.E., Major, A., 1966. Synthesis of Mg_2SiO_4 – Fe_2SiO_4 spinel solid solutions. *Earth Planet. Sci. Lett.* 1, 241–245.
- Scott Smith, B.H., Danchin, R.V., Harris, J.W., Stracke, K.J., 1984.

- Kimberlites near Orroroo, South Australia. In: Kornprobst, J. (Ed.), *Kimberlites I: Kimberlites and Related Rocks*. Elsevier, Amsterdam, pp. 121–142.
- Stachel, T., Harris, J.W., Brey, G.P., 1998. Rare and unusual mineral inclusions in diamonds from Mwadui, Tanzania. *Contrib. Mineral. Petrol.* 132, 34–47.
- Stachel, T., Harris, J.W., Brey, G.P., Joswig, W., 2000. Kankan diamonds (Guinea): II. Lower mantle inclusion paragenesis. *Contrib. Mineral. Petrol.* 140, 34–47.
- Wallace, M.E., Green, D.H., 1988. Experimental determination of primary carbonatite magma composition. *Nature* 335, 343–346.
- Wilding, M.C., 1990. A study of diamonds with syngenetic inclusions. Unpubl PhD thesis. University of Edinburgh, UK. 281 pp.