FERROPERICLASE – A LOWER MANTLE PHASE IN THE UPPER MANTLE

Gerhard P. Brey[1], Vadim Bulatov[2], Andrei Girnis[3], Jeff W. Harris[4,1], Thomas Stachel[5,1]

[1]University of Frankfurt, Germany; [2]Vernadsky Institute, Moscow, Russia; [3]IGEM, Moscow, Russia;
[4]University of Glasgow, UK; [5]University of Alberta, Edmonton, Canada

INTRODUCTION

Ferropericlase is a major constituent of the Earth. It resides mainly in the lower mantle below the 670 km discontinuity, where it becomes stable through the decomposition of silicate spinel via the reaction $Mg_2SiO_4 \rightarrow MgSiO_3(perov) + MgO(Fe\text{-}Per)$. Minor amounts of periclase occur also in the earth's crust, where it forms in high-temperature contact metamorphic processes. A considerable gap in its occurrence is the upper mantle and the transition zone where the above reaction lies to the left and MgO is not stable in the presence of pyroxene. Thus, when Fe-Per was found as inclusion in diamonds, it was considered as an indicator of a lower-mantle origin of the host diamond. However, Stachel et al. (2000) reported evidence that ferropericlase may form as inclusion in diamonds also at upper mantle conditions provided that Si-activity was low enough.

In a collection from the Kankan district, Guinea, a diamond (KK84) was found with ferropericlase and olivine as single inclusion each and also as a contacting pair. The single olivine inclusion is identical in composition to that in contact with ferropericlase and vice versa. This demonstrates their entrapment in a single stage of diamond growth as 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 had to transform to olivine with would necessitate Fe- and Mg-exchange of the touching pair. Thus, this diamond has grown in the upper mantle in a portion with a particularly low Si-activity. Yet, the ferropericlases have elevated concentrations of Na and Cr, which was considered so far to be indicative of a lower mantle origin (Kesson et al., 1998). Experimental evidence is lacking for this assumption which led us to study the solubility of Na at upper mantle pressures in the presence of the trivalent cations Al, Fe^{3+} and Cr.

EXPERIMENTS

Starting compositions along joins $MgO\text{-}NaAlSi_2O_6$, -$NaCrSi_2O_6$, -$NaFe^{3+}Si_2O_6$ were selected such that MgO was stable together with olivine, spinel (chromite, magnetite) and a Na-bearing phase, in our case melt. Only in the subsolidus run at 50 kbar and 1300 °C, a hitherto unknown Na- and Cr-rich phase grew. In order to generate large amounts of periclase, the bulk $MgO:SiO_2$ was chosen to 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 $NaCrSi_2O_6$ and $NaFeSi_2O_6$ 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 experiments were carried out under dry conditions in a belt apparatus at 30 and 50 kbar and 1300, 1400 and 1600°C.

Table 1: Run conditions and experimental run products

P	T	Run-Nr	Phases	Remarks
			$MgO - NaAlSi_2O_6$	
30	1300	295/2	P, ol, sp, L	
30	1300	299	P, ol, sp, L	held at 1450
50	1300	1214/2	P, ol, sp, L	
50	1400	1209/1	P, ol, sp, L	
50	1400			
50	1600	1218/1	P, ol, sp, L	MgO-richer
50	1600	1221/1	P, ol, sp, L	MgO-richer
30	1300	300	P, ol, sp, L	sandwich
50	1400	1216	P, ol, sp, L	sandwich
			$MgO - NaCrSi_2O_6$	
30	1300	295/1	P, ol, chr, L	
30	1300	296	P, ol, chr, L	high fo$_2$
50	1300	1214/1	P, ?, L	
50	1400	1209/2	P, ol, chr, L	
50	1400	1215/2	P, ol, chr, L	synthesis
50	1600	1218/2	P, ol, chr, L	MgO-richer
50	1600	1221/2	P, ol, chr, L	MgO-richer
			$MgO - NaFe^{3+}Si_2O_6$	
30	1300	292	P, ol, mt, L	

Experimental Results

Experimental run conditions and products are given in Table 1 und the compositions of the synthesized periclases in Table 2. The experimental products (except for the run at 50 kbar, 1300 °C) were always
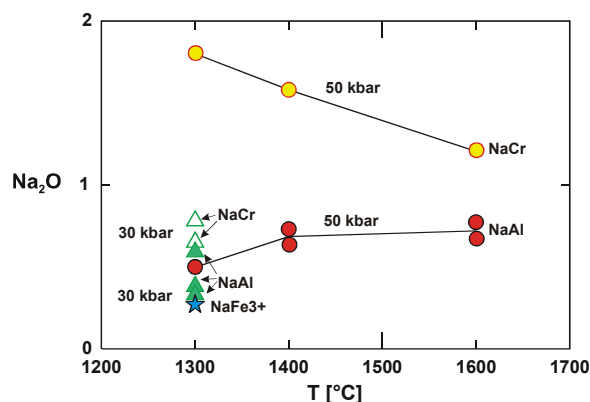
Table 2: Composition of synthesized periclases

Run-Nr	Al_2O_3	MgO	Na_2O
295/2	0.98	96.9	0.59
299	0.87	96.9	0.38
1214/2	1.06	96.1	0.5
1209/1	1.49	94.9	0.73
1218/1	3.64	94.9	0.78
1221/1	2.56	94.5	0.67
300	0.84	98.4	0.33
1216	1.63	97.3	0.64

Run-Nr	Cr_2O_3	MgO	Na_2O
295/1	6.18	89.3	0.78
296	7.1	89.6	0.65
1214/1	8.32	87.3	1.8
1209/2	11.5	84.8	1.58
1215/2	10.4	89.2	0.57
1218/2	20.7	77.2	0.77
1221/2	21.2	77	1.21

| Run-Nr	FeO	MgO	Na_2O
292	11.9	87.8	0.27

periclase, olivine, spinel (chromite, magnetite) and interstitial, quenchmodified liquid. Significant amounts of Na_2O were present in the synthetic periclases at all run conditions (Table 2 and Fig. 1). They duplicate the range of values observed in natural ferropericlases.
Sodium is lowest in the one Fe-bearing run, is higher at the same conditions when Al is present and highest in the Cr-bearing system. In the Al-bearing system Na-solubility 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 coexisting melt presumably varies in amount and composition.
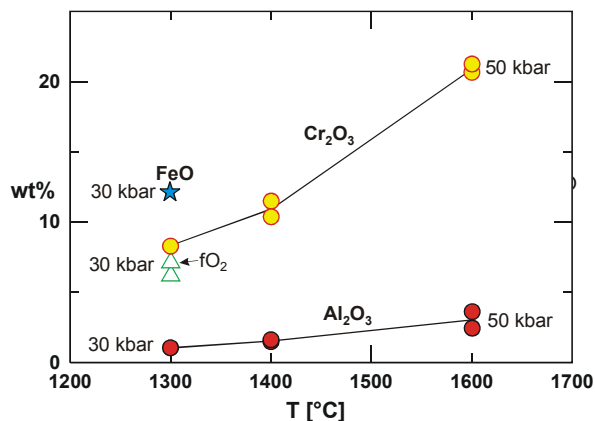
Fig.ure 2: FeO-, Al_2O_3- and Cr_2O_3-contents in periclase versus experimental temperature at 30 and 50 kbar

Al and Cr show a positive dependency on pressure and very pronounced on temperature (Fig. 2) with Cr reaching more than 20 % at 50 kbar and 1600 °C. These elements (esp. Cr) are incorporated into periclase in amounts far in excess of what is needed for charge balancing Na (Fig. 3). Al is present at 1300 and 1400 °C just in the correct amounts, but at 1600 °C it is double the amount of sodium and the ferropericlases must be non-stoichiometric. 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

Figure 1: Na_2O in periclase versus experimental temperature at 30 and 50 kbar
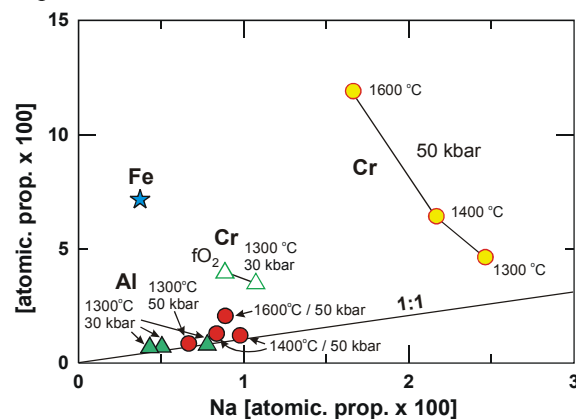
Figure 3: Atomic proportions of Fe, Al and Cr versus the atomic proportion of Na in periclase at the various experimental conditions. The 1:1 line is the reference line for charge balance

the amount necessary for charge balance, but much of it will be Fe^{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 MgO 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 $Na_2Mg_3Si_2O_8$ with significant 2Cr->MgSi and NaCr->2Mg isomorphism to yield $(Na,Mg)_2(Mg,Cr)_3(Si,Cr)_2O_8$.

FERROPERICLASE-OLIVINE PAIRS IN DIAMONDS

The olivines (structure confirmed by in-situ X-ray diffraction) in diamond KK84 are distinct from other olivine inclusions in diamonds world-wide (Fig. 4) 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 nickel contents, together with Cr and Na, fall within the range of the world-wide data base.

A second diamond (KK109) from Guinea Fig. 4) had a ferropericlase/olivine pair and two separate ferropericlases with differing composition to that from the touching pair (Stachel et al. 2000). Because of micron- to submicron spinel exsolutions and generally higher Cr- and Al-contents (and also Ni) 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 seems surprising at first 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. 4). This pair was 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, on final adjustment
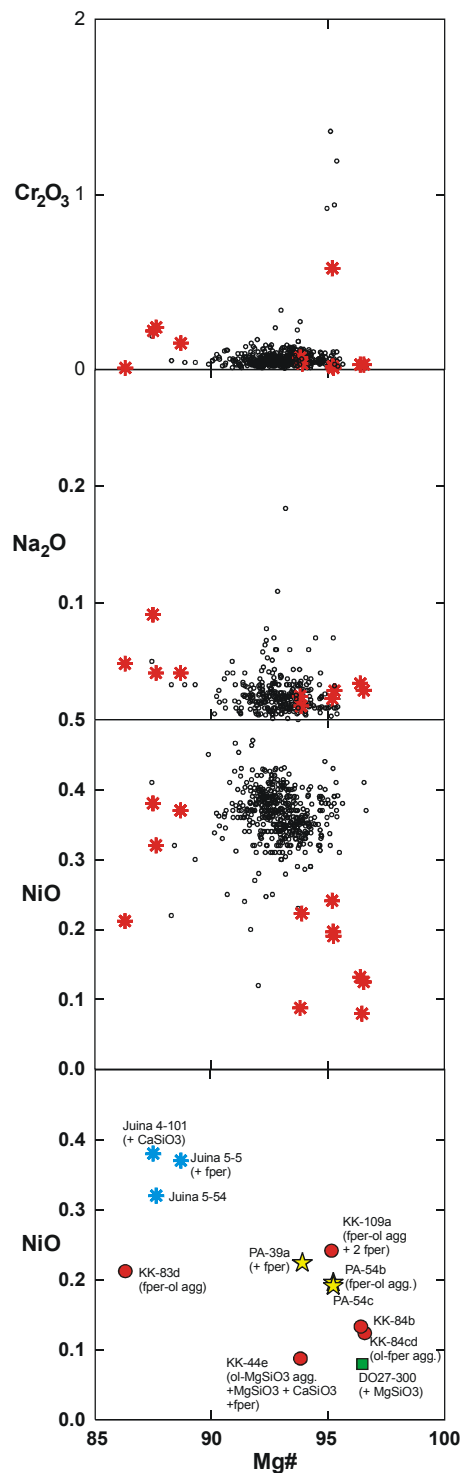
Figure 4: Composition of olivine inclusions from the world-wide data base. Olivines coexisting with ferropericlase plot away from the field of peridotitic olivines of upper mantle origin, both to low and high Ni- and Cr-contents. A number of olivines plot in the vicinity of these uncommon types.

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 one diamond are described from the Juina district in Brazil (Kaminsky et al., 2001 and Hutchison et al., 2001). In both cases, the ferropericlases are indistinguishable from the world data base (except for the relatively Fe-richer nature of the whole Brazilian suite), while the "olivines" show very high Ni, Co and Cr (Fig. 4). 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 CaSiO$_3$, fortying 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 54), but with much lower Ni-contents in the olivines than in those in the world wide data base, but similar to those olivine-ferroperclase pairs shown to be of upper mantle origin. Diamond DO 27-300 (Davies et al., in press) has olivine and Mg-perovskite as separate inclusions with the olivine being far too low in Ni and Cr (Fig. 4) to be a candidate as a former ringwoodite. Thus we would consider the inclusions in this diamond as a disequilibrium assembly.

From the above said, it appears that the chemistry of the ferropericlases does not allow to distinguish between an origin from the upper mantle, the transition zone or the lower mantle, but that olivines do carry this information.
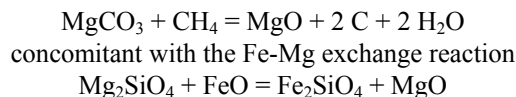
Single ferropericlases, single olivines

Single ferropericlases and their chemical compositions are not indicative for 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. Thus, low Ni, Co and Cr-contents at high Mg-values are indicative of an upper mantle origin and equilibrium with ferropericlase and high Ni, Co and Cr at intermediate to low Mg-values of an origin in the transition zone or the boundary to the lower mantle.

DISCUSSION AND CONCLUSIONS

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

$$MgCO_3 + CH_4 = MgO + 2\,C + 2\,H_2O$$
concomitant with the Fe-Mg exchange reaction
$$Mg_2SiO_4 + FeO = Fe_2SiO_4 + MgO$$

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 always generate orthopyroxene. Another scenario to be imagined is that ferropericlase crystallizes from a melt containing 8-10 wt % Na$_2$O (this number is deduced from our sandwich experiments not described further in this extended abstract – see table 1). Carbonated peridotite generates Na-rich carbonatite melts near the solidus (Wallace and Green, 1988) in the mantle, but it forms in equilibrium with orthopyroxene and olivine. Degassing at decreasing pressures will transform it to 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 extending 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.

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 only clear indication that diamonds come from the upper mantle, the transition zone, from the boundary to the lower mantle and its uppermost part – but not from any deeper.

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Contact: Gerhard Peter Brey, Institut für Mineralogie, Universität Frankfurt, D-60054 Frankfurt, Germany, e-mail: brey@em.uni-frankfurt.de