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PHASE RELATIONS OF ECLOGITE + 4.4% CO₂ AT 9-21 GPa: IMPLICATIONS FOR DIAMOND FORMATION IN THE DEEP MANTLE

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We have experimentally investigated the melting and phase relations of MORB eclogite with the addition of 4.4% CO₂ at temperatures 1100-1900°C and pressures 9-21 GPa. Multi-anvil experiments were conducted using the 3000 ton press at Tohoku University. The experimental compositions were two synthetic mixes GA1 and Volga. Volga is identical to GA1, but with 6.5% less SiO₂. Due to hydrothermal alteration, the upper part of the oceanic crust becomes enriched in carbonates. Usually, carbonate is present in the form of calcite. In some areas (mainly shallow, upper 500 m of the oceanic crust) the CO₂ contents may be as high as 6 wt% (Staudigel, 2003). In reality, calcite is probably heterogeneously distributed in the oceanic crust at various scales and any amount of carbonate in an experimental study will be to some extent arbitrary. The relatively high abundance of CO₂ in the experiments was intended to simplify the detection of carbonates in run products. The CO₂ was added to the starting mixture as CaCO₃ (cc). GA1+10%cc models altered oceanic crust, recycled into the convecting mantle via subduction. Volga+10%cc models subducted mafic crust, which may have lost a siliceous component during dehydration and/or silicate melting in the subduction zone. Compared to compositions previously selected for high-pressure studies (Table 1), the representative

	This work, GA1+10%cc	This work, Volga+10%cc	Vasuda et al., 1994	Wang and Takahashi, 1999	Okamoto and Maruyama, 2004	Litasov and Ohtani, 2005	Kashy and Gudfinnsson, 2010 ¹	Litasov and Ohtani, 2010
P (GPa)	9-21	9-21	3-20	2-27	10-19	18-28	12-25	10-32
SiO ₂	45.32	42.22	49.71	53.53	51.11	50.06	30.80	50.02
TiO ₂	1.34	1.43	1.71	1.44	1.76	1.47	—	—
Al ₂ O ₃	14.88	15.91	15.68	14.85	14.86	15.39	4.02	16.59
Cr ₂ O ₃	—	—	—	0.05	—	—	—	—
FeOT	8.85	9.46	9.36 ¹	7.92	10.3	9.61	—	—
MnO	0.15	0.14	0.18	0.16	—	—	—	—
MgO	7.15	7.64	8.43	7.64	7.68	7.59	22.49	14.82
CaO	14.24	14.85	11.73	9.12	11.23	11.28	21.23	11.49
Na ₂ O	3.14	3.36	2.76	2.64	2.94	2.43	—	2.08
K ₂ O	0.40	0.42	0.23	1.31	0.13	0.17	—	—
P ₂ O ₅	0.14	0.15	0.02	—	—	—	—	—
CO ₂	4.40	4.40	—	—	—	—	21.46 ²	5.00
H ₂ O	—	—	—	—	2.00	2.00	—	—
Total	100.00	100.00	99.81	98.66	102.01	100.00	100.00	100.00

¹ - additional 0.95 wt% Fe₂O₃ included in the value

² - one of the four compositions used in the study

³ - CO₂ measured by difference

compositions of the dry carbonated oceanic crust, such as GA1+10%cc and Volga+10%cc, are used experimentally for the first time. This allows constraints to be placed on the phase assemblages and melting character of carbonated eclogite along its subduction path into the upper mantle and transition zone. All experiments were conducted in the Au₂₅-Pd₇₅ capsules with 12-48 hours run durations.

The subsolidus mineral assemblage in the runs differed depending on the pressure. At 9 and 13 GPa, the major phases were garnet, clinopyroxene, magnesite, aragonite, high-pressure TiO₂ (only at 9 GPa) and stishovite (only at 13 GPa). Majorite garnet was the most abundant phase in all the experimental runs. At 17-21 GPa clinopyroxene was no longer stable; the mineral



assemblage consisted mostly of garnet with subordinate magnesite (only at 17 GPa), Na-rich aragonite, stishovite, Ca-perovskite (mostly at 21 GPa), and K-hollandite (mostly at 17 GPa). Na-carbonate crystallized in Volga+10%cc at 21 GPa.

In Volga+10%cc, the solidus curve is nearly constant between 1200 and 1300°C over the entire pressure range investigated. In GA1+10%cc, the solidus is located at similar temperatures at 9-13 GPa but at higher temperatures ~1300-1500°C at 17-21 GPa. The difference in solidi between the GA1+10%cc and Volga+10%cc compositions is explained by a change in Na-compatibility between 13 and 17 GPa as omphacitic clinopyroxene disappears, resulting in the formation of Na-carbonate in Volga+10%cc. The solidus temperature in GA1+10%cc also increases with increasing pressure as a consequence of carbonate reduction and diamond precipitation. The low degree melts are highly alkalic (K-rich at 9-13 GPa and Na-rich at 17-21 GPa) carbonate, changing towards SiO₂-rich melts with increasing temperature at constant pressure.

Diamond (or graphite) crystallized in most runs in GA1+10%cc composition, but never in experiments with Volga+10%cc composition. In the experiment with GA1+10%cc at 1400°C and 21 GPa diamond was identified with the Laser RAMAN technique (Fig.1). Structures of C-

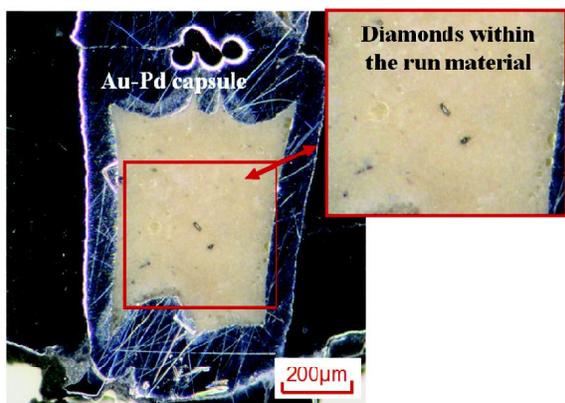


Fig. 1. Experimental capsule (GA1+10%cc at 1400°C and 21 GPa) with visually observed crystallized diamonds. The phase composition has been identified by Laser Raman technique.

bearing phases have not been identified in the other experiments, therefore we are unable to classify it precisely as diamond or graphite.

At both 17 and 21 GPa crystals are hard (scratching the polishing surface) (Fig. 2), while at 9 and 13 GPa they are much softer and exhibit a layered structure (Fig. 3).

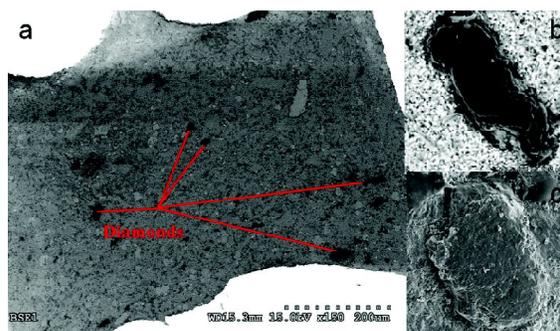


Fig. 2. Diamonds crystallized at 17-21 GPa with GA1+10%cc starting composition. (a) Experiment at 1300°C and 21 GPa. (b) Experiment at 1400°C and 21 GPa. (c) Experiment at 1200°C and 17 GPa. Grain size of diamond crystals is around 20-30 µm.

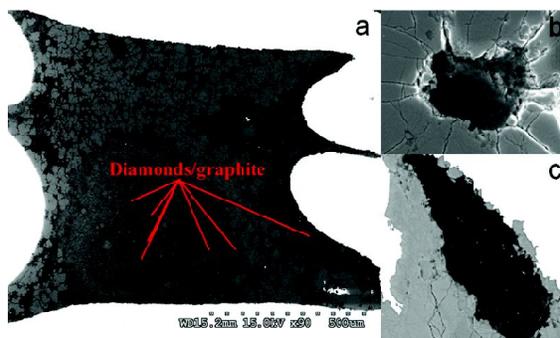


Fig. 3. Diamonds/graphite crystallized at 9-13 GPa with GA1+10%cc starting composition. (a) Experiment at 1400°C and 13 GPa. (b) and (c) Experiment at 1200°C and 13 GPa. Grain size of diamond crystals is around 20-40 µm.

This allowed the conclusion that at lower pressures graphite can be stable in GA1+10%cc at given oxygen fugacity. Most of observed diamond/graphite crystals are relatively large (up to 40 mm) and occur in both subsolidus and above solidus runs.

In most cases, diamond/graphite crystals are included in bigger garnet crystals (Fig. 3b) or



surrounded by fine-grained matrix of garnet and stishovite (Fig. 2a,b).

The diamond aggregates coexist either with compositionally variable crystalline carbonates (Fig. 4), or carbonate melts (Fig. 5).

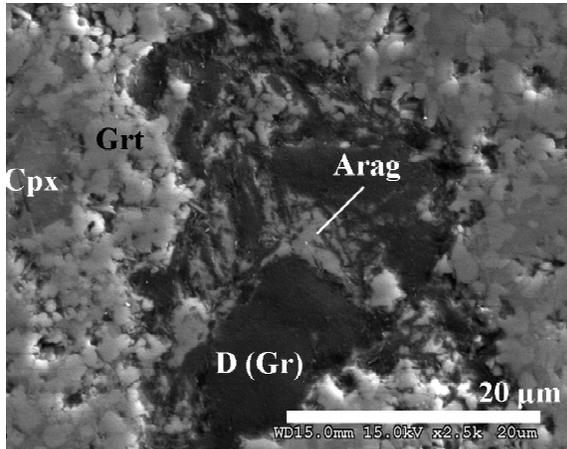


Fig. 4. Carbonate inclusions in diamond/graphite. SE images of the experiment with GA1+10%cc starting composition at 1200°C and 9 GPa.

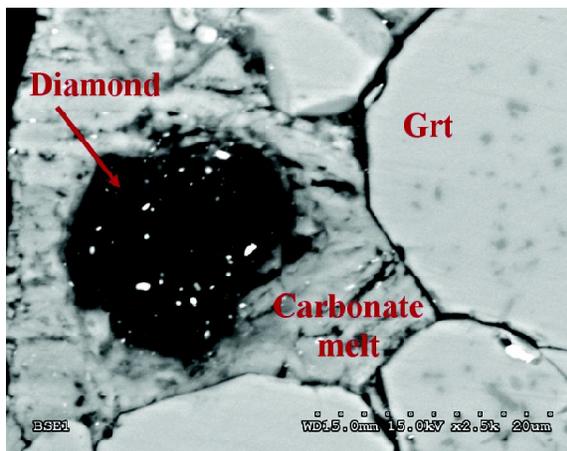


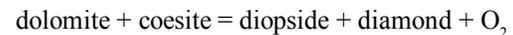
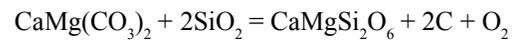
Fig. 5. Diamond/graphite crystal inside the melt pool in the experimental run at 1400°C and 13 GPa.

The fact that diamonds have crystallized only in the GA1cc bulk composition and not the Volga-cc bulk composition is of particular interest. A possible explanation for diamond crystallization in GA1cc is the oxidation of ferrous iron in silicate garnet as a consequence of the increased stability of the skiaigite component with increasing pressure

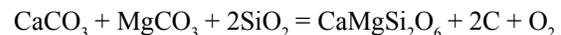
(Woodland & O'Neill, 1993, 1995). In calcium-rich eclogites the andradite component would predominate over the skiaigite component (Simakov, 2006). However, the composition and modal proportions of garnet in GA1+10%cc and Volga+10%cc at 17-21 GPa are almost the same.

Unfortunately, it was not possible to directly measure Fe³⁺ in the garnets from this study, although their cation sums are consistent with most if not all iron being present as Fe²⁺. Another reason would be partial contamination of the sample by hydrogen derived from cell assembly parts during the experiment. This is not very likely because then diamond formation would have been expected in both compositions, which is not the case.

The following reaction governing diamond-formation in eclogite systems has been proposed by Luth (1993):



Applying this reaction to the subsolidus experiments at 9 GPa, in which magnesite and aragonite coexists results in:



The equilibrium constant for this reaction is

$$K = \frac{a_{\text{CaMgSi}_2\text{O}_6} \times a_{\text{C}}^2 \times f_{\text{O}_2}}{a_{\text{CaCO}_3} \times a_{\text{MgCO}_3} \times a_{\text{SiO}_2}^2}$$

Given the presence of both coesite/stishovite and carbonates in all the experiments, it is possible to conclude that the denominator can be assumed to be 1 for almost pure carbonate components. Assuming that oxygen fugacity is similar in both starting compositions, K is dependent exclusively on the activity of the diopside component in clinopyroxene solid solution exclusively. With decreasing diopside activity, the reaction shifts to the right and leads to the formation of diamond/graphite. Indeed, the diopside component in GA1+10%cc clinopyroxene from subsolidus



experiments at 9 GPa is approximately 5-10 mol% lower than the Volga+10%cc clinopyroxene at the same P-T conditions. Only in the experimental run at 9 GPa and highest temperature conditions of 1400°C, diamond/graphite did not crystallize, but in that case the diopside component was higher for clinopyroxene crystallized in Volga+10%cc starting composition.

Thus, clinopyroxene composition at constant oxygen fugacity can possibly have an influence on diamond formation however this matter needs further experimental investigation.

The fact that carbon-bearing phases crystallized through the entire range of experimental P-T conditions in both subsolidus and above-solidus experiments, may indicate that carbonated eclogite can be a potentially suitable media for diamond crystallization along the entire path of subducted slab into the transition zone and even lower mantle. Observations of solid carbonate inclusions in the natural diamonds derived from the transition zone (e.g. Brenker, 2007) are in good agreement with our experimental results. On the other hand, even such a small difference in starting composition as between GA1+10%cc and Volga+10%cc can significantly influence diamond formation.

The solidus of both compositions remains at higher temperatures than the hottest estimated subduction geotherm, in good agreement with previous, lower pressure studies. Thus subducting carbonates in eclogite may reach the deeper convecting mantle, where they can be melted to produce alkali- and carbonate-rich liquids which could have a role in fertilizing the surrounding peridotite mantle and producing enriched magmas. On the other hand, because of relatively low solidus temperatures, extremely alkali-rich low-degree melts are estimated to segregate from the main eclogite body at the upper mantle depths. However, there is a high chance that refractory carbon-bearing eclogite may continue being subducted or stored at transition zone or even lower mantle pressures. We argue that such a

lithology may contain significant amount of carbon preserved in it even after several pulses of melting. Which form this carbon will be stored, will depend on oxygen fugacity, but at some more oxidized conditions diamonds may be an important accessory phase.

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