



MELTING PHASE RELATIONS IN THE SYSTEMS PERIDOTITE-H₂O-CO₂ AND ECLOGITE-H₂O-CO₂ AT PRESSURES UP TO 27 GPA

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INTRODUCTION

Oxidized fluid compounds, H₂O and CO₂, dominate in the upper mantle at depths to 100–200 km and have key importance to kimberlite magmatism. At greater depths CH₄, other hydrocarbons, and H₂ may become dominant, however, oxidized species may still be preserved at a depth up to 600–700 km at least in the subduction-related environments (Brenker et al., 2007). The simplified and complex systems with CO₂ or H₂O alone are studied experimentally up to pressures of 20–32 GPa (e.g. Litasov and Ohtani, 2002, 2009, 2010; Dasgupta and Hirschmann, 2006; Brey et al., 2008, 2011; Litasov, 2011). At the same time, the systems, containing both H₂O and CO₂, are studied only at low pressures to 3–5 GPa (e.g. Wyllie, 1978; Green and Falloon, 1998; Wyllie and Ryabchikov, 2000; Foley et al., 2009) and in few cases to 10–12 GPa under specific conditions (Girnis et al., 2011). In this contribution we report the results of the experimental study of the systems peridotite–H₂O–CO₂ and eclogite–H₂O–CO₂ up to a pressure of 27 GPa. Preliminary results of this study were reported in (Litasov et al., 2011).

EXPERIMENTAL

The starting compositions of peridotite (which is close to pyrolite) and eclogite (close to altered MORB) contained 3 wt % H₂O and CO₂

each (Litasov et al., 2011). The concentrations of Al₂O₃ and CaO are slightly lower, and the concentrations of Cr₂O₃ and NiO are higher in peridotite than those in pyrolite. Eclogite has a composition of altered MORB (slightly undersaturated in SiO₂). Experiments were performed at pressures of 3–27 GPa and temperatures of 800–1500°C (Fig.1) using a multianvil high pressure apparatus at Tohoku University (Sendai, Japan). The octahedral cell of ZrO₂ was placed in the center of eight cubic tungsten carbide anvils. The truncation edge length of WC anvils varied from 12 to 2 mm in different configurations (Litasov and Ohtani, 2009; 2010). Graphite or LaCrO₃ tubes isolated by a MgO sleeve from the capsule with the sample were used as heaters. The sample powder was loaded into the Au–Pd capsule and sealed using arc welding. The Pt–graphite capsule was applied at 3–6.5 GPa in the highest temperature experiments. Except for the runs at 27 GPa, each cell contained two capsules: the first one with peridotite, the second one with eclogite starting materials. The temperature was controlled by a W₉₇Re₃–W₇₅Re₂₅ thermocouple placed in the center of the heater. The pressure calibration and temperature gradients in capsules are described in (Litasov and Ohtani, 2009, 2010). The compositions of the phases were obtained using electron microprobe with the special attention for analysis of carbonates and aggregates of a quenched melt.

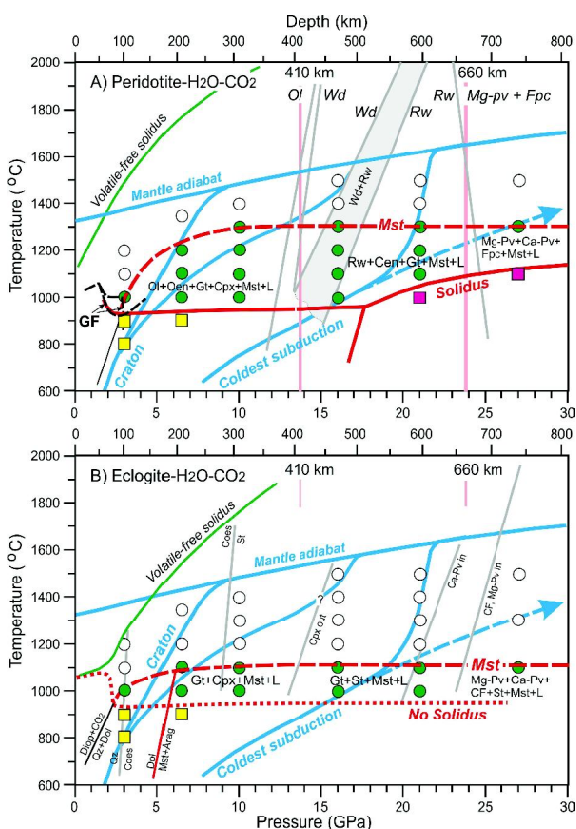


Fig. 1. Solidus and stability of magnesite in the systems peridotite-H₂O-CO₂ (A) and eclogite-H₂O-CO₂ (B) at pressures up to 27 GPa (Red lines). Stability of hydrous phases B and D (Pink) and fluid (Yellow) in subsolidus experiments, stability of magnesite (Mst) and melt (Green), and experiments at temperatures above the magnesite stability (Open symbols) are shown. GF, position of solidus and stability of amphibole in the system Hawaiian peridotite-H₂O-CO₂ after Green and Falloon (1998). Phase abbreviations: Ol – olivine, Oen – enstatite; Gt – garnet, Cpx – clinopyroxene, Wd – wadsleyite, Rw – ringwoodite, ; Fpc – ferropericlase; Ca-Pv – Ca-perovskite; Mg-Pv – Mg-perovskite; Diop – diopside; Dol – dolomite; Arg – aragonite; Qtz – quartz; Coes – coesite; St – stishovite; CF – Al-phase CF; L – melt or fluid. Blue lines – mantle PT-profiles.

RESULTS

The association of silicate minerals in the peridotite system includes olivine/wadsleyite/ringwoodite (at 16 GPa wadsleyite and ringwoodite coexist in the temperature range of 1100–1400°C, Fig.2) – orthopyroxene/clinoenstatite–garnet. Clinopyroxene occurs only at 3 and 6.5 GPa. Ringwoodite + garnet are stable at 21 GPa; at 1000–1100°C stishovite is added to

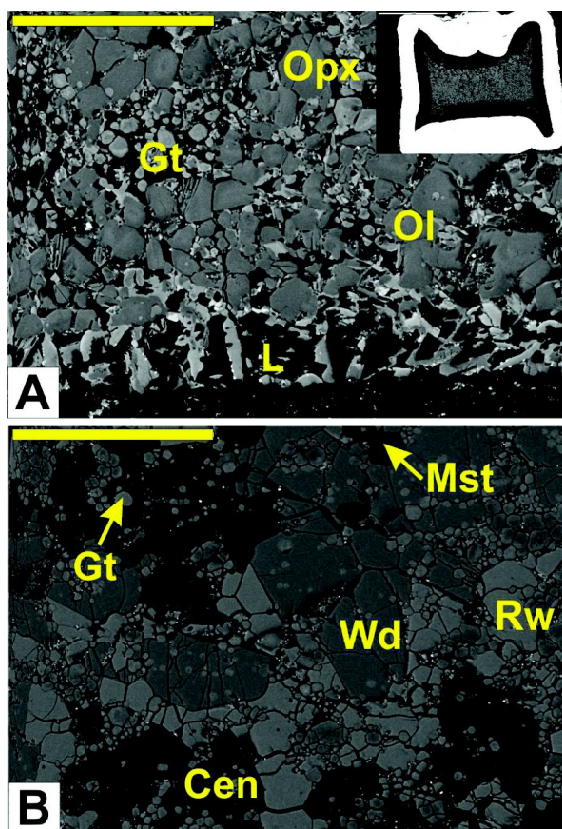


Fig.2. Back-scattered electron images of peridotite samples after experiments. A) Sample P-03-1200, quench melt (L) coexisting with olivine (Ol), orthopyroxene (Opx) and garnet (Gt); insert shows Pt-graphite capsule view. B) Sample P-16-1200, coexisting wadsleyite (Wd) and ringwoodite (Rw) also containing clinoenstatite (Cen), garnet (Gt) and magnesite (Mst). Sample number contains system (P – peridotite, E – eclogite), pressure (GPa), and temperature in °C. Scale bar is 100 μm.

them. The typical peridotite association of Mg-perovskite–Ca-perovskite–ferropericlase is stable at 27 GPa (Fig.1). Magnesite is the only carbonate phase over the entire pressure range. The temperature of magnesite stability is ~1300°C in the pressure range of 10–27 GPa and it decreases only at lower pressures (Fig. 1). Water-bearing superhydrous phase B and phase D were identified only at 21 and 27 GPa and 1000–1100°C. Since hydrous phases were not observed at lower pressures, the solidus temperature was not determined. Experiments at 10 and 16 GPa were not performed below 1000°C, because numerous



metastable phases are preserved at this temperatures even in long duration runs. Rare quenched carbonate crystals were obtained in runs at 800–900°C and 3–6.5 GPa, but it was not possible to analyse the melt compositions, because the samples contain cavities, which most likely provide evidence for the presence of a fluid phase (or melt with a high concentration of volatiles >50–60 wt %).

The representative phase compositions in the system peridotite–H₂O–CO₂ are given in (Litasov et al., 2011). In this paper we consider only melt compositions. Melts of low melting degrees (from 9 to 33 wt %) in the peridotite system occupy quite narrow compositional fields on the ternary diagrams (Figs. 3-4). It is important to note that the compositions of melts of low melting degrees are enriched in SiO₂ and alkalis, which is typical for the peridotite–H₂O systems, and differ from carbonatitic melts in the systems peridotite–CO₂. The temperature trends correspond to a decrease in the relative concentration of SiO₂ and alkalis and an increase in the (Mg + Fe)/Ca ratio.

The association of silicate minerals in the eclogite system includes garnet and clinopyroxene at 3–10 GPa, garnet and stishovite at 16–21 GPa, and a post-garnet assemblage of Mg-perovskite, Ca-perovskite, stishovite, and Al-phase CF at 27 GPa (Fig. 1). Garnet is a liquidus phase melting after clinopyroxene and stishovite with increasing temperature (Fig. 5). At 3–10 GPa rutile appears

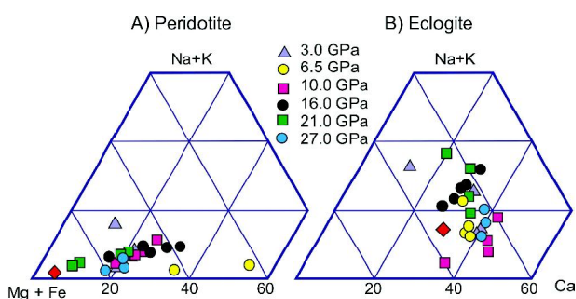


Fig. 3. Composition of melts in the systems peridotite–H₂O–CO₂ (A) and eclogite–H₂O–CO₂ (B) on the diagram (Mg + Fe)–(Na + K)–Ca. Diamonds denote the starting compositions.

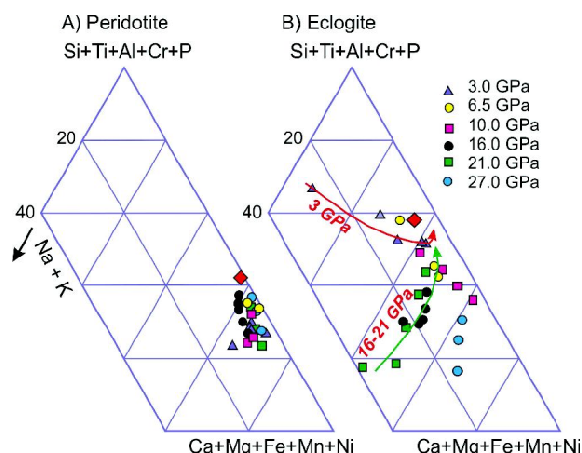


Fig. 4. Compositions of melts in the systems peridotite–H₂O–CO₂ (A) and eclogite–H₂O–CO₂ (B) on the diagram (Na+K)–(Ca+Mg+Fe+Mn+Ni)–(Si+Ti+Al+Cr+P). Diamonds denote the starting compositions. Trends of the evolution of melt compositions with temperature increase are shown for eclogite at 3 and 16–21 GPa.

as an accessory phase and at 16–21 GPa Fe–Ti-oxides appear episodically. Dolomite is stable at 3 GPa, but at higher pressures magnesite is the only carbonate phase. The temperature of magnesite stability in the eclogite system is ~1100°C in the pressure range of 10–27 GPa (Fig. 1), which is lower by 200°C than in the peridotite system. Hydrous phases were not observed even in the lowest temperature experiments. Thus, the solidus temperature was not determined and was estimated below 1000°C in the whole pressure range.

The representative phase compositions in the system eclogite–H₂O–CO₂ are given in (Litasov et al., 2011). In comparison with the peridotite system, melts in the system eclogite–H₂O–CO₂ have wider variations of the compositions on ternary diagrams (Figs. 3-4). Low degree melts are enriched in SiO₂ and alkalis to a greater degree in comparison with the peridotite system, which is also typical for the system eclogite–H₂O, and strongly differ from carbonatitic melts in the eclogite–CO₂ system. The temperature trends of melt compositions at 3 GPa significantly differ from the others. Rapid increase of the concentrations of FeO (5.2–10.7 wt %) and CaO

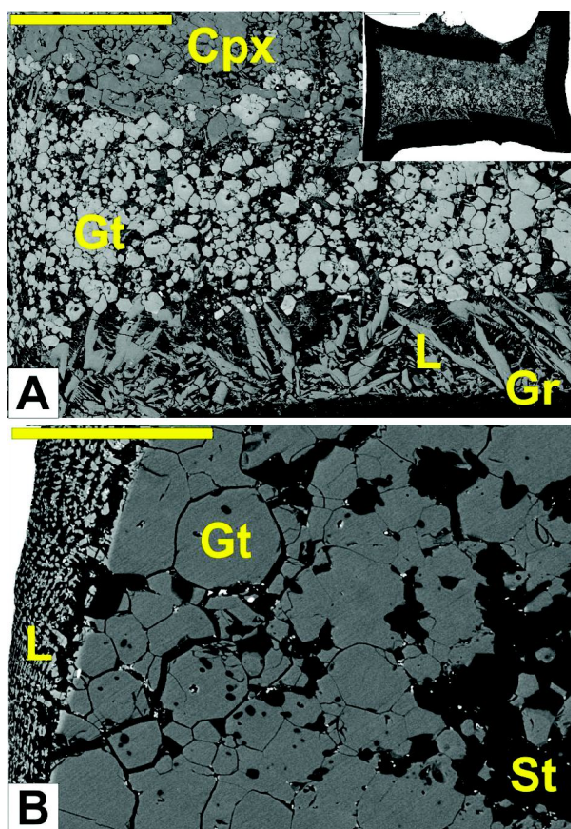


Fig. 5. Back-scattered electron images of eclogite samples after experiments. A) Sample E-03-1200, garnet (Gt) and clinopyroxene (Cpx) coexist with quench melt (L); insert shows Pt-graphite capsule view. B) Sample E-21-1200, garnet (Gt) and stishovite (St) coexist with quench melt (L). Scale bar is 200 mm.

(2.8–14.2 wt %) with temperature increase occurs at almost the same concentrations of SiO_2 (28–32 wt %) and MgO (5–7 wt %) (Fig. 4). Temperature increase at higher pressures results in increase of the concentration of SiO_2 (Fig. 4), except for the lowest temperature runs, for which it was impossible to analyse the melt composition. We can only estimate that based on the composition of quenched crystals, a melt or fluid with the melting degrees of <10% is enriched in Si, Na, K, and Mg. Melts at 16–21 GPa are strongly enriched in Na_2O (up to 10–16 wt%) in comparison with melts at 3–10 GPa (Fig. 4). This is explained by Na_2O incorporation into omphacite at low pressures and into CF-phase at 27 GPa, whereas

garnets at 16–21 GPa contains only up to 1.9 wt % Na_2O .

Peridotite and eclogite solidi in the studied systems have a flat slope to the pressure axis in the range of 6–27 GPa. Consequently this will result in melting of H_2O – CO_2 -bearing rocks at intersection of the solidi with PT-profiles of the subduction zones and hotter geotherms, which have a steeper slope to the pressure axis.

DISCUSSION AND CONCLUSIONS

Comparison of the results of experiments in the systems peridotite– H_2O – CO_2 and eclogite– H_2O – CO_2 with the data from previous studies of the systems with H_2O and CO_2 alone (Litasov and Ohtani, 2007; 2009; 2010) allows us to make the following important conclusions. Magnesite is the only carbonate phase in both systems at pressures above 6 GPa. The stability of aragonite in some eclogitic systems is possible at higher CaO concentrations, than in this study. In the eclogite system magnesite is stable at a temperature lower by 200°C than in the peridotite system; consequently, eclogite containing carbonates would melt preferentially to peridotite in the mantle, if there is a small portion of water in the system. The stability of magnesite and aragonite in the systems peridotite– CO_2 and eclogite– CO_2 has smaller differences by temperature (from 0 to 100°C). The temperature of stability of hydrous phases in the peridotite system decreases by 100–200°C in comparison with the peridotite– H_2O system. Hydrous phases, such as phengite or lawsonite were not observed in the experiments at 6.5 GPa and 900°C in the eclogite system as well. This provides evidence for the fact that addition of carbon or carbonates results in mobilization of structurally bonded hydrogen in peridotitic and eclogitic minerals and decreases the temperatures of melting of hydrous systems.

The compositions of the low-degree partial melts of peridotite and eclogite in the studied systems are SiO_2 - and alkali-rich and show



similarities with the melts from the H₂O-bearing-systems. This indicates that that carbonatite or SiO₂-undersaturated kimberlite melts cannot be formed in the deep mantle under H₂O-saturated conditions. SiO₂-undersaturated melts can be formed only from H₂O-free or H₂O-poor sources.

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References

- Brenker, F.E., Vollmer, C., Vincze, L., Vekemans, B., Szymanski, A., Janssens, K., Szaloki, I., Nasdala, L., Joswig, W., Kaminsky, F. (2007). Carbonates from the lower part of transition zone or even the lower mantle. *Earth and Planetary Science Letters* 260, 1-9.
- Brey, G.P., Bulatov, V.K., Girnis, A.V., Lahaye, Y. (2008). Experimental melting of carbonated peridotite at 6-10 GPa. *Journal of Petrology* 49, 797-821.
- Brey, G.P., Bulatov, V.K., Girnis, A.V. (2011). Melting of K-rich carbonated peridotite at 6-10 GPa and the stability of K-phases in the upper mantle. *Chemical Geology* 281, 333-342.
- Dasgupta, R., Hirschmann, M.M. (2006). Melting in the Earth's deep upper mantle caused by carbon dioxide. *Nature* 440, 659-662.
- Foley, S.F., Yaxley, G.M., Rosenthal, A., Buhre, S., Kiseeva, E.S., Rapp, R.P., Jacob, D.E., (2009). The composition of near-solidus melts of peridotite in the presence of CO₂ and H₂O between 40 and 60 kbar. *Lithos* 112, 274-283.
- Girnis, A.V., Bulatov, V.K., Brey, G.P. (2011). Formation of primary kimberlite melts – constraints from experiments at 6–12 GPa and variable CO₂/H₂O. *Lithos*, in press.
- Green, D.H., Falloon, T.J. (1998). Pyrolite: A Ringwood concept and its current expression, in: Jackson, I. (Ed.), *The Earth's Mantle*. Cambridge University Press, Cambridge, pp. 311–378.
- Litasov, K., Ohtani, E. (2002). Phase relations and melt compositions in CMAS-pyrolite-H₂O system up to 25 GPa. *Physics of the Earth and Planetary Interiors* 134, 105-127.
- Litasov, K.D., Ohtani, E. (2007). Effect of water on the phase relations in Earth's mantle and deep water cycle, in: Ohtani, E. (Ed.), *Advances in High-Pressure Mineralogy*. Geological Society of America Special Papers, pp. 115-156.
- Litasov, K.D., Ohtani, E. (2009). Solidus and phase relations of carbonated peridotite in the system CaO-Al₂O₃-MgO-SiO₂-Na₂O-CO₂ to the lower mantle depths. *Physics of the Earth and Planetary Interiors* 177, 46-58.
- Litasov, K.D., Ohtani, E. (2010). The solidus of carbonated eclogite in the system CaO-Al₂O₃-MgO-SiO₂-Na₂O-CO₂ to 32 GPa and carbonatite liquid in the deep mantle. *Earth and Planetary Science Letters* 295, 115-126.
- Litasov, K.D., Shatskiy, A.F., Pokhilenko, N.P. (2011). Phase relations and melting in the peridotite-H₂O-CO₂ and eclogite-H₂O-CO₂ systems at pressures of 3-27 GPa. *Doklady Earth Science* 437, 498-502.
- Litasov, K.D. (2011). Physicochemical conditions for melting in the Earth's mantle containing a C–O–H fluid (from experimental data). *Russian Geology and Geophysics* 52, 475-492.
- Wyllie, P.J. (1978). Mantle fluid compositions buffered in peridotite-CO₂-H₂O by carbonates, amphibole, and phlogopite. *Journal of Geology* 86, 687-713.
- Wyllie, P.J., Ryabchikov, I.D. (2000). Volatile components, magmas, and critical fluids in upwelling mantle. *Journal of Petrology* 41, 1195-1206.