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MELTING OF PERIDOTITE AND ECLOGITE COEXISTING WITH REDUCED C-O-H FLUID AT 3-16 GPA: FURTHER CONSTRAINTS FOR REDOX MELTING MODELS

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INTRODUCTION

The role of volatiles, mainly in the C-O-H system below levels of magma generations for typical rock types, ca. 40-200 km, is poorly understood. The study of redox state of peridotite xenoliths from kimberlite indicates that fO2 would gradually decrease with depth due to increasing solubility of Fe^{3+} in mantle silicates (Frost and McCammon, 2008). Besides, relatively reduced conditions in the mantle (more reduced than redox state of subsurface volcanic rocks) dictated by conditions of separation of metallic core, i.e. in equilibrium with molten/solid iron and by the basic concept of any melting process, when more oxidized species are distributed to the uprising melt or fluid phase. The C-O-H fluid composition at fO$_2$ near IW=0 would be significantly different from oxidized H_2O-CO_2 one and would correspond to CH_4-H_2O or CH_4-H_2 (Frost and McCammon, 2008). Thus, it is extremely important to model high pressure phase equilibria of mantle rocks coexisting with reduced fluid compositions.

The high-pressure experiments are the key instruments to study volatile behavior in deep mantle. Most experiments were conducted on the systems with oxidized volatiles, H_2O and CO_2 and covered pressure range up to 30-32 GPa (Dasgupta and Hirschmann, 2006; Green and Falloon, 1998; Litasov and Ohtani, 2002; Litasov and Ohtani, 2009, 2010; Wyllie and Ryabchikov, 2000). Experimental studies of the systems with reduced C-O-H fluid were performed in various systems at pressures up to 6-7 GPa using different modifications of a double-capsule method (e.g. Sokol et al., 2009). The double-capsule method allows dynamic control of fO$_2$, fH$_2$, and fH$_2$O in the experiment and can be described as follows. Welded outer capsule contains sufficient amount of oxygen buffer, e.g. Fe-FeO, and H_2O, which can be added as talc, brucite, or liquid water. Welded or pressure-sealed inner capsule contains sample with fluid source, which produce fluid of certain composition. The fluid source can be presented by different compounds producing C-O-H fluid by thermal decomposition. H_2O, graphite, stearic acid, silver oxalate are typical sources for components of the C-O-H fluid. The fO$_2$ is determined by the equilibrium $2H_2+O_2=2H_2O$ at the level close to inserted oxygen buffer by means of hydrogen exchange between buffer and inner sample capsule. In any case double capsule method can model only "dynamic" equilibrium, since buffer and fluid in the outer capsule and fluid in the inner capsule have limited "lifetime".

In present work we extended studies of the systems with reduced C-O-H fluid to higher pressures and report melting phase relations of the peridotite and eclogite systems at 3-16 GPa and 1200-1600oC. In order to perform these experiments the double-capsule technique with fO$_2$ control by outer Mo-MoO$_2$ or Fe-FeO buffer

capsule was designed. We determined the solidus temperatures and melt compositions and compare the results with those in the systems with oxidized H_2O-CO_2 fluid. The results were applied to the models of redox melting by change of oxidation state in the deep mantle regions.

EXPERIMENTAL

High pressure experiments were performed using a Kawai-type multianvil apparatuses at Tohoku University. The truncated edge length (TEL) of the tungsten carbide anvils was 12.0 (3–6.5 GPa) and 6.0 mm (12-16 GPa). We used modified double capsule methods (Sokol et al., 2009), where outer capsule was made of thick-walled buffer material (Fig. 1). Semi-sintered zirconia was used as the pressure medium for experiments. A cylindrical graphite (3–6.5 GPa) or $LaCrO_3$ (12-16 GPa) were used as the heater. A MgO insulator was placed between the capsule and heater. The outer buffer capsule was not welded before experiments, but become nearly impermeable for H_2O under the pressure as confirmed by imaging of recovered samples. The sample was placed into AuPd or Pt capsule and separated from the outer capsule by hydrogen transmitting medium – talc, which transforms to enstatite and H_2O-fluid or H_2O-bearing silicate melt upon heating. The size of the cell for TEL 12 mm is quite enough for placing two 3 mm wide and 2.5 mm tall outer capsule, which is well separated from inner capsule by HTM. However, experiments with the cell for TEL 6 mm were very difficult due to limited space in the cell (Fig. 1). The outer capsule in this cell should have enough wall and cap thicknesses (at least 0.2-0.3 mm) and should not be significantly deformed under compression to keep encapsulation. We performed cell check after each experiment including both inner and outer capsule conditions.

Starting materials for experiments were pure oxide mixture for peridotite and synthesized glass for eclogite (Table 1). 3 wt% of metallic Fe were
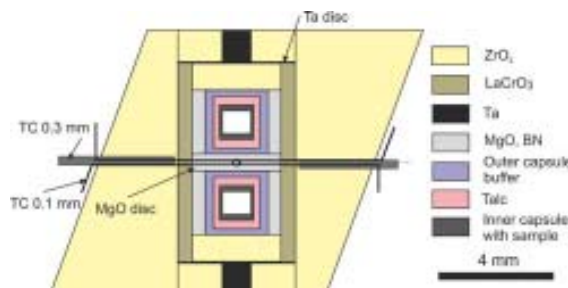

Fig. 1. Cell assembly for double capsule experiments at 12-16 GPa.

added to the starting material to reduce H_2O content in the sample. We used stearic acid, $C_{18}H_{36}O_2$, as a fluid source. It should decompose to $8CH_4 + 2H_2O + 8C$ upon heating to produce methane-bearing fluid. Total amount of stearic acid in the sample capsules varied between 8 and 12 wt%.

Temperature was measured with a W97Re3–W75Re25 thermocouple with a junction located at the center of the furnace. The thermocouple was isolated from the heater by Al2O3 inserts and from the capsules by thin 0.2 mm MgO discs. The pressure calibration and temperature gradients in capsules are described in (Litasov and Ohtani, 2009; 2010).

After experiments the sample capsule was mounted into epoxy, and polished using water-free materials. Mineral compositions were measured by electron microprobe at the Tohoku University.

RESULTS

Buffering technique and calculation the fO$_2$

We used 0.2-0.3 mm thick Molybdenum and Iron outer capsule for present experiments to control oxygen fugacity in the sample chamber near Mo-MoO$_2$ (MMO) and Fe-FeO (IW) oxygen buffers. MoO$_2$ at the inner walls of Mo-capsule and hydrous fluid inside the outer capsule was clearly identified after the experiments. However, this is not the case for FeO. The major

reaction products in most cases at the inner walls of the iron capsule were fayalite-bearing olivine. Besides, enstatite (as a reaction product of talc decomposition) was enriched by Fe in the boundary zone. This indicates that fO_2 was controlled by equilibrium enstatite + Fe + O_2 = olivine (OIE buffer) or Fe + SiO_2 + O_2 = fayalite (QIF), rather than by Fe-FeO buffer. In some cases we expect formation of iron hydride as revealed from bubbled zones in metal adjacent to inner walls boundaries. The fO_2 calculations for OIE and IQF buffers gives nearly same results and produces curves located close to the IW buffer. Thus, it can be assumed that using Fe-capsule in present experiments still controls the fO_2 near IW buffer within 0.5 log unit uncertainty.

Careful determination of the fO_2 depends also on the thermodynamic data for selected buffer. The position of a same buffer can vary for several orders of magnitude if different thermodynamic datasets are used. Overall, in this paper we assumed that Fe-capsule with talc transmitting medium model fO_2 at or slightly lower than IW buffer by O'Neill and Pownceby (1993) and Mo-capsule model fO_2 at MMO buffer, which is located at least 1 log units above this IW buffer.

Peridotite-COH-fluid

The experiments were performed in the peridotite and eclogite starting compositions. Maximum temperature of the experiments was restricted by 1600oC at 12-16 GPa due to melting of Fe or Fe-related eutectics at close temperature. Therefore, we could not obtain clear partial melts in some of the studied systems.

Subsolidus phase assemblage of peridotite includes olivine, orthopyroxene, clinopyroxene and garnet at 3-12 GPa, and wadsleyite, clinoenstatite and garnet at 16 GPa. These assemblages were the same for MMO and IW buffers. Stearic acid was decomposed to graphite/diamond and C-O-H fluid. All runs contained graphite or diamond crystals mixed with carbon

aggregate, which contain microinclusions (less than 2 µm in size) of silicate phases (Fig. 2). Graphite and diamond were identified by Raman spectroscopy. At 3 and 6.5 GPa we observed stability of graphite and at 12 and 16 GPa – diamond. The fluid was identified by rounded and irregular voids in the samples.

The compositions of minerals generally coincide with typical ones from volatile-free or H2O-bearing peridotite systems with slightly higher Fe-content according to starting composition.

Melting was detected by appearance of quenched crystals of pyroxene, feldspar and glassy silica (Fig. 2). Melt was quenched as large crystals, likely due to significant volatile fraction in it. In the Fe-systems melting was observed only in one sample at 3 GPa and 1300oC, whereas in the Mo-systems four samples revealed melting at all pressures except 16 GPa (Fig. 3). Using these samples we can constrain solidus for Mo-system at 1150oC at 3 GPa and 1600oC at 16 GPa. The solidus for Fe-systems was drawn parallel to that in Mo one and located at about 100oC higher temperatures in the studied pressure interval. These solidi are quite consistent with the data by Taylor and Green (1988) obtained at 3.6 GPa (Fig. 3).

Table 1. Calculated melt compositions (wt%) for the peridotite- and eclogite-COH-fluid systems.

| Peridotite | | | | | | | |
Sample No	SiO_2	TiO_2	Al_2O	Cr_2O	FeO	MgO	CaO	Na_2O
Starting	44.2	0.29	3.46	0.69	10.7	37.1	2.96	0.39
Mo-3-1200P	46.1	0.69	3.91	0.19	10.6	30.5	6.24	1.63
Mo-3-1300P	45.1	0.72	6.81	0.11	12.3	25.6	8.13	1.12
Mo-6-1300P	45.2	1.01	4.13	0.25	12.0	28.3	7.53	1.36
Mo-12-1600P	44.0	0.43	3.21	0.13	11.7	28.2	10.7	1.53
Fe-3-1300P	47.3	0.50	4.65	0.17	10.6	27.8	7.67	1.12

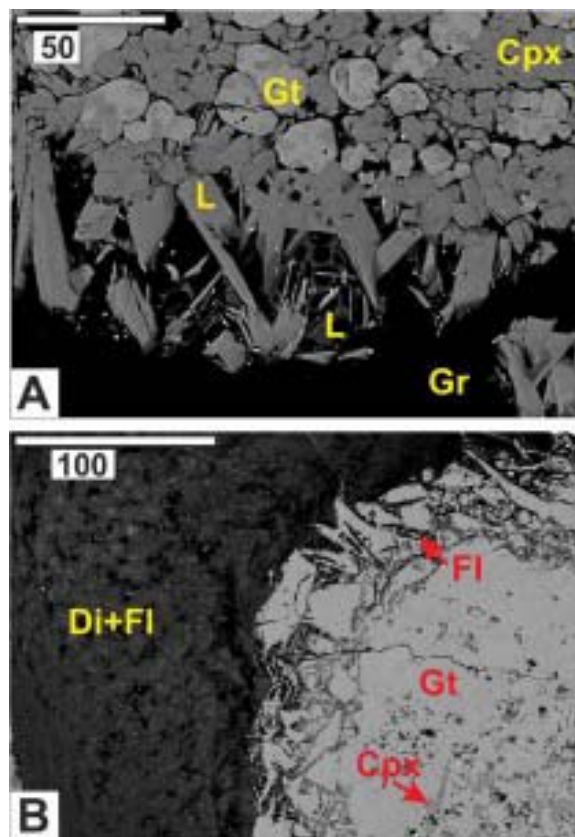| Eclogite | | | | | | | |
	SiO2	TiO_2	Al_2O	FeO	MgO	CaO	Na_2O	K_2O
Starting	44.7	1.76	13.7	13.1	10.8	12.7	3.03	0.39
Mo-3-1300E	48.2	3.87	8.34	11.5	4.79	14.6	7.39	1.34
Mo-6-1300E	47.8	3.54	4.69	14.1	5.49	13.0	9.71	1.63
Mo-12-1600E	46.4	2.48	6.11	15.8	4.53	15.1	7.32	2.23
Mo-16-1600E	46.0	2.87	6.45	13.5	3.93	16.0	9.38	1.97

Fig. 2. Back-scattered electron images of samples after experiments. A) Sample Ìi-3-1300Å, quenched crystals of Al-clinopyroxene and K-Na- feldspar+quartz+fluid bubbles (L), which show partial melting in eclogite; B) Fe-12-1200E, the boundary of carbon aggregate (diamond+fluid), impregnated by fine quench crystals, with eclogite. Scale bar in µm.

	SiO2	TiO$_2$	Al$_2$O	FeO	MgO	CaO	Na$_2$O	K$_2$O
Fe-3-1300E	48.9	4.25	3.87	15.1	6.65	8.04	11.5	1.71
Fe-6-1300E	49.2	5.25	4.07	16.2	3.18	6.57	13.9	1.66
Fe-12-1600E	48.5	3.64	4.48	14.6	4.01	10.8	12.0	2.08

All compositions are recalculated to 100%. Melt compositions are calculated from mass-balance. Sample number contains buffer (Mo or Fe), pressure (GPa), temperature in oC, and system: P – peridotite, E – eclogite.

It was very difficult to estimate the compositions of partial melts, because (i) it is quenched as large crystals, (ii) the fluid composition is unknown, and (iii) amount of silicate dissolved in the fluid is also unknown. Thus, we estimated approximate melt
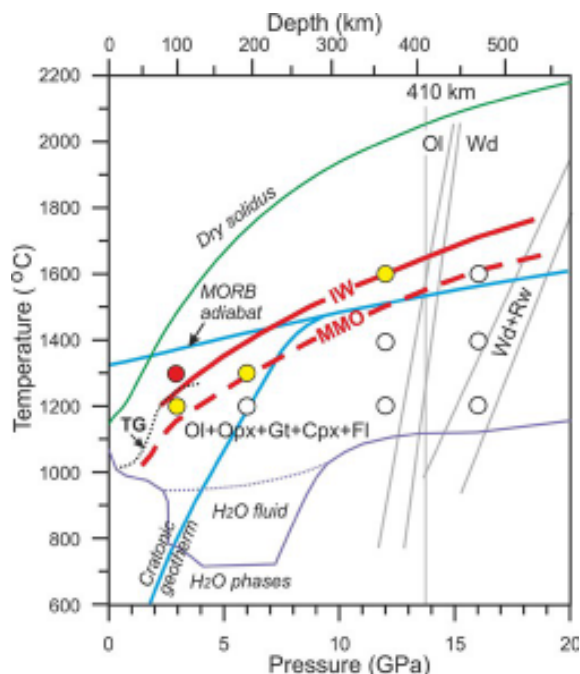

Fig. 3. Experimental results and solidi in the peridotite-COH-fluid systems with fO$_2$ monitored by MMO and IW oxygen buffers. *Red circles* – melting in the both systems, *Yellow circles* – melting in the Mo-system only, *Open circles* – no melting (no quench crystals). TG – solidus in the system peridotite-COH at fO$_2$=IW+1 (Taylor and Green, 1988). *Thin violet curve* shows stability of hydrous phases in the peridotite-H$_2$O system (Litasov and Ohtani, 2007). *Blue curves* show mantle PT-profiles.

compositions using mass- balance calculations (Table 1). Calculated melt compositions are characterized by relatively high SiO$_2$ contents (44-47 wt% in "dry" residue recalculated to 100%) at Mg#=80-83. In general melt observed in the present study are close to those in peridotite-H$_2$O systems rather than those in carbonated peridotite.

The carbon aggregate, which is finely mixed with graphite and diamond grains, was not investigated in details; however it was analyzed by defocused 50 µm electron microprobe beam in all samples. The total of analyses varies between 29 and 35 wt%. The measured compositions for peridotite samples reveal high similarity with calculated melt compositions from experiments with quench crystals (Fig. 4). At the same time carbonate aggregates contain less SiO$_2$ (32-40 wt%) and more TiO2 (up to 1.6 wt%) and Na$_2$O (up to 7.6 wt%) relative to quenched melts.
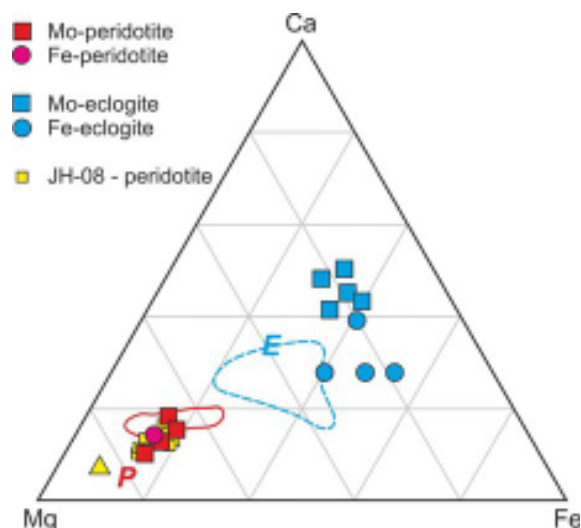
Fig.4. Calculated melt compositions in the systems peridotite-COH and eclogite-COH at Ca-Mg-Fe diagram. Ìî – ÌÌî buffer, Fe – IW buffer. *P* and *E* show starting compositions of peridotite and eclogite, respectively. JH-08 – melt compositions from peridotite-COH system at 5-12 GPa (Jakobsson and Holloway, 2008). Triangle shows starting composition from their work. The compositions of carbon aggregates, measured by electron microprobe for the peridotite-COH (*bold line*) and eclogite-COH (*dashed line*) systems are plotted.

We did not measure fluid composition after experiments. Modeling of C-O-H fluid composition is possible using real gas equations of state and Gibbs free energy minimization assuming no dissolved silicate components and same composition for the peridotite and eclogite systems. Fig. 5 show compositional dependences of C-O-H fluid from temperature at 3 and 10 GPa (Zhang and Duan, 2009). The major fluid components would be H_2O and CH_4. The H_2O content is higher in case of Mo-buffer and can be as high as 80-90 mol% at 16 GPa and 1200-1600oC. Methane is dominating in the Fe-system (up to 80 mol% at 3 GPa and 1200ºC), but became less important with increasing pressure. Ethane and hydrogen are subordinate components in the fluid.

Eclogite – COH-fluid

In the eclogite system garnet and clinopyroxene are present in all runs at 3-16 GPa.
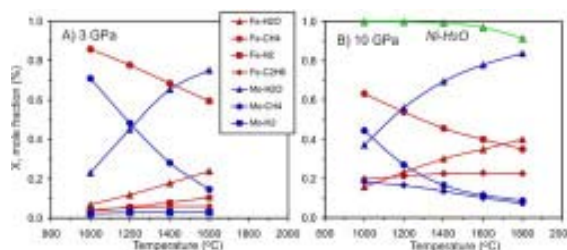

Fig.5. Temperature dependence of COH-fluid compositions at 3 and 10 GPa calculated using equations of state for real gases from (Zhang and Duan, 2009). Mo – fO_2 corresponds to MMO buffer, Fe – fO_2 corresponds to IW buffer, Ni – fO_2 corresponds to Ni-NiO buffer (H_2O only for comparison).
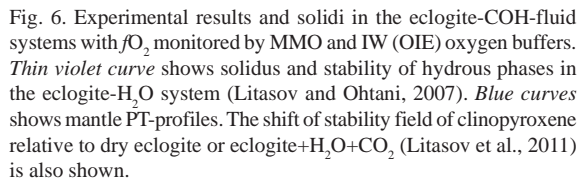
We observed disequilibrium features in garnet, with partially unreacted cores, which is typical for low-temperature experiments even with hydrous fluids (Fig. 2). Similarly to the peridotite system stearic acid was decomposed to graphite/ diamond, carbon aggregate and fluid phase. Clinopyroxene contains 3.6-7.1 wt% Na2O and jadeite component increases with increasing pressure. Quenched clinopyroxene is clearly different in composition by high TiO2 (>2.5 wt%) and Al2O3 (>11.5 wt%). Garnet has Na-bearing majoritic composition.

Melting in the eclogite system was detected in 5 samples including one at 16 GPa and Mo-system (Fig. 6). Thus, the solidi in eclogite systems are located at lower temperatures relative to peridotite ones. Estimated solidus temperatures for the Fe-system are 1100oC at 3 GPa and 1520oC at 16 GPa. As well solidus in the Mo-system is located at 50-100ºC lower than that in the Fe-system, but this difference is slightly less than in the peridotite systems. Calculated partial melt compositions are shown in Table 1.

DISCUSSION

Melting of peridotite and eclogite coexisting with reduced C-O-H fluid

The review of different solidi in peridotite and eclogite with various compositions of C-O-H fluids can be found in (Litasov, 2011). The

Fig. 6. Experimental results and solidi in the eclogite-COH-fluid systems with fO_2 monitored by MMO and IW (OIE) oxygen buffers. *Thin violet curve* shows solidus and stability of hydrous phases in the eclogite-H_2O system (Litasov and Ohtani, 2007). *Blue curves* shows mantle PT-profiles. The shift of stability field of clinopyroxene relative to dry eclogite or eclogite+H_2O+CO_2 (Litasov et al., 2011) is also shown.

obtained solidi for peridotite and eclogite coexisting with reduced C-O-H fluid are much higher (300-500°C) than those for peridotite/eclogite systems with H_2O and CO_2. However, they are still about 300°C lower than solidi of volatile-free peridotite and eclogite at studied pressures, e.g. near 15 GPa.

Although the solidi were obtained for particular systems with relatively high content of fluid phase they can be used for estimation of melting in the reduced asthenosphere. Melting of peridotite with C-O-H fluid buffered by IW buffer may occur at temperatures 50-100oC above the average mantle geotherm (Fig. 3), whereas for eclogite it is possible even along at 8-10 GPa cratonic geotherm. In this work we provide new

experimental evidences for redox melting by change of oxidation state across a mantle section in addition to those reported by Foley (2011) and Rohrbach and Schmidt (2011). The results have important implications for origin of kimberlite as well as for diamond crystallization in the cratonic roots.

Fluid and melt compositions

Composition of reduced C-O-H fluids in equilibrium with graphite/diamond was investigated in several different systems. Modeling of C-O-H fluid in equilibriums with graphite and diamond was performed at 2-7 GPa (Matveev et al., 1997; Sokol et al., 2009). The system peridotite-C-O-H at fO_2 controlled by WCWO buffer (WC-W-WO$_2$ = IW+1) was studied at 0.9-3.6 GPa. In this system the CH4/(CH$_4$+H$_2$O) ratio in the fluid decreases from 0.8 to 0.3in the temperature interval from 1050 to 1250oC at 1.5-3.6 system CaO-Al O -MgO-SiO -Na O-CO to 32 GPa and carbonatite GPa (Taylor and Green, 1988). The solidus in the system with reduced CH$_4$-H$_2$O fluid is located at higher temperature relative to the oxidized systems with H$_2$O and CO$_2$. This is connected with low solubility of silicate in methane- and hydrogen-bearing fluid and low solubility of reduced fluid species in silicate melt. The behavior of H2O in reduced fluid is poorly understood. It was shown that solidi of the silicate-C-O-H systems are high even if H$_2$O content in the fluid approach 90 mol% (Sokol et al., 2009; 2010), i.e. even if fH$_2$O is higher than aH$_2$O in hydrous silicate melt. In some cases the fluid composition measured in the experiments (Matveev et al., 1997; Taylor and Green, 1988) is consistent with that calculated from equations of state for real gases (e.g. Zhang and Duan, 2009), but in some others not. For instance Sokol et al. (2009) measured high concentrations of hydrogen in quenched fluid and low methane, which are not consistent with calculations.

In the work by Jacobsson and Holloway (2008) melting of peridotite coexisting with C-O-H fluid was modeled at 5-12 GPa and 1200-1500oC. The fluid source + buffer and sample were placed in the graphite capsules separated by Pt disc and then sealed to a single Pt capsule. The authors obtained compositions of silicate melts, however solidus of the systems was located at much lower temperatures (below 1200oC) if compare with the work by Taylor and Green liquid (1988) and our work. Surprisingly, the melt compositions for peridotite in this work are very consistent with those obtained by Jakobsson and Holloway (2008) (Fig. 4).

The nature of presumably subsolidus silicate inclusions in carbon aggregate is poorly understood. The likely explanation is that they are quenched from reduced fluid, indicating that it can dissolve significant amount of silicate components.

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