

Synthesize of boron-doped diamond cylinder as a heater in Multi-anvil apparatus

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Diamond is the hardest known material in the world. It is the first time to report synthesize of semi-conductor boron-doped diamond cylinder in the Kawai-type multi-anvil apparatus at 15 GPa and 2100°C. The dimension of the cylinder is 2.6 mm outer diameter, 1.5 mm inner diameter and 3.35 mm length. SEM image shows that the grain size of diamond is about 1 micrometer.

Those cylinders have been used for extremely high temperature generation (~3000°C) in a large sample volume (~0.1mm³) in the Kawai apparatus; the sample volume is ~1000 times larger than that in diamond anvil cell. High X ray transparency of boron-doped diamond is optimum as well for in-situ synchrotron X ray analysis. Although there have been several reports on boron-doped graphite heater, the present study is the first report on pure boron-doped diamond heater in Kawai-type apparatus. The reversibility of the heater was confirmed well through three times of repeated cycle of heating and cooling. The boron-doped diamond heater with 3 wt.% boron shows metallic behavior, i.e. increasing resistance with increasing temperature. This electrical characteristic is beneficial for stably generating temperature as high as 2700°C; the heating for higher temperature was failed because of failure of electrode. Therefore, succeeding optimization is required for higher temperature generation with this new heating element. Boron-doped diamond heater is more advantageous than B-doped graphite heater, because it is free from complicated power-temperature relationship and pressure drop associated with graphite to diamond conversion.

Keywords: diamond synthesize, B-doped diamond heater, ultrahigh temperature, Multi-anvil apparatus

Electrical conductivity of San Carlos clinopyroxene as a function of water content

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The high conductive region (50-100 km) obtained from magnetotelluric data at Southern East Pacific Rise has been interpreted by the high electrical conductivity of hydrous olivine. Though the fact that water could enhance the electrical conductivity orders of magnitude, the conductivity enhanced by hydrous olivine and orthopyroxene seems to be insufficient to account for this anomaly convincingly. Clinopyroxene, one of the main constituent minerals in the upper mantle, could be a possible candidate to raise the conductivity in this region because water tends to partition into this phase rather than olivine and orthopyroxene. In this study, we measured the electrical conductivity of clinopyroxene as a function of temperature and water content under the *P-T* condition corresponding to the conductivity anomaly region in the upper mantle.

Clinopyroxene aggregates with water contents ranging from ~0 to 2000 wt. ppm were synthesized from San Carlos clinopyroxene powder at 1270-1370 K and 1.5 GPa in a piston cylinder apparatus. The double capsule technique was used to realize the Ni-NiO buffer. The electrical conductivity measurements were performed at the same pressure and temperatures from 600 to 1200 K at the same oxygen fugacity, using a DIA-type apparatus. The water content of the sample both before and after electrical conductivity were determined by FTIR using Paterson calibration.

The electrical conductivity increases with increasing water content. Two conductive mechanisms were identified, i.e. proton conduction and hopping conduction. For hopping conduction, the activation energy is ~1.44 eV. For proton conduction, the activation energy differs by water content. At low water content, the activation energy is 1.28-1.36 eV; while at high water content, the activation energy is ~0.92 eV. All these data were fitted using the formula $\sigma = \sigma_{h0} \exp(-H_h/kT) + \sigma_{p0} C_w^r \exp(-H_p/kT)$. Compared with the electrical conductivity of olivine (Yoshino et al., 2006) and orthopyroxene (Zhang et al., 2012) under the same oxygen fugacity, electrical conductivity of hydrous clinopyroxene is comparable to those of the other major constitute minerals. To estimate electrical conductivity beneath the oceanic lithosphere as a function of water content, the Hashin-Shtrikman lower and upper bounds were used, and water-partitioning coefficients among olivine, orthopyroxene and clinopyroxene were also assumed. The model showed no obvious advantage to explain the high conductive anomaly. Thus, the conductivity anomaly predicted near the mid-ocean ridge cannot be originated from hydrated mantle. The conductivity anomaly region beneath the oceanic lithosphere should be explained by a presence of other conductive agents such as partial melt.

Yoshino et al. (2006), *Nature* **443**, 973-976.

Zhang et al. (2012), *EPSL* **357-358**, 11-20.

Keywords: clinopyroxene, electrical conductivity, water content, conductivity anomaly region, oceanic lithosphere

Defect chemistry and diffusion in hydrous forsterite

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The mass transport of olivine, which reflects the flow in the Earth's upper mantle, is controlled by the diffusion of structural elements. On the other hand, the diffusivity of an ion in the crystal is dominated by the motion of point defects of the corresponding sites. It is thus necessary to know the diffusivities of elements in olivine in the view of defect chemistry so as to investigate the behaviors in the upper mantle conditions.

Fei et al. (2013, 2014) systematically measured silicon and oxygen self-diffusion coefficients (D_{Si} and D_O , respectively) in iron-free forsterite as functions of water contents, showing that $D_{Si} \propto C_{H_2O}^{0.32(7)}$, $D_O \propto C_{H_2O}^{0.05(6)}$. These water-content exponents are much smaller than that expected on the basis of the assumption that self-diffusion coefficient of a chemical species is simply proportional to its defect density. Therefore, a new defect chemistry model is required to explain the above relationships.

Silicon diffusion:

The D_{Si} should be proportional to the density of silicon defects, namely, $D_{Si} \propto [V_{Si}''']$. On the other hand, Si^{4+} is tightly surrounded by four-coordinated O^{2-} , and therefore, migration of Si^{4+} should be enhanced if a surrounding O^{2-} is missing. We can expect that a certain proportion of V_{Si}''' is associated with $V_O \bullet\bullet$ due to their excess charges with the opposite signs. As a result, Si migration is probably dominated by $V_O \bullet\bullet$ -associated V_{Si}''' . D_{Si} is thus also proportional to $[V_O \bullet\bullet]$ and we have,

$$D_{Si} \propto [V_{Si}'''] \times [V_O \bullet\bullet]$$

Under the charge neutrality condition of $[(OH)_O \bullet] = 2[V_{Mg}'']$ in hydrous forsterite, we have $[V_{Si}'''] \propto (f_{H_2O})^{2/3}$ and $[V_O \bullet\bullet] \propto (f_{H_2O})^{-1/3}$. Therefore,

$$D_{Si} \propto [V_{Si}'''] \times [V_O \bullet\bullet] \propto (f_{H_2O})^{1/3},$$

which agrees well with the experimental results: $D_{Si} \propto (C_{H_2O})^{0.32(7)}$ (Fei et al., 2013).

Oxygen diffusion:

In hydrous olivine/forsterite, hydrogen exists as hydroxyl, $(OH)^-$. Oxygen ions could diffuse either by hopping of O^{2-} without H^+ or by hopping of O in $(OH)^-$. Because H^+ -associated O has a lower Coulomb force due to the excess charge by H^+ , the hopping probability of $(OH)^-$ should be higher than that of O^{2-} . Thus, the O diffusion should be dominated by O^{2-} of $(OH)^-$. As a result, we have,

$$D_O \propto [V_O] \times ([O^{2-}]^{hopping} + [(OH)^-]^{hopping}) \approx [V_O \bullet\bullet] \times [(OH)^-]^{hopping}.$$

There are mainly three types of $(OH)^-$ in hydrous olivine/forsterite: (a) $(OH)_O \bullet$ associated with V_{Mg}'' ; (b) $(OH)_O \bullet$ associated with V_{Si}''' ; (c) $(OH)_O \bullet$ un-associated with any cation vacancies. The un-associated $(OH)_O \bullet$ should have much higher mobility than V_{Si}''' or V_{Mg}'' associated ones due to the Coulomb force and therefore the O diffusion is probably dominated by un-associated $(OH)_O \bullet$. Thus,

$$D_O \propto [V_O \bullet\bullet] \times [(OH)^-]^{hopping} \approx [V_O \bullet\bullet] \times [(OH)_O \bullet]^{un-associated}.$$

Under the charge neutrality condition of $[(OH)_O \bullet] = 2[V_{Mg}'']$, we have $[V_O \bullet\bullet] \propto (f_{H_2O})^{-1/3}$ and $[(OH)_O \bullet]^{un-associated} \propto (f_{H_2O})^{1/3}$. Therefore,

$$D_O \propto [V_O \bullet\bullet] \times [(OH)_O \bullet]^{un-associated} \propto (f_{H_2O})^0.$$

This model suggests that D_O is independent from C_{H_2O} , which agrees well with the experimental results, $D_O \propto C_{H_2O}^{0.05(6)}$ (Fei et al., 2014).

Fei et al. (2013), *Nature* **498**, 213-215.

Fei et al. (2014), *JGR* **119**, 7598-7606.

Keywords: defect chemistry, self-diffusion coefficient, silicon, oxygen, water content, forsterite

D/H exchange in wadsleyite and ringwoodite: Implications for electrical conductivity

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Wadsleyite and ringwoodite, which are main constituent minerals of the mantle transition zone, can incorporate large amount of hydrogen in their structure (up to a few wt % H₂O). A knowledge of hydrogen self-diffusion in these minerals and its relationship with their electrical conductivity is critical to estimate the real amount of water present in the transition zone. Although only the hydrogen incorporation experiments in wadsleyite was performed using polycrystalline samples, the obtained diffusion coefficients cannot rule out the influence of grain boundary diffusion (Hae et al. 2006). Therefore, we have to investigate hydrogen lattice self-diffusion of wadsleyite and ringwoodite using single crystal at high pressure.

To estimate proton conduction from hydrogen self-diffusion, large single crystals (>1mm) of hydrogen (H) and deuterium (D)-doped wadsleyite and ringwoodite were synthesized respectively at high pressure and high temperature in Kawai-type multi-anvil apparatus.

We applied H/D exchange method to determine hydrogen self-diffusion coefficients because this method (Du Frane et al. 2012) has advantage to distinguish between incorporation and self-diffusion, and provides more accurate hydrogen diffusion coefficients contributing to proton conduction than traditional incorporation method (Kohlstedt and Mackwell, 1998, Demouchy and Mackwell, 2003, Hae et al. 2006).

After determination of crystallographic orientation, a pair of H and D-doped wadsleyite or ringwoodite crystals aligned to the same axis was placed together in gold capsule. The polished surfaces were tightly contacted each other. The inter-diffusion experiments were conducted at different temperatures (900-1300K) and the same pressure as synthesis condition. H/D inter-diffusion profiles were obtained by SIMS in Hokkaido University.

Hydrogen volume diffusion coefficients in wadsleyite determined from each single crystal pair are ~1 order of magnitude lower than those obtained from polycrystal wadsleyite (Hae et al. 2006). The hydrogen self-diffusion coefficients in ringwoodite are characterized by lower enthalpy and hydrogen mobility than wadsleyite at the temperature of transition zone.

Electrical conductivities of wadsleyite and ringwoodite estimated from the present diffusion coefficients based on the Nernst-Einstein relation. Our model suggests that hydrogen makes significant contributions to wadsleyite but insignificant contributions to ringwoodite due to large contribution of hopping conduction at the transition zone condition. Our proton conductivity values of wadsleyite are similar with those of Yoshino et al. [2012] at the transition zone condition but values of ringwoodite are lower especially at high water content. This model suggests that global average concentration of hydrogen in the transition zone of is ~1000 wt ppm H₂O.

Keywords: hydrogen, diffusion, wadsleyite, conductivity, ringwoodite

Thickness of the mantle transition zone beneath the Society hotspot

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We have conducted a seafloor geophysical observation from 2009 to 2010 near the Society hotspot. The observation network was composed of nine sets of broadband seismographs and electro-magnetometers, and two differential pressure gauges. In this presentation we show the mantle transition zone (MTZ) structure obtained with a receiver function method using the broadband seismograms. We employed a common-conversion point (CCP) stacking technique to map the MTZ thickness. A preliminary result indicates an area of a thin MTZ 200 km to the south of the Society hotspot (thinner than global average by 20-30 km). The lateral dimension of the thin MTZ area is about 200 km. There is another area of the thin MTZ 300 km EES to the hotspot. The thin MTZ areas are roughly correlated with slow P-velocities in the MTZ in the P-wave tomograms (Obayashi et al., 2014). They may represent hot mantle plumes ascending from the lower mantle.

Keywords: hotspot, ocean bottom seismograph, receiver function, French Polynesia

Experimental Study on the Hawaiian Plume with Recycled Eclogite: Part-1: Constraints on potential temperature

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Potential mantle temperatures (PMT) of plumes are thought to be significantly higher than shallow asthenosphere (200~300C). Excess PMT of the plume is very important in calculating the plume flux among the heat budget of the Earth dynamics (e.g., Sleep, 1990). In order to produce large amount of tholeiite magma in the shield building stage at the base of old Pacific plate, potential temperature of the Hawaiian plume is considered to be at least 300C higher than asthenosphere judging from the peridotite dry solidus at 3 GPa, base of the oceanic plate (e.g., Watson & McKenzie, 1991).

If large amount of recycled eclogite component is involved in the genesis of LIP magmas (e.g., Hawaii hot spot: Hauri, 1996; Takahashi & Nakajima, 2002, Sobolev et al., 2007, Columbia River flood basalt: Takahashi et al., 1998), PMT of the plumes which have been estimated based on peridotite dry solidus alone should be largely in error. For example, Takahashi et al.(1998) concluded that temperature of the initial emplacement stage of the Yellowstone plume may be only 100C higher than normal asthenosphere, based on melting study of the Columbia River basalts. In order to evaluate the role of recycled eclogite in magma genesis of Hawaiian plume, we carried out high-P and high-T melting experiments. Chemistry of the recycled eclogite will be discussed in Part 2.

High-pressure melting experiments were carried out under dry and hydrous conditions with layered eclogite/peridotite starting materials. Spinel lherzolite KLB-1 (Takahashi 1986) was employed as peridotite component in this study. Two basalt components were tested as recycled crust component: 1) Columbia River basalt (CRB72-180, Takahashi et al., 1998) which is relatively enriched in K, Ti and LREE (K₂O=1wt%, TiO₂=3.15wt%), N-type MORB (NAM-7, Yasuda et al., 1994) (for REE patterns, see Fig.1 of Gao et al. this conference, Part 2 of this work). The 2.85GPa experiments (corresponding to about 80km depth which is the top most horizon of the Hawaiian plume head) were carried out with Boyd-England type piston-cylinder apparatus at (1460~1540C for dry experiments; 1400~1500C for hydrous experiments), The 5GPa experiments (corresponding to about 150km depth on the plume axis) were conducted by Kawai-type multi-anvil apparatus (1550~1650C for dry experiments; 1350~1550C for hydrous experiments).

Melts formed by reactive melting of dry eclogite and peridotite changes dramatically in the temperature range across the solidus of peridotite KLB-1 from basalt (below dry solidus) to picrite (20-40C above dry solidus). Basaltic melts are not saturated with olivine both at 2.85 and 5 GPa and therefore they are separated by peridotite matrix by Opx film. Chemical reaction between the basalt melt and the peridotite matrix proceeds only slowly by solid-diffusion across the Opx film. In hydrous experiments, solidus of peridotite decreases significantly and therefore the reaction between hydrous melt and the partially molten peridotite matrix proceeds at temperatures below peridotite dry solidus.

Based on present experiments, we propose that potential temperature of the Hawaii plume may be only 100-150C above that of normal asthenosphere. Tholeiite magma in the shield building stage may be formed slightly under hydrous condition near the dry solid of peridotite (1450-1500C at about 3 GPa). Chemical distinction between Hawaiian shields (e.g., Mauna Loa and Kilauea) might correspond with difference in mixing ratio or degree of the chemical reaction between the recycled eclogite blocks and the ambient peridotite.

Potential mantle temperature in other mantle plume (OIB, flood basalt, etc) will be discussed in the light of present experiments. Our model predicts lower plume temperatures than most previous estimates. Plume flux may be related to the amount of entrained eclogite than potential temperature.

Keywords: Hawaiian plume, recycled eclogite, magma genesis, potential temperature

Experimental Study on the Hawaiian Plume with Recycled Eclogite: Part 2, Constraints on Chemistry of Recycled Component

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Introduction: It is believed that recycled oceanic crust is involved in the magma genesis of the Hawaiian mantle plume (e.g., Hauri et al., 1996; Takahashi & Nakajima, 2002; Sobolev et al., 2007). Takahashi & Nakajima (2002) proposed that magma produced near the axis of the plume head may be mixtures of two types of melts 1) basaltic andesite melt formed by melting of eclogite and 2) picritic melts formed by the reactive melting of eclogite and peridotite. However, geochemical feature of recycled oceanic crust component is still under disputed. A sequence of high-T high-P experiments were conducted to figure out constrains of such recycled component. Experimental details are shown in Part 1 of this presentation.

Phase and major elements features:

1) Anhydrous conditions: (CRB: 1460~1540C, 3h for 2.85GPa; N-MORB or CRB: 1550~1650C for 5GPa):

When peridotite remained subsolidus, molten basalt was separated from peridotite by thin Opx band formed by the chemical reaction between Si-rich partial melt of eclogite and olivine in the peridotite matrix, therefore the chemical reaction between basalt and peridotite layers proceeded only by solid diffusion. As peridotite reached its solidus between 1520C~1540C, fully molten basalt melt and melt pockets from peridotite layer linked, judging from sharp changes in MgO and FeO/MgO ratio. Extensive chemical mass transport took place by chemical diffusion and liquid percolation. However, Si-content remained nearly constant even at temperatures above solidus.

2) Hydrous conditions: 1400C~1500C, 2.85GPa 3h

In wet experiments (with 1wt% H₂O in peridotite layer originally), extraction of water took place from peridotite layer into basaltic melt (water was detected by FT-IR), giving little influence to the melting process of peridotite. On the other hand, in wet experiments (with 5wt% H₂O in peridotite layer), basalt started melting even at 1400°C. At 1480C and 1500C, melting process of both layers enhanced the chemical exchange of both sides. H₂O promotes melting of only basalt layer under low water concentration, while it enhances melting and chemical interaction between both layers leading to formation of Si-poor melts in basalt.

In the case 5GPa, 1wt% H₂O, coexisted hydrous vapor and hydrous silicate melt generated under temperature 1350~1450C (about 200C below peridotite dry solidus). Ti, K, P are enriched in the hydrous vapor.

REE features.

Rare earth element patterns: Columbia River basalt is enriched in LREE than N-MORB, run products of this study turned out to have a similar pattern (Fig.1, normalized pattern by CI chondrite) with their starting material (basalt). Since REE elements prefer to stay in the melt, increasing degree of partial melting will lower the whole REE elements abundance in the melt. REE abundance of lava from Kilauea and Mauna Loa is also plotted in this diagram, showing sharp decline of HREE components in these shield stage lava. Garnet (the key component of eclogite) is the only known mineral that prefers heavy REE. Although garnet together with Cpx are the residual phase at 2.85 and 5 GPa experiments, REE patterns of Kilauea and Mauna Loa are far more depleted in HREE than melts produced by our experiments. .

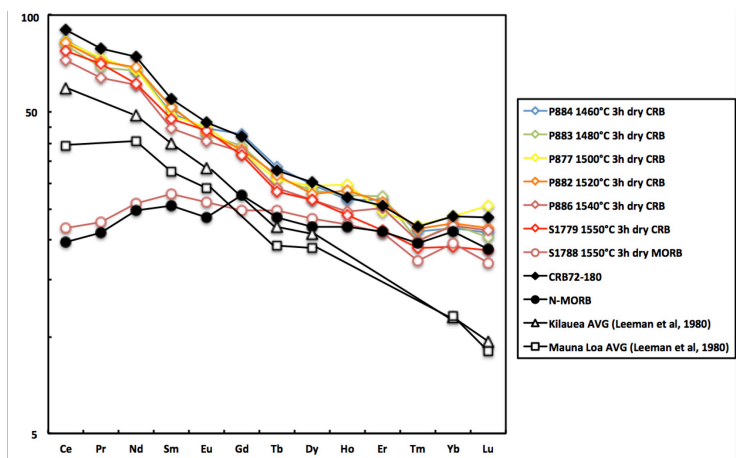
Discussion: In an upwelling mantle plume with recycled oceanic basalt components, both tholeiitic magma and alkali component could be obtained from hybrid melting of basalt and peridotite. H₂O promotes the melting process and generate more mafic melts. Very depleted HEE pattern of Hawaiian tholeiite might be explained by percolation of partial melt in vertically elongated eclogite blobs in the center of the plume (chromatographic effect). Enriched signature in K, Ti, and LREE in the Hawaiian tholeiite might indicate that source of recycled component in the Hawaiian plume is not NMORB but is more enriched in these incompatible elements (see Fig.1).

Keywords: Hawaii plume, magma genesis, recycled eclogite, chemistry, REE

SIT03-07

Room:106

Time:May 25 15:45-16:00



High-pressure and high-temperature polymorphism in the CaCO₃ at pressures to 30 GPa

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We determined phase transitions in CaCO₃ at pressures up to 30 GPa and high-temperatures using *in situ* X-ray diffraction and synchrotron radiation. In addition to geological importance this investigation has crystal-chemical and fundamental aspect as in this region enigmatic phase transitions from aragonite to disordered calcite or other phases takes place. The degree of orientational disorder in calcite drastically grow in the narrow temperature range of 1200-1230 K (at 1 bar) producing fully disordered phase (by orientation of CO₃ triangles) (Ishizawa et al., 2013). Despite of such apparent significance, there is just a few works where this phase transition was investigated by X-ray diffraction at high pressures (Suito et al., 2001). The results are not unequivocal, because disordered calcite was determined by only common similarity of diffraction patterns, whereas unit cell parameters were not determined. By the same reason the compressibility of disordered calcite is also unknown. The lack of the experimental results is explained by grain growth and disordering phase transitions in CaCO₃ at temperatures close to the melting point and as a result difficulties in getting relatively high quality diffraction patterns with amount of peaks enough for unit cell parameters determination. In present experiments we observed transition of aragonite to presumably disordered calcite phase at 1 and 3 GPa and 1273-1473 K, however at 5 and 8 GPa and higher temperature we observed transition to new phase, which we tentatively named disordered aragonite. At 14 GPa we did not observe transition of aragonite in the experiment to 1900 K, however at 20 GPa and at 31 GPa transition from aragonite to new phase(s) was observed at 1773 and 1373 K, respectively. The structures of the new phases will be refined based on diffraction data and subsequent *ab initio* computations.

Keywords: high pressure, calcium carbonate, phase transition, aragonite, X-ray diffraction

High-pressure decomposition of FeTiO₃, MgTiO₃ and ZnTiO₃ perovskites

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It is generally accepted that transition of MgSiO₃-rich perovskite (bridgmanite) to CaIrO₃-type postperovskite is responsible for formation of D'' layer in the lowermost mantle. Since discovery of the perovskite-postperovskite transition in MgSiO₃, numerous studies have been made to clarify high-pressure transitions of ABX₃ perovskites. FeTiO₃ and MgTiO₃ are endmembers of natural ilmenite, and ZnTiO₃ is an analogue for these compounds. Previous studies revealed that at 15-20 GPa range FeTiO₃ and MgTiO₃ ilmenites transform to perovskites, which are recovered as LiNbO₃-type phases at ambient conditions. In contrast to many perovskite-type oxides including MgSiO₃ perovskite, FeTiO₃ and MgTiO₃ perovskites do not transform to CaIrO₃-type postperovskite but decompose into two-phase assemblages. However, the transition behaviors of these perovskites are still in controversy, and little has been known on phase assemblage of ZnTiO₃.

We have examined high-pressure transitions in ZnTiO₃ and MgTiO₃ to about 25 GPa and those of FeTiO₃ to about 33 GPa using multianvil apparatus. Pressure was calibrated against press-load using pressure-fixed points at room temperature including GaP and Zr. The pressure was further corrected at high temperature using transition boundaries including dissociation of pyrope into Mg-rich perovskite + corundum. Quenched samples were examined by powder X-ray diffractometers and a scanning electron microscope with an energy-dispersive X-ray spectrometer. Some in-situ X-ray observations on ZnTiO₃ phases have also been made using a diamond anvil cell with synchrotron X-ray diffraction method.

The results by quench and in-situ experiments on ZnTiO₃ indicate that at 1200 °C ZnTiO₃ ilmenite transforms to perovskite at 10 GPa, which dissociates into rocksalt-type ZnO + baddeleyite-type TiO₂ at 22 GPa. On release of pressure, perovskite-type ZnTiO₃, rocksalt-type ZnO and baddeleyite-type TiO₂ are converted into LiNbO₃-type, wurtzite-type and αPbO₂-type phases, respectively. MgTiO₃ perovskite decomposes into MgO + baddeleyite-type TiO₂ at 20 GPa and 1400 °C. FeTiO₃ perovskite dissociates first into CaTi₂O₄-type Fe₂TiO₄ + TiO₂ phase at about 28 GPa. At about 30 GPa, this assemblage further changes into Fe₃Ti₂O₇ phase + TiO₂ phase below about 1100 °C, above which CaTi₂O₄-type Fe₂TiO₄ + FeTi₂O₅ phase were synthesized. These two assemblages have not yet been found in the previous studies. Combination of our results on ZnTiO₃, MgTiO₃ and FeTiO₃ with those of other titanate perovskites suggests that transition pressure of titanate perovskite increases with tolerance factor or ionic radius of divalent cation. It is also indicated that all the titanate perovskites studied dissociate into two-phase assemblages which are denser than hypothetical CaIrO₃-type postperovskites. This is consistent with the previously suggested tendency that ABX₃ perovskites with relatively ionic B-X bonds do not transform to postperovskites.

Keywords: perovskite, titanate, high pressure experiment, postperovskite

Phase relations of MgSiO₃-Al₂O₃ system in Earth's lower mantle

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Abstract

Aluminum oxide (Al₂O₃) is present in about 4-5 mol% for the Earth's mantle compositions, e.g., pyrolite, piclogite and chondrite (Ringwood, 1966; Sun, 1982; Anderson, 1989; Irifune et al. 1986, 2007). In the Earth's uppermost parts of lower mantle conditions, the Al₂O₃ is accommodated mainly in bridgmanite (Irifune 1994), which is the most abundant mineral phase in this region (Ringwood 1975). The MgSiO₃-Al₂O₃ system is a basis system to understand lower mantle phase equilibria in a more complex composition. Phase relations of MgSiO₃-Al₂O₃ system have since been extensively studied using the multi-anvil apparatus with tungsten carbide anvils from upper mantle to the uppermost parts of lower mantle conditions (Irifune 1986, 1996; Kubo et al. 2000; Hirose et al. 2001; Akaogi et al. 2002), and also further constructed by theoretical calculation (Panero et al. 2006; Tsuchiya et al. 2008). The phase relation of MgSiO₃-Al₂O₃, especially toward the Al₂O₃-rich side, in the lower mantle conditions is still relatively limited. Recent technique development of sintered diamond anvils in multi-anvils apparatus allow us to achieve the high pressures and high temperatures conditions of Earth's middle lower mantle (Tange et al. 2008, 2009; Irifune et al. 2010; Ito et al. 2010; Nishi et al. 2013; Yamazaki et al. 2014). Here, we further extend the phase relations of MgSiO₃-Al₂O₃ system between 31 GPa and 45 GPa at 2000 K using multi-anvil apparatus with sintered diamond anvils. Aluminum oxide solubility in bridgmanite is increasing with increasing pressure and temperature. These results can further confirmed previous experimental studies on the same system and pyrolite composition (Irifune et al. 1994, 1996, 2010), and the entire inventory of Al₂O₃ in pyrolite can be accommodated in bridgmanite in Earth's lower mantle.

Keywords: Aluminum oxide, bridgmanite, lower mantle, sintered diamond technique, phase relation

First principles study on the phase stability and elasticity of potassium-host hexagonal aluminous phases

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In order to understand the fate of the potassium-bearing phase subducted into the deep Earth's interior, we have studied the high-pressure stability and elasticity of $\text{KMg}_2\text{Al}_5\text{SiO}_{12}$ hexagonal aluminous phase (K-Hex) by means of the density functional computation method. The K-Hex phase is found to be mechanically stable up to 150 GPa and also energetically more stable than the calcium-ferrite (K-CF) type structure up to 150 GPa. In addition, calculations indicate that when the spinel composition coexists with the K-hollandite (K-Hol) phase, the K-Hex phase becomes more stable than the K-Hol phase at pressures above ~ 27 GPa. This suggests that the hexagonal aluminous phase be a potential host of the incompatible large-ion elements such as potassium in the lower mantle, especially in the subducted basaltic Mg and Al rich composition. Finally, seismic velocities of the K-Hex phase are found slower than Mg-perovskite (pv) in the lower mantle pressures, while its density is larger than Mg-pv over 70 GPa

Keywords: High pressure, Potassium, Lower mantle, Aluminous phase

Effect of Al content on electrical conductivity of bridgmanite

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Electrical conductivity is one of useful methods to prove temperature, structure and composition of the Earth's deep interior. Interpretation of electrical conductivity in the Earth has been done by comparison between conductivities obtained from geophysical observations and conductivities measured in the laboratory. Because bridgmanite is believed to be a dominant constituent mineral in the lower mantle, knowledge of electric conduction for bridgmanite to constrain the conductivity profile of the lower mantle. Xu et al. (1998) reported that Al incorporation to bridgmanite enhance the electron hopping conduction. Although there is a large variation of Al content in bridgmanite under the lower mantle, electrical conductivity of aluminous bridgmanite have not been measured as a function of Al content.

In this study, Impedance spectroscopy measurements were performed at 26 or 28 GPa and up to 2000 K in a Kawai-type multi-anvil apparatus in order to investigate effect of aluminium content on electrical conductivity of bridgmanite. The starting materials were synthetic orthopyroxene ($Mg_{0.9}, Fe_{0.1}$)SiO₃ powders with various amounts of aluminium (Al₂O₃ = 3, 6 and 10 wt.%). Electrical conductivity of aluminous bridgmanite increases with increasing Al content. At temperatures below 1700 K, the activation enthalpies of these samples are around 0.4 eV, which is consistent with that reported by Shankland et al. (1993), who measured the conductivity of quenched perovskite. At higher temperatures (>1800 K) corresponding to temperature conditions of the uppermost lower mantle, the conductivity of samples with relatively lower Al content abruptly increases with temperature and the resultant activation enthalpy is around 1 eV, which is consistent with that reported by Dobson (2003). At temperatures below about 1700 K, small polaron (electron hole hopping between ferrous and ferric iron sites) conduction with activation energy of 0.4 eV is considered as a dominant conduction mechanism of aluminous bridgmanite. At higher temperatures, a different conduction mechanism dominates with more than 1 eV of activation enthalpy.

To estimate ferric iron content in bridgmanite, synchrotron Mossbauer spectroscopy was performed at SPring-8 BL10XU. The ferric iron contents of all samples are estimated to be more than 60 % against total iron content. Proportion of ferric iron in A site tends to increase with increasing Al contents. Thus, increase of ferric iron content due to Al incorporation into bridgmanite can induce enhancement of conductivity. At high temperatures above 1800 K, the dominant conduction mechanism can change extrinsic oxygen ionic conduction when Al₂O₃ content is low. Xu and McCammon (2002) reported evidence that in aluminous perovskite with Mg#90, ionic conduction characterized by high activation energy (1.5 eV) becomes significant above 1700 K dependent on Al content. This is most likely due to the presence of oxygen vacancies, which charge-balance Al and ferric iron substituting onto the B site (Brodholt 2000; Lauterbach et al. 2000). The present results suggest that the electrical conductivity of a region at the top of the earth's lower mantle could be sensitive to amount of Al content in bridgmanite. On the other hand, when Al content in bridgmanite is low, the lower mantle conductivity will be more sensitive to temperature due to the extrinsic oxygen ionic conduction.

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Keywords: bridgmanite, lower mantle, electrical conductivity, Mossbauer spectroscopy, Al, electron hopping

Toward the unified image of the spin transition of iron in the lower mantle

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The pressure-induced spin transition of iron in the lower mantle minerals deeply affects the structures and physical properties of the lower mantle minerals, and thereby the dynamics of the lower mantle. So far, many experimental and theoretical studies have been carried out to clarify the spin transition of iron in the lower mantle minerals. However, there is still a controversy about the existence and the pressure dependence of the spin transition of iron in Mg-perovskite (Pv) and post-Mg-perovskite (PPv) at the lower mantle conditions. Pv and PPv in the lower mantle are considered to involve both Fe²⁺ and Fe³⁺, and Al as minor elements. Until recently, the controversy had been mainly about the spin transition of Fe²⁺. Now, the spin transition of Fe²⁺ in Pv and PPv seems to be settling down in the direction that Fe²⁺ in both Pv and PPv remains high spin (HS) at the dodecahedral site (A site) at the lower mantle conditions (Hsu et al., 2011; Yu et al., 2012).

On the other hand, with the spin transition of Fe³⁺ there are still large discrepancies among the reports, particularly related to the Al content involved in Pv and PPv. Some experimental results indicate that Fe³⁺ becomes low spin (LS) at the octahedral site (B site) in Al-bearing Pv (above ca. 70 GPa) and PPv (whole stability region) (Catalli et al., 2011; Fujino et al., 2012, 2013), while other experimental results indicate that Fe³⁺ coexisting with Fe²⁺ at the A site prefers to occupy the A site and remains HS even at high pressure (Mao et al., 2014; Dorfman et al., 2014). Meanwhile first-principles calculations indicate that Fe³⁺ remains HS at the A site in Al-bearing Pv and PPv (Hsu et al., 2012).

In the presentation, the possible explanations to resolve the above discrepancies among the previous reports to obtain the unified image of the spin transition of iron in the lower mantle minerals are proposed.

Keywords: spin transition of iron, ferric iron, Mg-perovskite, post-Mg-perovskite, Al content, cation exchange reaction

Deep structure and seismic anisotropy of the Western-Pacific subduction zones

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We determined high-resolution P and S wave tomography and 3-D P-wave azimuthal anisotropy of the Western-Pacific subduction zones by inverting a large number of P and S wave arrival-time data of local and regional earthquakes. Our results show some differences between P and S wave images for the stagnant Pacific slab in the mantle transition zone (MTZ) beneath Northeast Asia. The stagnant slab looks thicker in the P wave image than that in the S wave image, which may reflect the effects of both hydration and lower temperature in the MTZ, though differences in the resolution of P and S wave tomography may also have some effects. The Changbai and other intraplate volcanoes in NE Asia are caused by hot and wet upwelling in the big mantle wedge above the stagnant Pacific slab in the MTZ. Our P-wave anisotropy tomography shows that the fast velocity direction (FVD) in the subducting Philippine Sea plate beneath the Ryukyu arc is NE-SW (trench parallel), which is consistent with the spreading direction of the West Philippine Basin during its initial opening stage, suggesting that it may reflect the fossil anisotropy. A striking variation of the FVD with depth is revealed in the subducting Pacific slab beneath the Northeast Japan arc, which may be caused by slab dehydration that changed elastic properties of the slab with depth. The FVD in the mantle wedge beneath the Northeast Japan and Ryukyu arcs is trench normal, which reflects subduction-induced convection. Beneath the Kuril and Izu-Bonin arcs where oblique subduction occurs, the FVD in the mantle wedge is nearly normal to the moving direction of the downgoing Pacific plate, suggesting that the oblique subduction together with the complex slab morphology have disturbed the mantle flow.

Keywords: Subduction zones, Seismic tomography, Anisotropy, Slab, Earthquakes

Archean lithosphere in time and space: geophysical evidence on lateral and vertical heterogeneity in Siberia

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We present geophysical models for Precambrian cratons, including the structure of the crust and the lithospheric mantle, and the thermal structure of the Precambrian lithosphere based on surface heat flow data. A particular focus is on thermo-compositional heterogeneity of the lithospheric mantle. It is modelled as a non-thermal part of upper mantle seismic velocity heterogeneity based on a joint analysis of thermal and seismic tomography data, and as lithosphere density heterogeneity as constrained by free-board and satellite gravity data. The results are compared with xenolith data from the Siberian kimberlite provinces.

An analysis of surface heat flow indicates that many Precambrian cratons (particularly Siberia) are characterized by extremely low surface heat flow (<25-30 mW/m²), which is in apparent contradiction with a worldwide compilation of cratonic xenolith P-T arrays. In regions with very low heat flow, the depth extent of the lithospheric keels locally may reach the depth of 300-350 km.

An analysis of temperature-corrected seismic velocity structure indicates strong vertical and lateral heterogeneity of the cratonic lithospheric mantle. The lateral extent of depleted lithospheric keels diminishes with depth and, below a 150-200 km depth, is significantly smaller than geological boundaries of the cratons. In the Siberian craton, Proterozoic sutures and intracratonic basins are manifested by an increase in mantle density as compared to light and strongly depleted lithospheric mantle of the Archean nuclei.

We demonstrate that density structure of the cratonic lithosphere is well correlated with crustal structure and surface tectonics. The analysis of lithosphere seismic velocity and density structure allows for speculations on processes which formed and modified the Archean lithosphere.

Keywords: craton, lithospheric mantle, density, lithosphere thickness, depletion, metasomatism

Variable inertia method: A novel numerical method for mantle convection simulation

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It is important to understand mantle convection in the earth and the 3D numerical simulation has been a very useful tool. In almost all previous simulations of the mantle convection, the anelastic approximation and the (extended) Boussinesq approximation has been used. An implicit method should be used to solve the equation of motion applied above approximations to allow the use of long timesteps not limited by the CFL condition. However, the resulting matrix is ill-conditioned, in particular since the viscosity depends strongly on the temperature. Thus, 3D simulation of the mantle convection is not well-suited to modern large-scale parallel machines. We have developed an explicit method which can be used to solve mantle convection problem.

Recently, Rempel (2005) proposed the reduced speed of sound technique (RSST) to solve the thermal convection of our Sun. Previously, an incompressible approximation was used to solve the convection of the Sun, as a result, an implicit method was used. The basic idea of RSST is, as its name suggest, modify the continuity equation to reduce the sound speed, thereby allowing the long timestep not limited by the physical CFL condition. Hotta et al. (2012) applied RSST to the thermal convection of our Sun. They confirmed that the characteristic of the flow is not changed as far as the Mach number is smaller than ~ 0.7 , and successfully performed the high resolution simulation of our Sun (Hotta et al. 2014, 2015).

Since not only Mach number, but also the Reynolds number is very small in the mantle, we developed a new formulation which can change these two numbers independently. In order to reduce the sound speed, we multiplied the inertia term of the equation of motion by a large and viscosity-dependent coefficient. We also scale the thermal conductivity and the viscosity in a consistent way so that the characteristic of the flow is unchanged. Using these two modifications, we can change the Mach number and Reynolds number independently. Theoretically, we can expect that this modification would not change the flow as far as the Reynolds number and the Mach number are sufficiently smaller than unity. We call this method the variable inertia method (VIM).

We have performed an extensive set of numerical tests of the proposed method for thermal convection, and confirmed that the characteristics of the flow are not changed by VIM. In particular, it can handle the difference of viscosity of more than five orders of magnitude. Since we can use the long timestep with VIM, we can finish a simulation much faster than that without VIM without losing accuracy. Our new scheme is well suited for simulations on modern large-scale parallel machines since it is an explicit method and thus it opens a new door to very high resolution simulations of mantle convection.

Keywords: mantle convection, numerical simulation

Linear analysis on the onset of thermal convection of highly compressible fluids with variable physical properties

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A series of linear analysis was performed on the onset of thermal convection in a highly compressible fluid with variable physical properties, in order to study the fundamental nature of mantle convection of massive super-Earths in the presence of strong adiabatic compression. We consider the temporal evolution (growth or decay) of an infinitesimal perturbation superimposed to a highly compressible fluid which is in a hydrostatic (motionless) and conductive state in a basally-heated horizontal layer. As a model of spatial variations in physical properties, we employed an exponential dependence of thermodynamic properties (thermal expansivity and reference density), together with the spatial variations in transport properties (thermal conductivity and viscosity). The linearized equations for conservation of mass, momentum and internal (thermal) energy are numerically solved for the critical Rayleigh number as well as the vertical profiles of eigenfunctions for infinitesimal perturbations. The above calculations are repeatedly carried out by systematically varying (i) the dissipation number which measures the effect of adiabatic compression, (ii) the temperature at the top surface and (iii) the magnitude of spatial variations in physical properties of the modeled fluid.

By first analyzing the roles of thermodynamic properties, we found that the onset of thermal convection is strongly affected by the adiabatic compression, through the modulation of the static stability of thermal stratification in the fluid layer. For sufficiently strong adiabatic compression where a very thick “stratosphere” of stable stratification develops in the layer, for example, the critical Rayleigh number explosively increases with the dissipation number. The explosive changes in the critical Rayleigh number are associated with drastic decreases in the length scales of perturbations both in vertical and horizontal directions. In addition, when the effect of adiabatic compression is extremely strong so that the thermal stratification becomes stable in the entire layer, no perturbation is allowed to grow with time regardless of the Rayleigh number and/or the horizontal wavelength.

We also found that the critical states of thermal convection are greatly altered by introducing the depth-dependence in thermal conductivity: the increase in thermal conductivity counteracts the decrease in thermal expansivity with depth by raising the adiabatic temperature change and, hence, enhancing the stability of thermal stratification. In particular, for the cases where a “stratosphere” occurs at the mid-depth of the fluid layer owing to the moderate depth-dependence both in thermal expansivity and conductivity, we observed discontinuous changes in the structures of incipient flows with the dissipation number, depending on the concentration of flows either in the upper and lower “tropospheres”. Our findings suggest that a delicate interplay between the depth-dependent thermal expansivity and conductivity is of crucial importance in understanding the dynamic nature of the mantle convection of massive super-Earths.

Keywords: super-Earths, mantle convection, adiabatic compression, thermal expansivity, thermal conductivity

Post-perovskite phase boundary of Fe- and Al-bearing MgSiO₃

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The post-perovskite (PPv) phase transition of MgSiO₃ bridgmanite (Br) [1,2,3] occurs in the pressure (P) and temperature (T) conditions corresponding to the Earth's D' layer. Therefore, MgSiO₃ PPv is believed to be a key mineral to understanding the seismological properties in this layer. However, to date, it is still a challenging subject to determine the phase transition boundary precisely in the geophysically relevant Fe and Al-bearing compositions. Based on the first-principles methods combined with the internally consistent LSDA+*U* method and the lattice dynamics approach, the high-P and high-T thermodynamics of the MgSiO₃ phases are directly calculated with incorporation of 6.25 mol% of Fe²⁺, Fe³⁺Fe³⁺, Fe³⁺Al³⁺, and Al³⁺Al³⁺ [4,5]. Using calculated free energies, we determine the PPv phase boundaries for Fe and Al-bearing compositions. Our results show that at 2500 K, the Fe³⁺Al³⁺ and Fe³⁺Fe³⁺ incorporations span coexisting domains between Br and PPv significantly with lowering the transition pressure, in contrast to the Fe²⁺- and Al³⁺Al³⁺-bearing cases.

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Keywords: First-principles method, internally consistent LSDA+*U*, post-perovskite, phase transition

New constraints on S-wave velocity structure near the western edge of the Pacific LLSVP

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S-wave velocity structure near the edge of the Pacific Large-Low Shear Velocity Province (LLSVP) has been examined by many researchers (e.g., He et al., 2006; He and Wen, 2009; Takeuchi et al., 2008; Idehara et al., 2013). They have mainly used the differential travel times of ScS-S observed by global or local broadband networks (e.g., IRIS GSN, F-net, CNDSN and so on). Here we add the new data of ScS-S and S-SKS travel time data obtained by NECESSArray and a temporal broadband ocean bottom seismograph network in the Philippine Sea by the Stagnant Slab Project (SSP-BBOBS) (Shiobara et al., 2005).

ScS-S anomalies observed by NECESSArray in conjunction with those by F-net, which covers the region beneath the eastern Micronesia, are roughly explained by the existing 3D S-wave models. However, S-SKS anomalies, which are affected by S-waves propagated near the base of the mantle beneath the western Micronesia and the north of New Britain Island, suddenly changes from positive in the eastern area to almost zero or slightly negative in the western, whereas all the models predict large positive anomalies without significant changes. To confirm this S-SKS observation, we further examined ScS-S anomalies observed by the SSP-BBOBS. Some data indicate nearly zero in the corresponding area although the data are scattered and still sparsely distributed. Since a low velocity anomaly beneath the New Guinea Island are confirmed by Takeuchi et al. (2008) and Idehara et al. (2013), our observation suggests that the Pacific LLSVP is separated beneath the north of New Britain Islands. The models of 3D mantle structure are possibly insufficient near the western edge of the Pacific LLSVP.

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Keywords: LLSVP, Pacific, S-wave velocity structure, lower mantle

On the origin of a stably stratified layer below the CMB inferred from dynamo models

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The geodynamo is powered by the two agents, thermal and compositional buoyancy. The former is fueled by secular cooling of the Earth and/or latent heat upon solidification of the inner core, while the latter is by release of the light elements at the inner core boundary with inner core growth. Since these two buoyancy sources should behave differently due to the vast difference of their diffusivity based on the molecular values, double diffusive convection would occur in the Earth's core.

Apart from double diffusive convection, it is inferred from seismic observations that there is a thin stably stratified layer of O(100) km below the core-mantle boundary. However, it is not well constrained whether the origin of stable stratification is thermal or compositional. Here we investigate effects of a stable layer on dynamo action driven by double diffusive convection. Stably stratified layer is imposed by giving a sub-adiabatic temperature gradient. Thickness of the stable layer is assumed to be 10 % of the core radius. It is found that strength of the dynamo-generated magnetic field is significantly reduced by the thin stable layer in case of dipolar dynamos. On the other hand, the magnetic field is strengthened with the stable layer in case of weak multi-polar dynamos, consistent with a previous study. We discuss mechanisms responsible for such a difference and implications for the origin of the stably stratified layer.

Keywords: dynamo, core, stable stratification, double diffusive convection

Magnetic Rossby waves in the Earth's core

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Magnetohydrodynamic waves in rapidly rotating planetary cores can produce several secular variations of the planetary magnetic field. Some axisymmetric modes, including the torsional Alfvén waves, are thought to be responsible for certain observed features of the Earth's core dynamics and the geomagnetic variation. It is, on the other hand, possible for other waves to lead to the nonaxisymmetric variations. A potential candidate is the magnetic Rossby wave, which migrates in the azimuthal direction along the internal toroidal field. This can be related to the westward drift of the geomagnetic field, which has been observed in the Atlantic hemisphere for the past hundred years. Though the drift has commonly been believed to reflect advection due to large-scale lateral flows beneath the top of the core, propagation of the waves excited within the core may also account for it. This was originally proposed by Hide (1966), who showed that a slow mode of magnetic Rossby waves, sometimes called a slow MC-Rossby mode, could propagate westward on timescales of hundreds of years.

To investigate whether this mode can be relevant in the Earth's core, we extend Hide's linear theory to quasi-geostrophic cylinders and explore nonlinear dynamo simulations in rotating spherical shells. By performing tempo-spatial spectral analyses, we identify slow MC-Rossby waves that propagate at the correct speed, given by the Alfvén and Rossby speeds, with respect to the mean zonal flow. The result indicates that this mode could be excited in the planetary fluid core and that the wave propagation may indeed play a role in the magnetic drift. Taking geomagnetic drift speeds, the theory suggests the internal toroidal field of about 10 mT at the mid core radius. This could give a framework for inferring the physical properties in the fluid core, in terms of nonaxisymmetric waves.

Liquid iron alloys with light elements at outer core conditions by first-principles calculation

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Since the density of the outer core deduced from seismic data is about 10% lower than that of pure iron at core pressures and temperatures (P-T), it is widely believed that the outer core includes one or more light elements. Although intensive experimental and theoretical studies have been performed so far, the light element in the core has not yet been identified. Comparison of the density and sound velocity of liquid iron alloys with observations, such as the PREM, is a promising way to determine the species and quantity of light alloying component(s) in the outer core. Here we report the results of a first-principles molecular dynamics study on liquid iron alloyed with different concentrations of light elements, in order to clarify the effects of their impurities on the liquid density and sound velocity under outer core P-T conditions. We also discuss validity of empirical Birch's law between density and sound velocity in liquid iron alloys.

Keywords: outer core, liquid iron alloys, first principles

Sound velocity measurements of liquid Fe-C alloy under high pressure

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The liquid Earth's outer core consists predominantly of iron with c.a. 10 wt.% lighter elements, such as hydrogen, carbon, oxygen, silicon, and sulfur. Other terrestrial planets such as Mars, Mercury and Venus are also similar to the Earth in that they have central metallic cores, which are considered to be at least partially molten. Popular models for those planetary cores also favor the presence of lighter elements. The nature of the light elements is important for understanding the core formation processes and the present core structure and dynamics in terrestrial planets, both of which are still not well understood. The seismic wave speed is the primary information on the Earth's core. The sound velocity of liquid Fe alloying with light-elements is therefore key to constrain the lighter component in the Earth's core and provide a reference for future surveys of other planets. Recently we have developed the techniques for inelastic X-ray scattering (IXS) measurements combined with diamond-anvil cell (DAC) experiments at the SPring-8 IXS spectrometers in order to investigate sound velocities of liquid Fe alloying with light-elements under the high pressure and high temperature conditions relevant to planetary cores. We determined the sound velocity of liquid Fe-C alloy up to 70 GPa. We will discuss the effect of carbon on the sound velocity of liquid iron and implications for planetary cores.

Keywords: sound velocity, light element in the core, liquid iron carbide, high pressure

Melting experiments in the system Fe-FeS at core pressures

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Most of the Earth's core is iron and nickel alloy. However, the density of the core acquired from Preliminary reference Earth model (PREM) is smaller than that of pure iron. The amount of deficit is 6-10 wt % at the outer core and 1-3 wt % at the inner core. To explain this deficit, the core might contain one or more light elements (H, C, N, O, Si, S).

S is depleted in the crust and mantle compared to other volatile elements (Poirier, 1994). Moreover, iron meteorites contain S (Chabot, 2004), thus we focus on S. In order to discuss the composition of the core, the phase diagram is important. The bulk core composition must be Fe-rich side at inner core boundary (ICB) because the outer core incorporates larger amounts of light element than the inner core. Fe-FeS phase diagram is determined by X-ray diffraction (XRD) pattern (e.g. Morard et al. 2008) or chemical analysis of recovered sample (e.g. Kamada et al. 2012). However, no accurate determination of the eutectic composition has been obtained by XRD. On the other hand, constraining by chemical analysis has not been done using sample recovered from core pressure. Thus, we examine Fe-S phase diagram at higher pressure.

High pressure and temperature (P-T) conditions were generated in a laser-heated diamond-anvil cell. We used Fe-7.5, 13.5 wt.% S foil as a starting material. Angle-dispersive in situ X-ray diffraction (XRD) measurements at high P-T were conducted at BL10XU, SPring-8. The textural and chemical characterizations of recovered samples were made with a field-emission-type scanning electron-microprobe (FE-SEM) equipped with energy dispersive x-ray spectrometry (EDS) and with a field-emission-type electron probe microanalyzer (FE-EPMA). Cross sections of samples were carefully examined by combining a focused Ga ion beam (FIB) with FE-SEM.

From quantitative analysis, we observed the trend that the amount of S in melt decreases and that the amount of S in the solid Fe increases with increasing pressure.

Observing the sample using Fe-7.5 wt % S by SEM, we can see the 3 textures; melt, solid Fe, subsolidus phase. Melt includes more S than solid Fe. The content of S in liquid is between 12.5 and 10.4 wt. % in the range of 38-138 GPa. The eutectic composition is expected to have S than molten iron. Moreover, according to the experiment using S rich starting material, the texture of recovered sample contain melt, Fe₃S, subsolidus phase. The S content in melt is larger than that in eutectic composition. Using both of S-rich and S-poor starting material, we can constrain the eutectic composition.

Assuming that the negative pressure dependence of S content in melt is retained up to ICB pressure, the content of S in liquid Fe at ICB pressure is lower than 10 wt %. The S amount required to explain core density deficit (CDD) is 11.9-13.9 wt.% at outer core and 6-6.6 wt. % at inner core (Sata et al. 2010). In this condition, the S content of eutectic composition is more than 11.9 wt.%. However, this value is great comparing to the eutectic composition expected from this study. Therefore, S is not the only light element in the Earth's core.

Keywords: High pressure and temperature, melting experiments, the Earth's core, light element, core density deficit

Inner core dynamics inferred from grain growth of epsilon-iron

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The inner core is thought to be composed of Fe-Ni alloy with hcp structure based on the high pressure experiments (Tateno et al., 2012) and hence the physical properties of hcp iron (epsilon-iron) are keys for understanding the dynamics of the inner core. Recent seismic observations suggest the variation in grain size in the inner core (Monnereau et al., 2010). It is important to understand the variation in grain size for constraints of the dynamics of the inner core because grain size is controlled by the growth rate and growth rate gives us information on time scale of the inner core growth and/or deformation. In this study, we experimentally determine the grain growth rate of epsilon-iron to understand the dynamics of inner core.

epsilon-iron is only stable at high pressure and it is unquenchable to an ambient condition. Therefore, in this study, we conduct in situ high pressure experiments to determine the grain growth rate of epsilon-iron. We prepared polycrystalline iron of starting material by multi-directional forging (MDF) on highly purity iron rod to avoid oxidation during sintering. In the high pressure experiment, the starting materials was compressed in a Kawai-type high pressure apparatus equipped with sintered diamond anvils with 1.0 truncated edge length at BL04B1, SPring-8. At the pressure of 50-60 GPa, sample was heated for several hours to determine the grain growth rates. Grain growth can be detected by the reduction of number of diffraction spots on the two-dimensional detector with monochromatic X-ray (Offerman et al., 2002) with annealing time.

In the experiments, we observed the reduction of the number of diffracted spots, meaning that grain growth occurs during annealing experiments. For example, the number of diffraction spots reduced to 50 % after annealing at 1300 K for two hours. By extrapolating the present data, we may constrain the translation dynamics of the inner core (Alboussiere et al., 2010) in comparison with seismic observation.

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