SIT02-01 Room:104 Time:May 21 13:45-14:00

Sound velocity measurement of hcp-Fe at high pressure and temperature

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The sound velocity is one of the most important physical properties which can be assessed by seismology. In spite of its importance, the technical difficulty provides limitation of the measurements under the core conditions. Here we show the results of measurements of the sound velocity of hcp-iron by the inelastic X-ray scattering (IXS) method using DAC at high pressure and temperature. Inelastic X-ray scattering spectra were taken at BL35XU, Spring-8. The dispersion of longitudinal acoustic phonons of hcp-Fe was measured by three spectrometers for 4 values of the momentum transfer. The average acoustic sound velocities were thus simply fitted by the sine curve using the equation with free parameters of Vp and Qmax (Fiquet et al., 2001). We used the symmetric diamond anvil cell for the measurements at high pressure and room temperature. Whereas we used the external heating diamond anvil cell for the measurements at high temperature.

We made the inelastic scattering measurements of hcp-iron at pressures up to 167 GPa at room temperature, which is the highest pressure for the IXS measurement. Sound velocity measurements at high pressure and temperature were made at 53 GPa and 87 GPa at 400 K, 54 GPa and 91 GPa at 700 K, and at 62 GPa and 1000 K using the external heating diamond anvil cell. The pressure scale used is a Pt scale by Matsui et al. (2009). When we plot sound velocity and density of hcp-Fe measured in this work in the Birch diagram, we found that the Vp-density relation at 300 K is consistent with the trend reported by Mao et al. (2001) by NIRIXS, and slightly higher in velocity compared to that reported by Fiquet et al. (2001) using IXS method. The temperature dependency obtained in this work shows almost no temperature effect, i.e., the Birch law is applicable up to the temperature at least 1000 K up to c.a. 100 GPa contrarily to the previous NIRIXS work by Lin et al. (2005).

Reference:
Matsui et al. J. Appl. Phys. 105, 013505 (2009).
Mao et al., Science, 292, 914-916 (2001)
Fiquet et al., Science 291, 468 (2001);DOI: 10.1126/science.291.5503.468
Lin et al. Science 308, 1892 (2005); DOI: 10.1126/science.1111724

Keywords: sound velocity, inelastic X-ray scattering, hcp-Fe, high pressure and temperature, Birch law, inner core

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SIT02-02 Room:104 Time:May 21 14:00-14:15

Melts in the Deep Mantle: Insights from First Principles Molecular Dynamics

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As the primary medium through which planetary differentiation occurs, silicate melts are a key entity in the study of the thermal and chemical evolution of Earth. Over the past few years we have used first-principles molecular dynamics simulations to investigate the liquid state physics of the magnesio-, calsio- and aluminosilicate melts at pressure and temperature conditions relevant to the entire mantle. First-principles methods characterize bonding directly in terms of the electronic charge density computed via density functional theory, and is equally robust at ambient and extreme pressure and temperature conditions. This allows accurate predictions of the physics of melts at extreme conditions to be made.

Liquid state diffusion and thermodynamics have been investigated in detail, with special attention to dependence on pressure, temperature and composition. Comparison to corresponding changes in liquid structure enables us to understand thermodynamic and diffusive behavior in a detailed atomistic context. Our results provide a rigorous test for a new fundamental thermodynamic relation for melts, which we derived to accurately describe liquid state thermodynamics. The relation is unique in that it accounts for electronic free energy contributions and displays the correct limiting behavior at extreme volume and temperature, capturing the thermodynamics of liquid-vapor coexistence.

Our work has allowed for deeper insight into the evolution of terrestrial planets, including the thermal state and mode of crystallization of magma oceans, the possible presence of melt in the deep earth, and their relative buoyancy. This insight in turn acts as a guide for questions to be addressed in the future, as first-principles simulations of systems of larger numbers of atoms and complex chemical compositions representative of natural systems become feasible.

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SIT02-03 Room:104 Time:May 21 14:15-14:30

On seismic properties in the deep mantle in mantle convection with the self-consistetly calculated mineralogy

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Numerical thermo-chemical mantle convection simulations in a spherical geometry with mineral assemblages self-consistently calculated using the free energy minimization are used to check the validity of detection on the post-perovskite phase as the seismic discontinuity in the deep mantle, in terms of 1-D seismic profiles at various locations. The assumed compositions of mid-ocean-ridge-basalt (MORB) and harzburgite are composed of six oxides (Na2O-CaO-FeO-MgO-Al2O3-SiO2: NCFMAS) system but the harzburgite composition is calculated from ideal mantle (pyrolite) and MORB compositions. Results indicate that the post-perovskite can be detected as a consequence of the anti-correlation between S and P profiles in the deep mantle, which has the faster jump in S but slower jump in P. The 1-D seismic profiles calculated from our simulations also suggest that the multiple discontinuities in the deep mantle can be interpreted as the folding of subducting slabs above the basaltic piles but, at some exceptional points, they can be interpreted as the multiple crossing due to the post-perovskite phase transition, which would be consistent with various seismic waveform analyses. The anti-correlation of seismic anomalies between S and P in the basaltic piles is also found in our simulations but not very clear because the P anomalies calculated from our models are very noisy. In conclusion, the various seismic properties in the deep mantle could be reproduced from numerical mantle convection with a self-consistently calculated mineralogy, which includes the multiple crossing related to the post-perovskite phase and anti-correlation between S and P anomalies as an evidence for existing the compositional heterogeneities in the deep mantle.

Keywords: core-mantle boundary, thermo-chemical mantle convection, post-perovskite, 1-D seismic structure, seismic discontinuity

SIT02-04 Room:104 Time:May 21 14:30-14:45

Relationship of crystallographic orientation between perovskite and post-perovskite in CaIrO3 and its implication

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After discovery of post-perovskite phase in MgSiO3 by Murakami et al. (2004), main constituting material in the D” layer is considered to be post-perovskite phase. Therefore, transformation mechanism from perovskite to post-perovskite is a key factor to understand the rheology of subducted slab in this region because transformation mechanism often controls the relationship of crystallographic orientation and grain size contrast before and after transformation.

In this study, we focused on the relationship of crystallographic orientation between perovskite and post-perovskite caused by the phase transformation from perovskite to post-perovskite. To access this topic, we used analogue material of CaIrO3, which has a same crystal structure as MgSiO3, becasue MgSiO3 post-perovskite is only stable over ~120 GPa and unquenchable to ambient conditions, meaning the experimental difficulty.

We first prepared the starting materials of large-grained polycrystalline CaIrO3 perovskite at 2 GPa and 1430-1450 C for 12-15 h in piston cylinder apparatus. By using these starting materials, we conducted transformation experiment at 2 GPa and 1100-1400 C for less than 1 min. After experiments, samples were investigated by XRD, SEM and EBSD for phase identification and microstructural observations.

Two important results were obtained in this study: 1) significant grain-size reduction occurs due to phase transformation from perovskite to post-perovskite. 2) topotactic relations, such as a-axis of perovskite accordance with the a-axis of post-perovskite, b-axis of perovskite accordance with the c-axis of post-perovskite, c-axis of perovskite accordance with the b-axis of post-perovskite, were observed on partially transformed sample.

Our results can explain the strong seismic anisotropy in the D” layer of VSH>VSV in circum Pacific region (Panning and Romanowicz, 2006). If perovskite forms lattice preferred orientation by dislocation creep with slip system of [100](010) (Karato et al., 1995) in the subducting slab, phase transformation also yields lattice preferred orientation of post-perovskite due to topotactic relation even if diffusion creep is dominant for post-perovskite due to grain size reduction. As a result, the expected lattice preferred orientation of post-perovskite of c-axis normal to flow plane and a-axis parallel to flow direction suggests that strong seismic anisotropy of VSH>VSV is immediately formed after phase transformation corresponding to the circum Pacific region.

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SIT02-05 Room:104 Time:May 21 14:45-15:00

Pore effect on macroscopic physical properties II: three-dimensional composite elasticity and its application to a porou

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A porous system has distinct macroscopic proprieties that are very different from those of a non-porous matrix. In the present study, a three-dimensional buffer-layer finite element method (FEM) model was developed to investigate the porosity effect on macroscopic elasticity without introducing assumptions or approximations. This is the natural extension of a previous two-dimensional study by Yoneda and Sohag [2011]. Using the three-dimensional buffer-layer FEM model, the porosity effect was systematically analyzed by changing the degree of porosity, aspect ratio of the ellipsoidal pore, and elasticity of the matrix. Consequently, various useful relations were found through three-dimensional analysis of porosity effects. Derivatives of normalized elastic stiffness constants over porosity are integers, if the Poisson ratio of a matrix is zero. These derivatives are nearly constant below 5% porosity, suggesting that the interaction between neighboring pores is insignificant if the representative size of the pore is less than one-third of the mean distance between neighboring pores. The relations we obtained in this work were applied to correct ultrasonic velocities measured on a porous sintered specimen of Cmcm-CaIrO3, which is a well-known analog of the post-perovskite phase of MgSiO3. The resulting rigidity of Cmcm-CaIrO3 after correction for the porosity effect was significantly higher than values predicted by theoretical calculations, and the Poisson ratio of 0.284 is consistent with ratios predicted by theoretical calculations made for the post-perovskite phase of MgSiO3. Considering the similarity of the Poisson ratios, Cmcm-CaIrO3 may be a good analog for the post-perovskite phase of MgSiO3 at around 120 GPa.

Keywords: composit elasticity, finite element method, CaIrO3, post perovskite

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SIT02-06 Room:104 Time:May 21 15:00-15:15

Two-stage evolution of the Earth’s mantle under decaying internal heating

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The Earth’s mantle convection with magmatism and tectonic plates are numerically modeled in a two-dimensional rectangular box of aspect ratio 4 to 6 to understand how the mantle evolves owing to decaying internal heating. Both plate tectonics and magmatism as a migration of magma generated by decompression melting are self-consistently modeled. The mantle evolves in two stages. On the earlier stage, the abundant heat producing elements (HPEs) in subducted basaltic crusts strongly heat the deeper part of the lower mantle, and the hot materials enriched in the basaltic components frequently ascend to the surface as bursts to cause vigorous magmatism; the mantle bursts strongly stirs the mantle and split the lithosphere into small fragments that chaotically move. As HPEs decay on the later stage, however, mantle bursts stop, and subducted basaltic crusts formed by ridge volcanism accumulate on the core mantle boundary to form compositionally dense thermo-chemical piles. Hot plumes ascend from the thermo-chemical piles only occasionally to cause mild magmatism, and a limited number of large plates develop to move more steadily. When water injection into the mantle by subducting slabs is taken into account, chemical differentiation of the mantle is promoted to some extent by enhancing magmatism. The overall features, however, do not depend much on whether or not water circulation is implemented within the model. The overall features of mantle evolution do not depend on the choice of the initial temperature, too, provided that the initial temperature is high enough to induce the magma ocean.

Keywords: mantle evolution, mantle convection, magmatism, decaying heat producing elements, water

SIT02-07 Room:104 Time:May 21 15:30-15:45

Spin crossover and thermodynamic properties of ferric Fe-bearing MgSiO3 perovskite at lower mantle P-T conditions

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(Mg,Fe)SiO_3 perovskite is thought to be the most abundant phase in the Earth lower mantle. Mineral physical studies on this phase is therefore of significant importance in investigating structure and dynamics of the Earth deep mantle. Several studies suggest that Fe is primarily in the ferric oxidation state in silicate perovskite (McCammon, 1997; Frost et al., 2004). In addition, Fe^{3+} could undergo a spin transition, from high spin to low spin, and induce large changes in the thermodynamic properties of the phase, in particular, its bulk modulus (Catalli et al., 2010). However, due to some technical difficulties for the Fe-bearing phases, the high-P,T thermodynamics of ferric Fe-bearing $MgSiO_3$ perovskite are yet to be well understood both experimentally and theoretically. In particular, all the ab initio studies on Fe^{3+}-bearing $MgSiO_3$ perovskite conducted so far are limited at static condition.

Here, we present the results of a computational study on the thermodynamic properties of ferric Fe^{3+}-bearing $MgSiO_3$ perovskite up to 150GPa. We perform density functional calculations beyond conventional methods based on the internally consistent LDA+U technique (Tsuchiya et al., 2006) to describe local interactions between the d-states in Fe in more appropriately that give rise to Hubbard splitting. In this study, ferric Fe is incorporated as substitutional single-point defects in both Mg and Si sites, which can be present in different spin states (low or high) and magnetic states (ferro-, ferri-, and antiferromagnetic). The calculations are performed for several Fe-Fe interatomic distances in order to investigate the effects of the Fe configuration. We calculate the phonon dispersion relations of the Fe^{3+}-bearing phases based on the direct method, where the force constant matrices are determined by directly applying small but finite atomic displacements, similarly to our previous study in ferrous Fe^{2+}-bearing $MgSiO_3$ perovskite and post-perovskite (Metsue and Tsuchiya, 2011, 2012). Then, we determine several important thermodynamic quantities such as the vibrational entropy, free energy, heat capacities, bulk moduli and thermal expansion coefficient within the quasiharmonic approximation. These results are compared to those reported by Tsuchiya et al. (2005) for pure $MgSiO_3$ and by Metsue and Tsuchiya (2012) for ferrous Fe^{2+}-bearing $MgSiO_3$ perovskite. Our results suggest that ferric Fe undergoes a spin transition in the Si-site at pressures ˜50 GPa. The thermodynamic properties of $MgSiO_3$ perovskite are more affected by the incorporation of Fe^{3+} compared to Fe^{2+} but remain limited. Although the spin crossover pressure is consistent with experiments, it does not induce large changes on the thermodynamic properties, contradicting the previous experimental study of Catalli et al. (2010).

Keywords: MgSiO3 perovskite, spin transition, mineral physics

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SIT02-08 Room:104 Time:May 21 15:45-16:00

Spin transitions of iron in the lower mantle minerals - new approaches to settle the spin transition problems of iron -

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Although pressure-induced spin transition of iron is very important to understand the mineralogy and dynamics of the lower mantle, spin transitions of iron in the lower mantle minerals have long been unclear except for ferropericlase. In particular, the spin transition of iron in Mg-perovskite (Pv) has been the issue of a lot of controversy. However, very recently there is a sign that this chaotic state of spin transition problems of iron in Pv will be improved or settled through the following two approaches. One is through the theoretical works on quadrupole splitting (QS) of Fe^{2+} at the A-site in Mossbauer spectra and the other is through the experimental works on cation exchange reaction of Fe^{3+} and Al between the A- and B-sites. We are contributing to the latter approach. This time I will talk about these two approaches to the spin transition problems of iron in the lower mantle minerals.

We measured spin states of Fe^{3+} in Al-bearing Pv and post-Mg-perovskite (PPv) by X-ray emission spectroscopy (XES) and X-ray diffraction (XRD) using the well qualified samples. XES and XRD of Pv indicate that high spin (HS) Fe^{3+} occupies the A-site below 50-60 GPa but above 50-60 GPa Fe^{3+} replaces Al at the B-site by cation exchange reaction and becomes low spin (LS), while Fe^{3+} remaining at the A-site is HS up to 200 GPa. Meanwhile XES and XRD of PPv indicate that LS Fe^{3+} occupies the B-site above around 110 GPa, suggesting that cation exchange reaction of Fe^{3+} and Al between the A- and B-sites occurs below around 110 GPa. The important point here is that the spin state of Fe^{3+} is not determined only by pressure and temperature but also determined by the synthesis and annealing conditions of the samples, and cation exchange reaction of Fe^{3+} and Al between the A- and B-sites plays an important role on it.

As the other approach, Bengtson et al. (2009) and Hsu et al. (2010) reported, based on *ab initio* simulations, that high QS of Fe^{2+} at the A-site in Mossbauer spectra of Pv, which has long been used as the evidence of the intermediate spin (IS) or LS state of Fe^{2+} in the previous reports, is attributed to the HS state of Fe^{2+} at the A-site, just opposite assignment to that of the previous reports. In the presentation, based on these new approaches, spin transitions of iron in the lower mantle minerals are discussed.

Keywords: spin transition, ferric iron, Mg-perovskite, post-Mg-perovskite, X-ray emission spectroscopy, cation exchange reaction

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SIT02-09 Room:104 Time:May 21 16:00-16:15

High-pressure rhombohedral Fe2SiO4 and structure change with spin state

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Motivation High-pressure transformations of various iron bearing spinel solid solutions have been performed by X-ray diffraction measurements (XRD), magnetic measurement, electric conductivity measurement and Raman spectroscopy[1, 2]. Fe_2SiO_4 spinel is decomposed with a reaction of Fe_2SiO_4 (spinel) = 2FeO (wustite) + SiO_2 (stishovite) by high-pressure and temperature experiments [3]. Recently a new structural of a rhombohedral phase has been reported by XRD and Mossbauer spectroscopy measurement at pressures above 30 GPa at ambient temperature [4].

High-pressure transition In the present experiment the structure transition of Fe_2SiO_4 from cubic spinel to rhombohedral (R- Fe_2SiO_4) phase and compression mechanism of spinel phase were elucidated by Rietveld profile fitting analyses and X-ray emission spectra study under high pressure up to 65 GPa at ambient temperature in order to clarify the correlation between structure transition and spin transition.

The rhombohedral-to-cubic back transformation is confirmed by decompression study, indicating the reversible structure transition. Spinel and R- Fe_2SiO_4 were heated to 1500 K by laser heating, proving a decomposition to rhombohedral FeO and SiO_2 stishovite.

New rhombohedral structure A new phase different from spinel was observed above 44 GPa at ambient temperature. Rietveld profile fitting analysis of the pattern taken at 55 GPa confirms the high-pressure rhombohedral structure with R3m space group symmetry and Z=6. There are two Fe sites with six-fold coordination: Fe1 with site symmetry of 2/m (9e) and Fe2 with m (3b). Si atom has a four-fold coordination with 3m (6c). Fe1 site is considerably deformed and Fe1-O average bond distance of 1.935 A, which is smaller than Fe2-O of 2.001 A. A topotactic relation between spinel and R- Fe_2SiO_4 is preserved.

Fe_2SiO_4 spinel at 39 GPa, cubic Fd3m, z = 8, a_c = 7.855 A
R- Fe_2SiO_4 at 55 GPa, hexagonal R3m, z = 6, $a_h = b_h$ = 5.380 A, c_h = 13.814 A
$a_{h,cal} = b_{h,cal} = d_{c,110}$ = 5.554 A, $c_{h,cal} = d_{c,111}$ = 13.685 A

Compression in the <110> direction of spinel structure and simultaneous elongation to <111> direction creates a high-pressure R- Fe_2SiO_4 phase from the spinel structure. The density of R- Fe_2SiO_4 at 55 GPa is D=5.867 g/cm^3, about 5 % larger than D=5.584 g/cm^3 of spinel at 39 GPa.

X-ray emission spectra XES of Fe^{2+} ($3d^6$) ion at the octahedral site of Fe_2SiO_4 shows an intermediate spin state. The spin transition from high spin (HS) to low spin (LS) started at 23 GPa in Fe_2SiO_4. The transition started at much lower pressure than the most of iron-bearing silicate and oxide structural transitions observed by XRD. The LS electronic state increases with compression. Electron spin state gives a great influence on effective ion radii of the transition elements [5].

Fe^{2+}-O distance of Fe_2SiO_4 is 2.16 A in the high spin state at low pressures and 1.99 A at low spin state under high pressures. The bond distance changes induce the polyhedral distortion. The Si-O bond is little compressed, while the Fe-O bond is enormously compressive. Fe-O bond distance shows a distinct change in the spinel phase at 23 GPa. It is consistent with the spin transition pressure.

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Keywords: New rhombohedral Fe2SiO4, Rietveld structure analysis, X-ray emission spectra, High-low spin transition, Spin and structure correlation

SIT02-10 Room:104 Time:May 21 16:15-16:30

High-pressure transitions and the density of subducted continental crust to the upper part of lower mantle

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It has been suggested that the slab materials composed of oceanic crust, harzburgite and peridotite are heterogeneous components in mantle. But subduction of continental crust materials to the deep mantle with the slab has been suggested from the mineralogical, petrological and geochemical evidences. High-pressure phase relations of upper continental crust (UCC) have been determined from the uppermost mantle to the upper lower mantle conditions (Irifune et al., 1994; Wu et al., 2009). But the phase relations of UCC at around upper-lower mantle boundary conditions have not yet been studied in detail. In this study, we have demonstrated high pressure and high temperature phase relations of UCC at P-T conditions around 660-km discontinuity.

The starting material of UCC was prepared by mixing following oxides and silicates: SiO_2 (68.0), TiO_2 (0.6), Mg_2SiO_4 (2.6), Fe_2SiO_4 (3.0), $NaAlSiO_4$ (11.9), $CaAl_2Si_2O_8$ (4.8), $KAlSiO_4$ (6.8), $CaSiO_3$ (2.3), where numbers in parentheses are contents in mol%. High-pressure experiments using a Kawai-type 6-8 multianvil high-pressure apparatus were made at 20.6-28.0 GPa and 1200-1800C. UCC and pressure marker (one of Mg_2SiO_4, $MgSiO_3$ and $MgAl_2O_4$) were packed in two holes in a Re capsule, kept simultaneously at desired P-T conditions for 2-3 hours, quenched and recovered after the run. Phase identification of each sample was made with a microfocus X-ray diffractometer, and compositional analyses of them were made with a SEM-EDS.

The stability fields of five different mineral asembleges of UCC were found as follows: (1) clinopyroxene (Cpx) + garnet (Gt) + hollandite (Hol) + stishovite (St), (2) $CaAl_4Si_2O_{11}$-rich phase (CAS) + Cpx + Gt + Hol + St, (3) calcium ferrite (Cf) + $CaSiO_3$-perovskite (Cpv) + Gt + Hol + St, (4) CAS + Cf + Cpv + Gt + Hol + St, (5) Cf + Cpv + Hol + St. The mineral assemblages of (1) or (2) change to (3) or (4) at 21-22.5 GPa. The mineral assemblages of (3) or (4) change to (5) at 24-25 GPa. At 1200C, CAS does not exist. At pressures above 24-25 GPa, recovered samples were easily crushable. It indicates that Hol (II) which is probably stable above the pressure transforms to Hol (I) during decompression. We also estimated mineral proportions from the compositions, and densities of UCC were calculated and compared with density profile of PREM. The density of UCC at 1400C is the same as that of PREM at 24-28 GPa. Therefore, we suggest that UCC can be subducted into the lower mantle if the slab surface temperature is lower than 1400C.

Keywords: continental crust, high pressure experiment, high pressure transition, hollandite, calcium ferrite, slab

SIT02-11 Room:104 Time:May 22 09:00-09:15

Redetermination of high-temperature heat capacity of Mg2SiO4 ringwoodite

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It is accepted that (Mg, Fe)$_2$SiO$_4$ ringwoodite is an major constituent mineral in the mantle transition zone. Since Mg$_2$SiO$_4$ ringwoodite is a dominant endmember of the ringwoodite phase, its physical and thermochemical properties are very important to discuss the deep mantle. In a thermodynamic calculation, heat capacity at constant pressure (C$_P$) is used to calculate enthalpy and entropy at given temperature and 1 atm. Measured high-temperature C$_P$ data of Mg$_2$SiO$_4$ ringwoodite have been already reported by Watanabe (1982) and Ashida et al. (1987). However, the C$_P$ calculated by several theoretical studies were not consistent with them. In this study, the high-temperature C$_P$of Mg$_2$SiO$_4$ ringwoodite was remeasured using differential scanning calorimetry (DSC) in a temperature range of 298-850 K. At temperatures above about 900 K, the C$_P$ data were not available due to the back transformation to Mg$_2$SiO$_4$ forsterite. Therefore, the C$_P$ at temperatures higher than 850 K were calculated using a lattice vibrational model calculation.

A Mg$_2$SiO$_4$ ringwoodite sample for the C$_P$ measurement was synthesized using a Kawai-type multi-anvil high-pressure apparatus at GRC, Ehime University. A starting material of Mg$_2$SiO$_4$ forsterite was heated at 22 GPa and 1473 K for one hour, and then quenched and decompressed to ambient pressure. Powder XRD and SEM-EDS measurements confirmed that the recovered sample was single phase of stoichiometric Mg$_2$SiO$_4$ ringwoodite. The C$_P$ measurement was performed using a differential scanning calorimeter. In a temperature range from 300 to 573 K, a heating rate was 10 K/min and data were obtained with a step of 5 K. In a range of 553-843 K, the step was 20 K with the heating rate of 20 K/min. Observed heat data were calibrated by corundum based on the C$_P$ of Ditmars et al. (1982). The 3-7 data were averaged at each temperature. For the lattice vibrational model calculation, the Kieffer model with the vibrational density of states model for Mg$_2$SiO$_4$ ringwoodite, which well reproduces the low-temperature C$_P$ from 1.8 to 304.7 K reported by Akaogi et al. (2007), was used.

The C$_P$ data measured in this study are about 3-5% larger than those reported by Watanabe (1982) and Ashida et al. (1987) over the measurement temperature range and are very consistent with those determined from the vibrational model calculation by Chopelas et al. (1994) and from the ab initio calculation by Ottonello et al. (2009). The C$_P$ calculated by the Kieffer model shows very good agreement with those measured in this study. The re-determined C$_P$ of Mg$_2$SiO$_4$ ringwoodite is represented as C$_P$ = 164.30 + 1.0216x10^{-2}T + 7.6665x10^{3}T^{-1} - 1.1595x10^{7}T^{-2} + 1.3807x10^{9}T^{-3} (J/mol K) in a range of 250-2500 K. The result gives a larger entropy at high temperature than those calculated using the C$_P$ measured in the previous works, suggesting more gentle, negative slope of the thermodynamically calculated post-spinel phase boundary in Mg$_2$SiO$_4$ than those of previous thermodynamic studies.

Keywords: ringwoodite, Mg2SiO4, heat capacity, high temperature, DSC, lattice vibrational model calculation

SIT02-12 Room:104 Time:May 22 09:15-09:30

Majorite-ringwoodite strength contrast: Implication for the separation of crustal material from slab near 660 km depth

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Many seismic observations have shown that some of subducting lithospheres penetrates into deeper mantle across 660 km discontinuity. Former oceanic crust, which forms uppermost layer of the slab, consists mainly of majorite-rich garnet (hereafter majorite) near 660 km depth. Majorite is denser than surrounding mantle at shallower depth than 660 km where the ambient mantle consists mostly of ringwoodite, but is less dense at deeper part of the mantle where the Mg-perovskite is the dominant phase. Thus the crustal component may separate from the slab near 660 km depth. Karato (1997) discussed that the separation of crustal component can occur when the crustal component is significantly stronger than surrounding mantle based on dynamic calculation. However, it is unclear whether the separation of the crustal material occurs because plastic strength of related materials at the deep mantle conditions has not been known. In this study, we conducted deformation experiments at pressure and temperature conditions corresponding to the Earth's deep mantle in order to determine strength contrast between majorite and ringwoodite.

Deformation experiments at pressure of ˜15 GPa and temperature of 1473-1673 K were carried out using SPEED-MkII-D installed at BL04B1, SPring-8, Japan. Majorite (Mj) synthesized from a gel with chemistry of the majoritic garnet in oceanic crust and $(Mg_{0.6}Fe_{0.4})_2SiO_4$ ringwoodite synthesized from olivine were placed vertically and deformed uniaxially under same temperature, pressure and stress conditions. Strain measurements were done during deformation based on X-ray radiography using synchrotron radiation. Strain rates were 0.7-2.4 x 10^{-5} s^{-1} for Mj and 1.2-14.5 x 10^{-5} s^{-1} for Rw. Relative strain rate of Rw and Mj (strain rate for Rw divided by that of Mj at same condition) determined at 6 different deformation conditions were 1.3-2.5 (Mj was always stronger in the present experimental conditions). However, an extrapolation of present results to realistic strain rate in the mantle suggests that strength of Mj is similar to that of Rw or lower. Assuming that the dominant deformation mechanism in the Earth's mantle is same as that in present experiments (most probably power-law dislocation creep), the separation of the oceanic crust component may not occur at near the 660 km discontinuity.

SIT02-13 Room:104 Time:May 22 09:30-09:45

Intracrystalline nucleation of post-garnet transformation in deep subducting plate

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Untransformed metastable garnet possibly exists in the plates subducted into the lower mantle because the kinetics of the post-garnet transformation is very slow. Although the post-garnet transformation may affect the density profiles and rheological structure of subducting slab, the realistic depths of the transformation considering the kinetic effects has not been discussed well. Here we report experimental results on the mechanisms of the post-garnet transformation under the large overpressure conditions using single crystalline garnet and sintered diamond anvils. Based on the experimental results, the post-garnet transformation kinetics in the deep subducted plate was discussed.

Natural pyropic garnet single crystals cut to the 0.250 mm cubes were used as the starting material. The material was surrounded by a fine powder of MgO and enclosed in an graphite capsule. All experiments were carried out using a Kawai-type high-pressure apparatus (MADONNA-II, Ehime University). The sintered diamond anvils with the truncated edge length of 1.5 mm were used as the second stage anvils in order to generate high pressure over ˜30 GPa. The sample assembly is composed of sintered (Mg,Co)O pressure mediums, a cylindrical LaCrO3 heater, and a Mo electrode. Temperature was monitored with a W3%Re-W25%Re thermocouple. Transformation microstructures of recovered samples were examined using a field emission-scanning electron microscope (FE-SEM, JSM-7000F) and transmission electron microscopy (TEM, JEOL JEM-2010). Thin foils for TEM analyses (ideally 100 nm) were prepared using a focused ion beam (FIB) system (JEOL JEM-9310FIB).

We found that the intracrystalline nucleation occur above ˜ 35-38 GPa although only grain boundary nucleation occurs at the lower pressure conditions. Also, growth rate of the transformed phases increased with increasing pressure due to the change of the mineral assemblages. Both of the nucleation and growth process at large overpressure conditions would strongly enhance the transformation kinetics, and therefore the post-garnet transformation may proceed rapidly in the subducted plate at around the depth of 900-1000 km. The seismic discontinuities are observed at depth of 900-1080 km beneath subduction zone (the mid-mantle discontinuity). This may be caused by the metastable post-garnet transformation at the large overpressure state.

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SIT02-14 Room:104 Time:May 22 09:45-10:00

Elastic wave velocities of Al-bearing stishovite at high P and T

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Like continental crust, mid-oceanic ridge basalts and sediments are enriched in Silicon. It has been suggested that subduction processes provide a way of enriching the mantle with silica. Above 10 GPa, SiO_2 transforms to stishovite with a tetragonal rutile structure (space group $P4_2/mnm$), which is believed to be a major mineral of mid-oceanic ridge basalts subducted to the mantle transition zone [1]. Previous studies have shown that stishovite has a relatively high-density compared to other constituent minerals of subducted slabs, and could generate chemical and density heterogeneities in the deep mantle. For this reason, numerous studies reported the physical properties of pure stishovite (see [2], and references therein). However, in the subduction context, stishovite can contain up to 2.5 wt% Al_2O_3 in dry systems [3] and up 9 wt% Al_2O_3 in hydrous systems [4]. Therefore stishovite is proposed to be an important carrier of Al and H_2O into the transition zone and lower mantle. The incorporation of even small amounts of Al and its possible coupling with oxygen vacancies can influence the stability, density and compressibility of SiO_2[5-7].

The pressure and temperature dependences of the elastic properties of stishovite + 1 to 6 wt% Al_2O_3 were examinated *in situ* up to 24 GPa and 1700 K by using a Kawai-type multi-anvil press apparatus coupled with synchrotron X-ray diffraction and ultrasonic interferometry. The collection of P-V-T-V_P-V_S data simultaneously provided a strong constraint on the pressure, temperature and Al-content dependences of velocities and elastic properties of Al-stishovite. Generally, we found that sound velocities of P- and S-waves are substantially slower for SiO_2 + only 1wt% Al_2O_3. Thermoelastic data are extrapolated to higher P, T and Al-content and used to directly estimate density and velocity profiles for various composition and temperature profiles. Our results are discussed in regards with the structure and composition of slabs subducted to the depths of the mantle transition zone and lower mantle.

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Keywords: Elastic wave velocity, X-ray diffraction, high-pressure and high-temperature, stishovite, aluminum

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SIT02-15 Room:104 Time:May 22 10:00-10:30

On the onset of plate tectonics in the very early Earth

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Plate tectonics is a particular mode of mantle convection in a planetary mantle, and so far it is observed only on Earth. Most of geological activities, such as earthquakes, volcanic eruption, and mountain building, occur when different plates interact at plate boundaries, and the realization that Earth's surface is actively deforming via plate tectonics was achieved through 1960s and 1970s, revolutionizing almost all branches of earth sciences. Plate tectonics is such an essential process, but we still do not understand the physics of plate tectonics in a satisfactory manner. The current situation may be paraphrased by the following three unresolved questions: (1) how did plate tectonics evolve in the past? (2) why does plate tectonics take place on Earth? and (3) when did plate tectonics first appear on Earth? Considerable progress has been made on the first question in the last decade, and this progress turns out to help better address the second and third questions as well. In this contribution, I will present a synthesis of the current status by combining theoretical considerations and a range of geological and geochemical observations, with a focus on the likelihood of initiating plate tectonics in the early Earth.

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SIT02-16 Room:104 Time:May 22 10:45-11:00

Seismic tomography and mantle dynamics of the Western-Pacific and East Asia regions

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We have used multiscale seismic tomography to determine the detailed 3-D seismic velocity structure of the crust and mantle under the Western-Pacific subduction zones and the East Asian continental regions. The subducting Pacific and Philippine Sea (PHS) slabs are imaged clearly from their entering the mantle at the oceanic trenches to their reaching the mantle transition zone and finally to the core-mantle boundary (CMB). High-resolution local tomography of Northeast Japan has imaged the shallow portion of the slab from the Japan Trench down to about 200 km depth under Japan Sea. The 3-D Vp and Vs structures of the forearc region under the Pacific Ocean are constrained by locating suboceanic events precisely with sP depth phases. Strong structural heterogeneity is revealed in the megathrust zone under the forearc region, and there is a good correlation between the heterogeneity and the distribution of large thrust earthquakes including the great 2011 Tohoku-oki earthquake (Mw 9.0). A joint inversion of local and teleseismic data imaged the subducting Pacific slab down to 670 km depth under the Japan Islands and the Japan Sea. The PHS slab is detected down to 500 km depth under SW Japan. A mantle upwelling is found under SW Japan that rises from about 400 km depth right above the Pacific slab up to the PHS slab. Regional and global tomography revealed the Pacific slab that is stagnant in the mantle transition zone under Eastern China. A big mantle wedge (BMW) has formed in the upper mantle above the stagnant slab. Convective circulations in the BMW and deep dehydration of the stagnant slab may have caused the intraplate volcanoes in NE Asia, such as the Changbai and Wudalianchi volcanoes. The active Tengchong volcanism in SW China is caused by a similar process in the BMW above the subducting Burma (or Indian) slab. Global tomography shows pieces of fast anomalies in the middle and lower mantle as well as in the D” layer above the CMB, suggesting that the stagnant slab finally collapses down to the lower mantle and CMB as a result of very large gravitational instability from phase transitions. Prominent slow anomalies are also revealed in the mantle under the subducting slabs, which may represent either mantle plumes or upwelling flows associated with the deep subduction of the slabs.

Keywords: slab, arc volcanoes, intraplate volcanoes, tomography, earthquakes

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SIT02-17 Room:104 Time:May 22 11:00-11:15

Pressure-induced enhancement of proton migration in brucite

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Proton migration plays a key role in the macroscopic properties of hydrous minerals. Knowledge about proton migration in hydrous minerals is critical for understanding point defects, defects-dominated processes and electrical conductivity in the hydrous minerals. Brucite, which is a stable phase in a wide pressure range, has the simple crystal structure, and therefore it is the best material to understand proton migration process in hydrous minerals with layered structure. Pressure effect on the crystal structure of brucite has widely been investigated by high pressure experiments. Regarding the large compressibility anisotropy of brucite between c and a-axis, brucite is expected to show different conductive behavior with compression. However, there have been no experimental studies about the pressure effect on the hydrogen diffusivity in the hydrous minerals. Here we report the mechanism for proton migration in brucite.

To understand the proton migration process in brucite as a function of temperature and pressure, two different experimental approaches were used: (1) Hydrogen-deuterium (H-D) exchange diffusion experiments and (2) electrical conductivity measurements.

Raman spectroscopy was used to determine the hydrogen concentration. H-D exchange diffusion experiments at pressures from 3 to 15 GPa and 950 K show that the hydrogen diffusivity in brucite is enhanced about one order by compression. The relationship between Log D (m^2/s) and P (GPa) can be described by an asymptotic model: LogD=-11.73-2.38$*$0.78^{P}. Arrhenius parameters for proton diffusion in the direction of perpendicular and parallel to c-axis of brucite at 3 GPa and 750-1050 K yielded a pre-exponential factor of 1.53$*10^{-9}$ and 6.86$*10^{-11}$ m^2/s and an activation enthalpy of 0.69 and 0.59 eV, respectively. Brucite single crystal shows strong anisotropy of electrical conductivity. Measurements of the electrical conductivity of brucite polycrystals at 2.2- 14.7 GPa and 600 to 750 K show that the conductivity of $Mg(OH)_2$ increased about one order of magnitude with increasing pressure. The proton migration in brucite within its stability is likely to be an n-type mechanism. The enhanced proton migration might correspond to the reduction of O...O$'$ distance with increasing pressure. The mobile proton concentration over the total proton concentration in brucite [x (%)= mobile proton/total proton $*$100] was calculated from the Nernst-Einstein equation. At 3 GPa in a temperature range from 550 to 750 K, x is less than 2.5%, whereas, it reaches to about 10% at 14.7 GPa and 950 K.

Keywords: proton migration, hydrous minerals, brucite, electrical conductivity, diffusion, Raman

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SIT02-18 Room:104 Time:May 22 11:15-11:30

Phase relations and melt compositions in hydrous pyrolite system

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Many studies suggest that there could be significant amount of water in the deep Earth, especially in the mantle transition zone (Inoue et al., 1995; Kohlstedt et al., 1996). Water plays an important role in understanding the geodynamics process in the mantle, such as the melting behavior (Inoue, 1994; Kawamoto and Holloway, 1997), phase transformation (Ohtani and Litasov, 2006), and so on. To clarify the effect of water for the mantle peridotite, a series experiments were carried out in pressure range from 12 to 21 GPa and temperatures from 1400 degree C to 1600 degree C in pyrolite+water system, by using a Kawai-type multianvil apparatus with 3mm TEL second stage WC anvils in Ehime University. Some different compositions (Mg/(Mg+Fe)) of olivine were used for pressure calibration under high temperature, and 2cpx-geothermometer was used to estimate the temperature gradient in the run charge. The starting samples were the mixtures of ”pyrolite - MgO” glass, MgO and $Mg(OH)_2$, thus the water contents were adjusted by the $Mg(OH)_2$/MgO ratio. The samples were sealed by AuPd capsules to prevent the loss of water. The recovered samples were polished, and the phases were identified by micro-Raman spectroscopy and X-ray diffraction pattern, the textures were observed by BEI, and the chemical compositions were measured by SEM-EDS system. Under hydrous condition, the phase boundary of olivine/wadsleyite moved to lower pressure, while the appearance of ringwoodite moved to higher pressure, and both phase boundaries became much sharper, compared with dry condition. Liquidus phase changed from garnet to garnet and stishovite, and finally magnesium perovskite at 21GPa.

Compositions of partial melts at 12-21 GPa had high Ca/Al ratio (4-13), and magnesium-rich with (Mg+Fe)/Si ratio larger than 1.7, which is beyond komatiite composition, and quite different from that of the partial melt from dry system. The water contents of hydrous melt were determined by mass balance calculations. It shows that the water content of melt is more than 10wt.% at 410km depth, even along the hot geotherm, which is much larger than the critical value reported by Matsukage et al.(2005) and Sakamaki et al.(2006). That means the hydrous melt may not be stable atop the 410km depth, and should migrate upwards into the mantle. Density calculation also gave the same conclusion. Thus the low velocity zone atop the 410 km depth reported by Revenaugh and Sipkin (1994) may not come from the melting of the mantle minerals.

Keywords: pyrolite, partial melt, water content, low velocity zone

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SIT02-19 Room:104 Time:May 22 11:30-11:45

Generation of ascending flows in the Big Mantle Wedge (BMW) induced by retreat and stagnation of subducted slabs

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We conducted numerical experiments of mantle convection in order to study the mechanism for the generation of ascending flows in the ”Big Mantle Wedge” (BMW), which has been recently proposed by Zhao and coworkers in order to relate the stagnant Pacific slab with the intraplate volcanism in East Asia. In this study, we consider a time-dependent convection of fluid under the extended Boussinesq approximation in a model of a two-dimensional rectangular box of 2000 km height and 6600 km width. We have included both the exothermic olivine to spinel and the endothermic post-spinel phase transitions at around 410 and 660 km depths from the top surface, respectively. The viscosity of mantle material is assumed to be exponentially dependent on temperature and pressure (or depth). We also take into account the effects of the sudden increase in viscosity at the 660 km depth. The plate subduction is modeled by a downward flow of cold and viscous fluid along with a pre-assigned conduit which mimics the path of the descending slab from the top surface to the mantle transition zone (MTZ). In addition, we take into account the effect of trench retreat, by imposing a oceanward migration of the conduit with respect to the deep mantle. Our calculations demonstrated that the retreating motion of trench is of the primary importance on the slab stagnation: For a sufficiently fast trench retreat, the subducting slab tends to stagnate near the 660 km depth. In addition, the horizontal extent of the stagnant slab, once it forms in the MTZ, increases with time almost in proportion to the trench retreat. This means that the BMW is extended oceanward in response to the retreating motion of trench and slab and, in other words, the toe of stagnant slab is significantly anchored in the mantle. We also found that the oceanward extension of BMW has a strong control on the flows in the region. In particular, there occurs a local but strong circulation near the oceanward end of the BMW just above the stagnant slab. This local circulation is driven by the subducting and retreating motion of slab, and induces an ascending flow which pulls up cold fluids near the stagnant slab. Our findings suggest that ascending flows in the BMW can be mechanically-triggered most easily near the oceanward end (or a neck) of the stagnant slab, which is in good accordance with the occurrence of several Cenozoic volcanoes in East Asia above the stagnant Pacific slab.

Keywords: stagnant slab, mantle convection, trench retreat, East Asia, volcanism, Big Mantle Wedge

SIT02-20 Room:104 Time:May 22 11:45-12:00

Subduction of oceanic asthenosphere: evidence from sub-slab seismic anisotropy

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The oceanic asthenosphere is characterized as a low viscosity channel down to 200-300km depth separating the cold lithosphere from above, and it is intimately linked to a layer of low seismic velocity and prominent seismic anisotropy observed globally beneath ocean basins. While subduction of tectonic plates in convergent margins is well recognized, the fate of oceanic asthenosphere remains enigmatic. We demonstrate that the entrainment of the oceanic asthenosphere with its inherited azimuthal anisotropy and strong radial anisotropy explains most of the sub-slab shear-wave splitting patterns, where the fast splitting direction changes from predominantly trench-parallel under relatively steep subduction zones to frequently trench-normal under shallow subduction zones. Substantial amount of oceanic asthenosphere, on the order of 100km, is likely entrained down to the deep upper mantle, which suggests that the mass flux associated with subduction as well as geochemical recycling and mixing may deserve to be revisited. The origin of the asthenospheric fabric consistent with the observation will be also discussed.

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SIT02-21 Room:104 Time:May 22 12:00-12:15

Electrical conductivity of hydrous Ca-free aluminous pyroxene: Implications for the electrical structure in the upper ma

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It was reported that the top of the asthenosphere shows high conductivity anomaly (Evans et al., 2005). Although this kinds of anomaly has been often explained by olivine hydration, it is reported that hydrous olivine is unable to account for this conductivity anomaly (Yoshino et al. 2006). Orthopyroxene is thought to be one of the main constituents of the upper mantle. Although it is less abundant than olivine, Mierdel et al. (2007) observes aluminous pyroxenes can contain strikingly high amount of water, hence, it can be the most important host of water in the shallow part of the upper mantle. It is necessary to measure electrical conductivity of hydrous aluminous orthopyroxene.

The electrical conductivity of Ca-free aluminous enstatite with various water contents has been determined at a pressure of 3 GPa in a Kawai-type multi-anvil apparatus. Impedance spectroscopy was performed for both hydrogen-doped and -undoped samples in a frequency range from 0.1 Hz to 1 MHz to examine the effect of water on conductivity. Two conduction mechanisms were identified for hydrogen-undoped samples at temperature of 1000-1723 K and for hydrogen-doped samples at relatively lower temperature range of 500-900 K to minimize dehydration of samples. For the hydrogen-undoped samples, the activation enthalpy is around 1.9 eV at the higher temperatures range ($>$ 1300 K) suggesting that the dominant charge transfer mechanism is Fe^{2+}-Fe^{3+} hopping (small polaron) conduction. For the hydrogen-doped samples measured below 900 K, the activation enthalpy decreases from 1.11 to 0.70 eV, and the conductivity values systematically increase with increasing water content, suggesting that proton conduction is the dominant conduction mechanism. Using the present results, a laboratory-based conductivity-depth profile in the upper mantle has been constructed as a function of water content. Comparison of our model with the currently available geophysical observations beneath the Eastern Pacific Rise indicates that hydrous aluminous enstatite cannot account for the high conductivity anomaly at the top of the asthenosphere as well as olivine.

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Keywords: electrical conductivity, water, orthopyroxene, asthenosphere

SIT02-22 Room:104 Time:May 22 13:45-14:00

Electrical conductivity of volatile-bearing partial molten peridotite

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The softness of oceanic asthenosphere that allows mobility of overlying lithosphere has been explained by partial melting, hydrolytic weakening of the constituent minerals or just high temperature. Electrical conductivity is a key physical valuable to examine these hypotheses.Recent laboratory electrical conductivity measurements have shown that proton conduction in olivine can elevate the electrical conductivity compared to the dry condition. However, the latest two studies have shown that electrical conductivity of hydrous olivine is not high enough to explain the conductivity anomaly at the top of the asthenosphere, even if the olivine crystal contain a certain amount of water.

Partial melt is the most attractive agent to raise the conductivity at that depth. Recent geoelectromagnetic studies showed conductibility structures of the upper asthenosphere under the Pacific Ocean and required high melt fraction (˜2 vol. %) in the presence of the anhydrous basaltic melt, which is not consistent with the melt fraction estimated from the seismic studies. Volatile components such as water and carbon dioxide in partial molten peridotite can largely reduce the melting temperature and can largely increase the conductivity. However, there have been no systematic study for electrical conductivity of volatile-bearing partial molten peridotite.

In the present study, effect of volatile components such as H2O and CO2 on electrical conductivity of the partial molten peridotite was investigated to consider as a cause of the high conductivity anomaly. The starting materials were KLB1 + 2 wt.% H2O and KLB1 + 1.5 wt.% CO2. The electrical conductivity measurements were performed at 3 GPa and various temperature conditions to obtain a vriation of melt fraction. We found that water- and carbonate-rich partial melts have extremely high conductivity. Electrical conductivity of hydrous partial molten peridotite showed huge enhancement of the conductivity (more than three orders of magnitude) just above the solidus. The conductivty decreased with increasing both temperature and melt fraction. This trend implies that the conductivity decreases with decreasing water conetnt in partial melt. Electrical conductivity of partial molten carbonate peridotite showed that the conductivity of the carbonate melt is nearly one order of magnitude higher than those of silicate melt in peridotite. The high conductivity of the upper asthenosphere beneath the young oceanic lithosphere is not caused by mineral hydration, but by presence of trace amount of volatile-rich melt due to trace amount of volatile components in the asthesnospheric mantle.

Keywords: volatile component, electrical conductivity, partial melting, upper mantle, peridotite, water

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SIT02-23 Room:104 Time:May 22 14:00-14:15

Experimental investigation of the thermal transport properties of omphacite under high pressure and high temperature

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Temperature is a key parameter controlling physical and chemical properties of earth. Knowledge of thermal transport properties (diffusivity, conductivity, and heat capacity) of mantle mineral is indispensable because of its important implications for mantle convection, subduction dynamics and the origin of deep earthquakes (e.g. Mosenfelder et al., 2001; van Keken, 2004; Marton et al., 2005). Pyroxene is an important mineral not only in the upper mantle but also the deep subduction zone (eclogite). Its thermal transport properties at mantle pressure and temperature conditions will provide key insights into these dynamic processes. However, we currently know little of such information.

Eclogite is the major rock in deep subduction zone and lowermost crust of thickened continental (e.g., Ringwood, 1982; Gubbins and Snieder, 1991; Peacock, 1996; Anderson, 2005). The thermal property of eclogite is key information to constrain thermal structure of continental crust and mantle convection. Dobson et al. (2010) measured the thermal diffusivity of eclogite at 3.5 GPa with changing temperature. Considering the stability fileld of eclogite (up to about 15 GPa), it is not sufficient to discuss eclogite properties regarding with subduction process. Thermal property of garnet, which is one of tow major component of eclogite, has already been measured by Osaka (2004). Therefore, we intend to study the thermal property of omphacite, which is also major component of eclogite, at pressures up to 15 GPa, above which pyroxene will dissolved into garnet to form majorite.

We have measured thermal properties of omphacite at pressures to 14 GPa, applying a pulse heating method for simultaneous thermal conductivity and thermal diffusivity measurement. The measurements were conducted using 14/8 cell assembly on a Kawai-type high-pressure apparatus at the ISEI, Misasa. The result shows that omphacite has lower (around 10 %) thermal conductivity than jadeite, and its pressure derivative is 5.1 % per 1GPa, which is higher than than that of jadeite (2.5%, Osako, unpublished data) and olivine (4.5%, Osako et al., 2004).

Keywords: Thermal tansfer, High pressure and high temperature, Omphacite

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SIT02-24 Room:104 Time:May 22 14:15-14:30

The crystal structures of two Zn_2SiO_4 high-pressure polymorphs

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Introduction

The M_2SiO_4 group (M: divalent cations e.g. Mg, Fe) includes the most important constituent minerals of the deep Earth, and thus many of them have been extensively studied. However, some systems containing less common cations (e.g. Zn) are not yet fully understood. The Zn_2SiO_4 system is of special interest from the crystal chemical point of view, because Zn is a strongly tetrahedral coordination preferred element. The phase relation of Zn_2SiO_4 has been reported by Syono et al. [1]. Five phases were identified in the pressure range up to 13 GPa (denominated as phase I to V in the order of increasing pressure) [1]. The crystal structures of phases I (willemite), II and V (modified-spinel structure) have been determined. Phase III and IV have been suggested to be non-stoichiometric [1], but their structures remain undetermined. Here, we report the crystal structures of Zn_2SiO_4 III and IV determined via an ab initio structure determination technique from synchrotron powder X-ray diffraction data utilizing local structural information from NMR as constraints.

Experimental

The Zn_2SiO_4 polymorphs (phase III-6.5 GPa and 1273 K, phase IV-8 GPa and 1273 K) have been synthesized employing a Kawai-type double-stage uniaxial split-sphere multi-anvil apparatus at ISEI, using willemite as starting material. The latter was synthesized at ambient pressure and 1523 K from a mixture of 2ZnO + SiO_2. All the samples have been confirmed to give consistent X-ray diffraction patterns as those reported previously. ^{29}Si MAS NMR spectra have been obtained using a Varian Unity-Inova 9.4T spectrometer at a resonance frequency of 79.5 MHz at ISEI. Synchrotron powder X-ray diffraction data were acquired under ambient condition at the beamline BL19B2 of SPring-8. Chemical analyses have been performed using a JEOL JXA-8800 electron microprobe. The crystal structures were solved using an ab initio structure determination technique by FOX [2] from the synchrotron powder X-ray diffraction data, using the information from ^{29}Si NMR as constraints. The obtained structures were further refined with the Rietveld method using the RIETAN-FP program [3].

Results and Discussion

The ^{29}Si MAS NMR spectra for both phases III and IV contain a single peak for tetrahedral Si. Electron microprobe analyses showed that the Zn/Si ratios are within uncertainty of 2.00 for these two phases, indicating that both of them are stoichiometric, contrary to previous report [1]. The space groups of phase III & IV were determined to be Pnma and Pbca, respectively. Their cell parameters are consistent with those reported by Syono et al. [1]. Both of them contain tetrahedral Si and Zn, like phases I and II. Phase III shows an approximately hexagonally close-packed structure with Si in tetrahedral sites, closely related to that of olivine. Unlike the latter, Zn cations in phase III occupy tetrahedral, rather than octahedral positions. The volume per unit formula of phase III is somewhat larger than that of 'virtual olivine' for Zn_2SiO_4 [1]. Phase IV contains unique edge-shared Zn-O tetrahedral dimers, in contrast to phases I to III that contain only corner-shared Zn-O tetrahedra. The volumes per unit formula for phases III and IV are somewhat larger than that of the lower-pressure polymorph, phase II [1]. This suggests that phases III and IV could have undergone structural changes during decompression. Further in situ high-pressure high-temperature measurements are necessary to resolve this issue.

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Seismic anisotropy in the mantle wedge estimated by numerical simulations

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Understanding the detailed structure of the mantle wedge is difficult, because there are a variety of factors, such as water and melt, which should be taken into account. As a first step to constrain the structure in this region, it is a good way to focus on a simple model, and estimate observable output. In this presentation, we consider the small-scale convection (SSC) in the mantle wedge as an example of the models which may explain the spatial and temporal distribution of volcanoes on the NE Japan and see its effects on seismic anisotropy, that is, the observations which has a close relationship with the mantle flow.

The mantle flow is calculated with composite rheology (i.e., a combination of linear and non-linear rheology) and by using the obtained flow, we estimate P-wave anisotropy based on a theory of LPO development.

Results in the horizontal cross-sections show that the fast direction of P-wave propagation is almost the same as the direction of plate motion. This implies that the large-scale mantle flow associated with subducting slab is still dominant even in the presence of SSC. Results in the vertical cross-sections show that the fast direction of P-wave propagation tends to tilt vertically particularly near the downwellings of SSC. However, the present studies of P-wave azimuthal anisotropy determine the fast direction of P-wave propagation only in the horizontal cross-sections. Therefore, the seismological technique to determine the P-wave anisotropy including the vertical direction (or in 3D) gives us the essential information to know the mantle movement of any kind in the mantle wedge. We also discuss the observation with surface waves which show large V_{SH}/V_{SV} in the mantle wedge and its implications based on our modeling results.

Keywords: mantle wedge, small-scale convection, seismic anisotropy