

Towards co-evolution model of water ocean and deep Earth' s interior –Constraints for total amount of water in Earth' s system

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Revealing an evolution of Earth' s system in terms of co-evolution of surface environment and deep interior, an interaction between water ocean and plate motion is very crucial. In a series of our previous studies, a boundary condition for water migration equation caused by hydrous mantle convection has been assumed that the amount of water ocean is an infinite. With this assumption of boundary condition, the mantle water content may increase rapidly ('burst' of mantle water content), which is caused by efficient heat and mass transfer due to vigorous plate motion but not so efficient with episodic and stagnant lid mode of hydrous mantle convection. However, this assumption is not realistic. Here we set a new boundary condition for water transport equation in mantle convection simulation that can be addressed with a 'finite' amount of water ocean. The input parameter of this type of modeling is the total amount of water in both surface and deep interior, which is assumed as 2 Ocean Masses (1 Ocean Mass = 1.4×10^{21} kg), 5 Ocean Masses and Infinite mass. Applying a finite amount of water ocean, the 'burst' of mantle water content may also occur with vigorous plate motion and water ocean is drought up in about a few billion years of time-scale that is shorter than the age of Earth if the total amount of water in Earth' s system is assumed as 2 Ocean Masses. To get around 1 Ocean Mass at the age of the Earth, at least 3 to 5 Ocean masses of water in Earth' s system seems to be required, which is still consistent with formation theory of water ocean in evolution of early Earth.

Keywords: ocean, plate motion, Earth's system dynamics

Deformation mechanisms and rheology of hydrous phases in subduction

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Hydrous phases are major components of sedimentary, mafic and ultramafic rocks that interact with aqueous fluids released at depths in convergent margins. They play an especially important role at subduction interface where the presence of thin layers with high seismic anisotropy suggests intense deformation in phyllosilicates bearing-rocks such as serpentinites, blueschists and metasediments. I review the current knowledge on plastic deformation of hydrous phases with emphasis on phyllosilicates and their high-pressure transformation products (phase A). While the properties measured in experiments point to mechanical weakness of many hydrous phases, extrapolation of experimentally determined deformation laws to natural conditions is problematic. Comparison with natural samples points to the need for further experimental investigation of deformation laws in context where mechanisms other than plasticity, especially pressure-solution under fluid-saturated conditions, are at work at the high-pressure (1-4 GPa) and moderate temperatures (300-500°C) conditions of the brittle-ductile transition along the subduction interface.

Fluid migration in poro-viscoelastic slab

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Fluids play a key role in controlling seismic and volcanic activities in subduction zones, and many previous studies have investigated where in the slab fluids are released. However, the detailed fluid behavior after its release is still an open question. A recent numerical study suggested that a large part of fluids does not simply go up vertically but rather migrates in high-permeability layer in the slab. They assumed, however, that the slab behaves as viscous fluid when it changes its volume in response to fluid migration. In this presentation we will show how fluid migration changes when the slab is treated as poro-viscoelastic medium.

We use numerical approach based on a theory of two-phase flow, which allows us to simultaneously consider the movement of matrix and fluid phases. We consider 2D model domain inside the slab. A thin layer of fluid source is assumed. Bulk modulus and bulk viscosity which characterize elastic and viscous deformation with volumetric change, respectively, are assumed to be constants. We fix bulk modulus to be 130 GPa and change only bulk viscosity to see its effects on fluid behavior.

Preliminary results show that when the viscosity is lower than $\sim 10^{22}$ Pa.s, viscous deformation is dominant in the slab and almost all the fluids go up vertically soon after its generation, producing porosity waves. When we use bulk viscosity of 10^{24} Pa.s, the slab behaves as an elastic medium and a large part of fluids is trapped in the slab. Considering that the slab has a high shear viscosity due to its low temperature and that bulk viscosity is at least as high as shear viscosity, bulk viscosity in the slab is likely to be very high. Therefore the slab may deform as an elastic medium in response to fluid migration and a large part of fluids will remain in the slab.

Keywords: fluid migration, poro-viscoelasticity, subduction zones

Preferential orthopyroxene serpentinization in the fore-arc mantle and implications for seismic velocity interpretation

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The hydration state of the stagnant fore-arc mantle has been estimated from seismic velocity observations based on the petrologically estimated hydrous mineral phase and modal compositions. When interpreting seismic tomography data, antigorite serpentine is often assumed as the only hydrous mineral in the hydrated fore-arc mantle (e.g., Reynard 2007). However, our recent experimental study showed that the preferential orthopyroxene (Opx) reaction results in the formation of talc along with serpentine at most in the same amount as for serpentine (Nakatani and Nakamura, 2016). In this study, we further examined the P-T conditions for preferential Opx reaction in the olivine (Ol) + aluminum-bearing Opx system in the range of 400–580°C and 1.3–1.8 GPa. We found that the preferential Opx reaction is expected to produce talc in more than one-third of the serpentine in the shallow fore-arc mantle at hot subduction zones, such as Cascadia and Nankai (i.e., $P < 1.3$ GPa and $T > \sim 500^\circ\text{C}$). We then calculated the isotropic seismic velocity for hydrated harzburgite using a volumetric proportion of Ol:Opx = 7:3 and the Voigt-Reuss-Hill average. Using these calculations, we can evaluate the influence of talc formation on seismic velocity.

Seismic velocity calculations indicate that V_p and V_s of hydrated harzburgite decrease monotonically with increasing reacted H_2O content; the rate of decrease does not depend on the extent of the preferential Opx reaction. However, the harzburgite hydration reaction reaches completion at a relatively low H_2O concentration (as low as 2.6 wt%) in the preferential Opx reaction because the talc H_2O concentration (4.8 wt%) is lower than that of serpentine (13 wt%). For example, V_p decreases from 8.3 to 7.7 km/s when all the Opx reacts (i.e., 100% reaction progress) at 580°C and 1.3 GPa. However, it corresponds to a reaction progress of only 33% when the hydration reaction proceeds stoichiometrically to produce serpentine alone. Another important effect of talc formation is that, due to its lower V_p/V_s (~ 1.60) compared with that of serpentine (~ 1.78), the bulk rock V_p/V_s does not change significantly with talc formation along with serpentine. Regions with low V_p and V_s but no conspicuous V_p/V_s perturbation might be explained by the presence of talc, which may contribute to weakening of the mantle (Hirauchi et al., 2016). We also found a case of preferential Opx reaction and resultant talc formation in natural samples; peridotite from the Lower Zone of the Horoman complex, which is assumed as hydrated at pressures below 0.5 GPa. This observation supports the possibility of preferential Opx reactions occurring in the fore-arc mantle.

Keywords: fore-arc mantle, serpentinization, orthopyroxene, talc, seismic velocity

In-situ IR high pressure experiment on hydrous forsterite

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The uppermost mantle is mainly composed of olivine and pyroxene. These minerals can contain small amount of water from a few wt.ppm to a few 1000 wt.ppm (e.g. Mosenfelder et al., 2006). Presence of even such small amount of water can change some physical properties (e.g. rheological properties; Hirschmann and Kohlstedt, 2012; electrical conductivity; Zhang et al., 2012, Schlechter et al., 2012). Many water incorporation mechanisms of olivine were suggested by experimental studies (e.g. Bai and Kohlstedt 1993, Berry et al., 2005) and theoretical studies (e.g. Umemoto et al., 2011) and were controversial. On the other hand, the mechanism by which water influences physical properties is not well understood. In order to study the role of water, the positions of hydrogen ions in crystal sites should be investigated at first.

FT-IR spectra are sensitive to the strength of OH covalent bond. A clue to reveal the positions can be obtained by using the FT-IR method. However, the experimental FT-IR spectra were obtained from quench polycrystalline recovered samples. Since hydrogen atom is very light, therefore, quenched recovered sample may not hold positions of original hydrogen atoms. In fact, Faust and Williams (1996) reported behavior of hydroxyl bonding of phase B at high pressure using in-situ IR spectra. Phase B, which is known as hydrous phase in the subduction zone, have the two bands of 3345 and 3404 cm^{-1} in IR spectra associated with the two hydroxyl sites. They reported the pressure dependence of the peaks. In their experiment, opposite peak shifts of the two bands of 3345 and 3404 cm^{-1} were observed and it is demonstrated that hydrogen position in phase B changes with pressure.

In this study, we performed in-situ IR observations at high pressures for forsterite (Fo) single crystals using DAC. At first I developed in-situ IR observation method at high pressure for low water content of nominally anhydrous minerals in the upper mantle. Using this technique, polarized IR spectra parallel to crystal axis of synthetic hydrous Fo were obtained under high pressure for the first time. First principle calculation (DFT calculation) for hydrogen position in Fo was carried out at various pressures. Hydrogen position in Fo was estimated based on the comparison of the vibrational frequencies measured by the FT-IR methods and simulation by the first-principles methods. The band shift observed in experiments under high pressure could be explained by the hydrogen position change in Si Site with pressure calculated by DFT.

Keywords: FT-IR, DFT calculations, nominally anhydrous minerals, in-situ IR observation, upper mantle

Impact of subduction of H₂O on intermediate depth seismicity, slow slip, and mantle wedge hydrology.

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Metamorphic dehydration of H₂O from hydrated rocks going down in the Earth's subduction zones is known to affect a large number of physical and chemical processes, including arc volcanism, intermediate-depth seismicity, slow slip, and deformation of the mantle wedge. I will provide an overview of recent progress on our understanding of such processes by the combined use of geodynamical modeling, metamorphic petrology, and seismology.

Intermediate-depth seismicity in a number of well-studied subduction zones appears to be related to the dehydration of blueschist-facies rock in cold subduction zones and that of antigorite in warm subduction zones. In the case of the cold Alaska subduction zone seismicity appears to be limited to the predicted dehydration boundary, but seismicity is wide spread and occurs more shallowly in Tohoku and Hokkaido, suggesting rehydration embrittlement is favored over dehydration embrittlement.

Two-phase flow models confirm that fluids tend to at least partly flow back up the slab supporting such mechanism for intermediate-depth seismicity. Focusing of flow in the lowermost mantle wedge in subduction zones with concave geometry may be responsible for the patches of high rates of slow slip events observed in Cascadia and Nankai.

Fluids originating from the slab below arc depth are also expected to cause serpentinization of the cold fore-arc corner in the mantle wedge, although the most effect serpentinization is observed in warm subduction zones where dehydration below the fore-arc also contributes free fluids.

Keywords: subduction zones, intermediate-depth seismicity, two-phase flow

Whole mantle dynamical simulation for aqueous fluid transportation and Pb–Sr–Nd isotopic evolution

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Introduction

Subduction zone fluids are regarded as an essential factor in global isotopic heterogeneities of mantle rocks (e.g., Tatsumi, 2005; Iwamori & Nakamura, 2015). However, it is still controversial how the heterogeneities have been created, distributed, and developed through Earth's history (e.g., layered vs. hemispherical; long-term accumulation vs. effective propagation). We aim at constructing a numerical model that incorporates consistently both geochemistry and physics of fluid-solid two-phase mantle convection.

Methods

On the basis of Nakao et al. (2016, EPSL), we newly construct a 2-D fluid dynamical model with the direct method plus marker-in-cell techniques, including:

- (1) Spontaneous plate subduction and whole mantle convection;
- (2) Water transportation via solid and aqueous fluid phases;
- (3) Water-content-dependent viscosity and density;
- (4) Advection, fractionation, and radioactive decay of U, Th, Pb, Rb, Sr, Sm, and Nd in both solid and aqueous fluid phases. Partition coefficients are based on Kessel et al. (2005) for the upper mantle, and are parameterized for the lower mantle.

Results and Discussion

Mantle wedge process: The simulation results reproduce dehydration of MORB and the overlying serpentinite, as well as the corresponding extraction of hydrophiles in mantle wedge. The aqueous fluids bearing the incompatible elements ascend towards the base of the overlying continental plate. However, the spatial distribution of chemical heterogeneity with variable U/Pb generated in this process is limited to a region around the subducting slabs. They sink into and pile up at the bottom of the mantle due to their large density and viscosity. This may account for an origin of the hidden reservoir with an extremely high Pb isotopic ratio (e.g., Tatsumi, 2005).

Lower mantle process: On the other hand, the simulation shows that dehydration of hydrous ringwoodite just below the 660-km discontinuity (e.g., Schmandt et al., 2014) causes efficient propagation of the hydrophilic heterogeneity. The boundary works as a filter of water and hydrophiles carried by penetrating oceanic slabs, creating hydrous ringwoodite piles enriched in the hydrophiles (i.e., small U/Pb) along the bottom of the transition zone. By contrast, depleted residues (i.e., large U/Pb) are continuously generated at 660 km, sinking into the lower mantle. Since the chemical heterogeneity around the 660 is located in a hotter, less viscous region, it can be transported widely within a short period of time. The hydrous ringwoodite piles over the 660 occasionally generate hydrophile-rich wet plumes due to their small density. We consider the wet plumes from the 660 during continent gathering as a possible origin of the hemispherical isotopic heterogeneity (Iwamori & Nakamura, 2015) because continental collision (i.e., trench advance) and slab penetration at the 660 tend to occur simultaneously.

Keywords: mantle convection, water transportation, chemical evolution, dehydration of ringwoodite, wet plume, isotopic ratio

Chemical geodynamics of subduction zones: geochemical mass balance approach with Arc Basalt Simulator version 5

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A forward geochemical/petrological model created by Arc Basalt Simulator version 5 (ABS5) is used to examine the element mass balance in arc magma genesis including the dehydration of slab materials and flux melting of wedge mantle peridotite that form primary arc magmas. The inverse problem approach using the forward ABS5 model allows for estimation of intensive and extensive geophysical variables in arc magma genesis. The intensive variables are slab dehydration depth (P_{ss}) and temperature (T_{ss}) and mantle melting pressure (P_{perid}) and temperature (T_{perid}). The extensive variables are the amount of slab liquid added to the mantle ($F_{\text{slab liq}}$) and the degree of melting of the mantle (F_{perid}) along with the amounts of water in the slab liquid ($XH_2O_{\text{slab liq}}$), mantle (XH_2O_{perid}), and magma (XH_2O_{melt}). The subordinate geochemical variables are the degree of chemical reaction of the slab liquids to the solid slab ($\%R$); the slab liquid fractions from igneous oceanic crust ($F_{\text{liq}}(\text{AOC})$), sediment ($F_{\text{liq}}(\text{SED})$), and metasomatized mantle peridotite layers ($F_{\text{liq}}(\text{DMM})$); and the degree of depletion of the wedge mantle ($\%MORB_{\text{ext}}$). The mass balance of 26 incompatible elements, 6 major elements including H_2O , and Sr–Nd–Hf–Pb isotopes are calculated by the same scheme. Monte Carlo calculations are used to estimate the aforementioned variables by fitting the calculated magma composition to that of observed values. This paper describes the ABS5 calculation scheme and presents its application results. The geophysical variables are compared with those estimated by other methods, and the control of magma productivity and formation mechanism of the volcanic front are discussed.

Keywords: Geochemistry, Arc magmas, Role of water, Mass balance model

Effect of Al on stability of DHMS up to uppermost lower mantle

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A series of dense hydrous magnesium silicate phases (DHMS) such as phase A (PhA), phase E (PhE), superhydrous phase B (SUB) and phase D (PhD) have been suggested as potential water carriers to transition zone and even to the lower mantle under the conditions present in the cold subducting slabs [e.g. Kawamoto, 2004; Komabayashi and Omori, 2006]. Recently, the newly reported Al-bearing PhD is stable at temperatures up to 2,000 °C at 26 GPa, which indicates aluminum increases stability region of DHMS [e.g. Pamato et al., 2015]. To systematically study the effect of Al on the stability of hydrous phases, we conducted experiments using nature clinocllore, which contains about 15 wt% H₂O and about 14 wt% Al₂O₃. The Al-bearing hydrous PhE, SUB and PhD were observed with P-T increasing according to our results. Following the P-T path of cold subduction, the phase assemblage PhE + PhD is stable at 14-23 GPa, and even a trace of PhE is detected at 1150°C and 25 GPa coexisting with PhD. The phase SUB is stable between 16-22 GPa coexisting with PhE + PhD. Following the P-T path of hot subduction, the phase assemblage PhE + Gt is observed at 14-18 GPa coexisting with fluid or melt. The phase assemblage SUB + PhD is stable at 18-25 GPa, which may extend to higher pressures and temperatures. In addition, it is found that PhE contains 8.5-15 wt% Al₂O₃, SUB contains 3-8.5 wt% Al₂O₃ and PhD contains 8-18 wt% Al₂O₃ in present studies. It is obvious that Al enhances the stabilities of these three hydrous minerals, which are stable even in the hot subducting conditions, and the water content drastically increases estimated from deficit of total weight percent. On the other hand, the Al substitution mechanism in PhE, SUB and PhD were clarified according to chemical compositional relationship between Mg, Si, Al. This shows that they can hold a significant amount of H (water) in their structure. Our results may indicate that the wide stabilities of Al-bearing DHMS increase the chance of obtaining water after antigorite (serpentine) decomposes at the shallow region of the subduction zone and transporting water to the deep lower mantle.

Keywords: phase A, phase E, superhydrous phase B and phase D, aluminum bearing dense hydrous magnesium silicate phases

Speciation of water in basaltic to rhyolitic glasses investigated through ^1H MAS NMR

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Water plays a significant role in the chemical and physical properties of silicate melts, the stability of mineral phases, and magmatic eruptive style. Understanding the mechanisms by which water is incorporated into melts [as molecular water ($\text{H}_2\text{O}_{\text{mol}}$) or hydroxyl (OH^-)] is critical to interpreting water's role in magmas^[1] in subduction zones. We performed ^1H solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy on a suite of glass compositions from basalt to rhyolite and water contents from 1-20 wt. pct. H_2O at lower crustal pressures (1.5 GPa) to assess the influence of glass chemistry on the incorporation mechanisms and structure of water in volcanic glasses and melts.

The ^1H MAS NMR spectra contain information on the speciation of water and the bonding environment of ^1H in quenched glasses at their glass transition temperature. The ratio of the area of the centerband to that of the centerband plus the spinning side bands in ^1H MAS NMR spectra has been demonstrated as a technique to estimate $\text{H}_2\text{O}_{\text{mol}}/\text{OH}^-$ in glasses^[2], because an increase in the amount structurally-bound $\text{H}_2\text{O}_{\text{mol}}$ in quenched glasses increases the intensity of the sideband peaks. The NMR spectra from basalt, andesite and rhyolite glasses with the same water content (e.g., 5 wt. pct.) exhibit similar centerband/sideband area ratios suggesting a near-constant $\text{H}_2\text{O}_{\text{mol}}/\text{OH}^-$ with a slight shift toward larger sidebands suggesting a minor increase in $\text{H}_2\text{O}_{\text{mol}}$ with increasing NBO/T. FTIR observations of water speciation in quenched silicate glasses^[3] suggest that at high water contents, a majority of water in a melt should be incorporated as $\text{H}_2\text{O}_{\text{mol}}$. However, the low sideband intensities of a water-saturated rhyolite glass indicate that most of the water in the glass is incorporated as OH^- . Furthermore, at high water contents (50 mol pct.), OH^- interacting with alkali and alkaline earth species (M-OH) could cause an increase in the polymerization of the melt compared to OH-groups formed by interaction with tetrahedral cations (Si-OH or Al-OH), which will significantly lower melt polymerization. While ^1H NMR cannot directly resolve which cations are bonded to OH^- , future experiments using ^{23}Na and ^{29}Si NMR of these glasses will allow us to determine the degree to which OH^- is interacting with alkalis, alkaline earths, silicon and aluminum, yielding information on water solubility mechanisms and coincident melt polymerization as a function of bulk composition and bulk water content of the glasses. Combined, these datasets will provide critical information on the influence of water on melt polymerization.

In addition to information on water speciation, the frequency of the centerband in ^1H NMR spectra is directly proportional to the average O-H-O distance in the glasses. Increasing NBO/T of glasses from rhyolite to basalt results in a marginal decrease in the centerband frequency from 4.2 ppm to 2.7 ppm suggesting a slight overall decrease in O-H bond length with increasing NBO/T. Combined with Raman, ^{29}Si and ^{23}Na NMR, this peak shift could shed light on the specific solution mechanisms governing OH^- incorporation in silicate melts.

The results of this study are consistent with ^1H NMR investigations of simple systems that suggest the activities of cationic species in the melt influence the solubility mechanisms of OH^- ^[4]. Given that water is a critical component in the generation and evolution of subduction zone magmatism, this study is an important step toward a better understanding of the behavior of water in melts.

¹Mysen, "Water-Melt Interaction in Hydrous Magmatic Systems at High Temperature and Pressure"

²Eckert et al., "Water in Silicate Glasses: Quantification and Structural Studies by ^1H Solid Echo and MAS NMR Methods."

³Ihinger et al., “The speciation of dissolved water in rhyolitic melt.”

⁴Xue, “Water Speciation in Hydrous Silicate and Aluminosilicate Glasses: Direct Evidence from Si-29-H-1 and Al-27-H-1 Double-Resonance NMR.”

Keywords: water, NMR, rhyolite, basalt

Grain growth-induced channelization of non-wetting fluids in synthetic quartzite

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The migration mechanisms of intergranular fluids in deep-seated rocks are of fundamental importance in geological and geophysical processes. Grain-boundary wetness, often characterized by a dihedral angle, is a parameter used to determine the grain-scale geometry, and accordingly, the migration mode of the fluids. When the dihedral angle is larger than 60° in a fluid-rock system, an interconnected fluid network is not established along the grain edges and corners at low fluid fractions, and thus pervasive permeable flow is not assumed to occur. In such a case, the processes that allow fluids to migrate within rocks are poorly understood. To address this issue, we performed sintering experiments on aqueous-fluid-bearing quartzite and observed the evolution of the fluid distribution with time. The experiments were conducted with various fluid fractions and compositions (3.21–15.1 vol% of aqueous fluid, $\phi = 0, 0.35\text{--}0.85$) at 900 °C and 1.0 GPa for up to 192 hours.

In the end products (from experimental runs under CO₂ saturation) that had greater than 60° dihedral angles between the fluid and the quartz grains, fluid pockets (grain-scale fluid reservoirs surrounded by faceted quartzite grains) were found to have formed via fluid expulsion during grain growth. These fluid pockets were likely formed by smaller grains, surrounded by fluid-filled triple and multiple junctions, that were consumed by grain growth, followed by the coagulation of the fluid-filled junctions [1], [2]. In some of the product runs, the fluid pockets were aligned to be in proximity with one another. These fluid pockets are likely to be interconnected three-dimensionally. The spatial distribution of smaller quartz grains measured with the line-transect method revealed that smaller grains tend to acquire network-like arrangements; probably due to a geometrical (packing) requirement in self-organizing fluid-rock systems that have grain size variations. Such a grain arrangement may result in the increased interconnectivity of fluid pockets via consumption of the small grains during extensive grain growth, a process that would significantly increase the permeability of non-wetting, fluid-bearing systems.

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Keywords: Grain growth, Fluid expulsion, Dihedral angle, Minimum energy fluid fraction

Raman spectroscopic investigation of α - β quartz phase transition in hydrothermal diamond-anvil cell and acquisition of equation of states of aqueous solutions

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The α - β quartz phase transition temperatures ($T_{tr,qtz}$; s; up to ~ 781 °C) were determined at various pressures (P ; s; up to ~ 802 MPa) in a hydrothermal diamond-anvil cell (HDAC; Li et al., 2016; Rev. Sci. Instrum., **87**, p. 053108-1) by monitoring the Raman shift of the α -quartz band near 128 cm^{-1} (at 24.2 °C). When compared with the commonly used α -quartz band near 465 cm^{-1} (e.g., Schmidt and Ziemann, 2000; Am. Mineral. **85**, p. 1725), the rate of reduction in wavenumber during H_2O isochoric heating is about five times higher. In addition, the sudden change of the rate of reduction in wavenumber at $T_{tr,qtz}$ is much more sharp and clear, making the α -quartz band near 128 cm^{-1} a much better choice for detecting the phase transition.

Our experimental procedures were similar to those of Shen et al. (1993; Am. Mineral. **78**, p. 694), except Raman spectroscopic method instead of laser interferometry was used to determine $T_{tr,qtz}$. A quartz wafer (prepared from a natural crystal from Asikaerte Be pegmatite in Xinjiang, China) together with or without H_2O were loaded in the sample chamber, which was a hole in a Re gasket between two diamond anvils; H_2O pressure medium was not needed for experiments at 0.1 MPa total pressure.

Raman spectra were acquired during a heating cycle of the experiments after the sample was kept at a constant T for more than 3 minutes. We used a JY/Horiba LabRam HR Evolution Raman system, with 532.06 nm (frequency doubled Nd:YAG) laser excitation, a SLWD 50x Olympus objective having 0.35 numerical aperture, a 1800-groove/mm grating with a spectral resolution of about 0.2 cm^{-1} , and $\sim 14\text{ mW}$ laser light was focused on the sample during the measurement. Spectra were collected in one spectrographic window (from 77 to 593 cm^{-1}) for either 30 s (below 700 °C) or 60 s (above 700 °C) with two accumulations per spectrum.

The bulk density of H_2O in the sample chamber for the observed $T_{tr,qtz}$ was determined by measuring the homogenization $T(T_h)$ after the liquid-vapor phase separation during isochoric cooling. The two K-type thermocouples in HDAC were calibrated with the melting points of NaNO_3 (306.8 °C) and NaCl (800.5 °C), and the uncertainties in T measurements are ± 1.5 °C. The associated pressures at T_h (P_h) and $T_{tr,qtz}$ ($P_{tr,qtz}$) were calculated based on the equation of state (EOS) of H_2O (Wagner and Pruβ, 2002; J. Phys. Chem. Ref. Data **31**, p. 387). The straight line connecting (T_h, P_h) and $(T_{tr,qtz}, P_{tr,qtz})$ in a P - T space is near the isochore of that bulk density of H_2O . Similar approach was successfully applied to obtain isochores of 2 m ZnCl_2 solution (Bassett et al., 2000; Zeitsch. Kristallogr. **215**, p. 711), and will be extended to other geologically important aqueous solutions at T s up to 1000 °C using HDAC and Raman spectroscopy. The α - β quartz phase boundary obtained in this study can be represented by: $(P_{tr,qtz}) (\pm 8.8\text{ MPa}) = 0.0015 (T_{tr,qtz})^2 + 1.8268 (T_{tr,qtz}) - 1544.5$, where $(T_{tr,qtz})$ is between 574 and 781 °C; with $R^2 = 0.9998$. Our results agree, within experimental uncertainties, with those reported by Mirwald and Massonne (1980; J. Geophys. Res. **85**, p. 6983), but with some deviations from other previous data.

Keywords: α - β quartz phase transition, Raman spectroscopy, Equation of states of aqueous solutions, Hydrothermal diamond-anvil cell, Isochore

Noble gas and major element composition of deep groundwater in the fore-arc region of southwest Japan; widespread distribution of fluids dehydrated from the Philippine Sea Plate

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Chemical and isotopic studies including analyses of noble gases were conducted on the groundwater in the fore-arc region of southwest Japan (Kii Peninsula and Shikoku Island) where the Philippine Sea Plate is subducting. High $^3\text{He}/^4\text{He}$ ratios relative to the atmospheric value (up to 6.7 Ra) were observed throughout the studied area, covering a wider area than documented previously. From the wide distribution of high $^3\text{He}/^4\text{He}$ values and the associated ^{20}Ne and Cl^- concentrations, Morikawa et al. (2016) infer that aqueous fluids derived from dehydration of the subducting slab are present at depth beneath the entire peninsula. These aqueous fluids may ascend along the major north-dipping boundary faults. The variety of water types documented may be due to water-gas separation and the subsequent incorporation of gaseous species into shallow meteoric groundwater. The observed high $^3\text{He}/^4\text{He}$ ratios in the absence of a mantle wedge below the southern part of the Kii Peninsula may reflect the oblique ascent of these fluids along north-dipping boundary faults.

As already reported by Dogan et al. (2006) and Umeda et al. (2006), moderately high- $^3\text{He}/^4\text{He}$ groundwater has been observed on Shikoku Island, west of the Kii Peninsula, although no sampling point exceeded 4 Ra. By analogy with the Kii Peninsula, incorporation of the ascending fluids along faults accounts for the groundwater of this area, but this moderately high $^3\text{He}/^4\text{He}$ ratio (< 4 Ra) is possible to relate the slab configuration. The depth of the slab surface is relatively shallow, and therefore the thickness of the mantle wedge beneath Shikoku Island is less than that below the Kii Peninsula, resulting in a low mantle-He budget around the pathway of the fluids.

References: Dogan et al. (2006) *Chem. Geol.*, **233**, 235-248, Morikawa et al. (2016) *Geochim. Cosmochim. Acta*, **182**, 173-196, Umeda et al. (2006) *Geochem. Geophys. Geosyst.* **7**, Q04009, doi:10.1029/2005GC001210

Keywords: noble gas, groundwater, Philippine Sea Plate, helium, Kii Peninsula

Characteristics of slab-derived fluids beneath Kii Peninsula, southwestern Japan inferred from seismic tomography

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1. Introduction

In order to investigate behavior and nature of slab-derived fluids discharged from the Philippine Sea plate subducting beneath Kii Peninsula, southwestern Japan, we carried out linear array seismic observations, receiver function analyses and seismic tomography. We estimated the geometry of the slab and the seismic velocity structure beneath the Kii Peninsula, and discussed the behavior of the fluids with the distribution of low velocity anomalies. We are now understanding relations between the fluids and deep low frequency events and active micro seismicity beneath the northern Wakayama Prefecture.

2. Receiver function analysis

We carried out linear array seismic observations in the Kii Peninsula from 2004 to 2013. We deployed seismometers along profile lines with an average spacing of ~ 5 km. We applied receiver function analyses and obtained images of S wave velocity discontinuities. We estimated 3D configurations of the continental Moho, the slab top and the oceanic Moho from receiver function images for four profile lines in the NNW-SSE direction which is the dip direction of the Philippine Sea slab and for two profile lines in the NNW-SSE direction that is almost perpendicular to the dip direction.

The continental Moho, the slab top and the oceanic Moho are clearly found in the receiver function images. A new knowledge obtained by the analysis is that the continental Moho dips upward in the southeast direction above the Philippine Sea slab.

3. Seismic tomography

We carried out seismic traveltimes tomography with FMTOMO (Rawlinson et al., 2006) in which a robust wavefront tracking (de Kool et al., 2006) is implemented for the theoretical travel time calculation and the ray tracing. We used a velocity model with the 3D geometries of the three discontinuities derived from the receiver function analysis. We also used observed travel times at temporary stations in the dense linear arrays in addition to permanent stations. A dense distribution of the temporary stations contributed to higher resolutions of tomographic images. We used 231,650 P travel times and 210,142 S travel times from 3,445 local events during May 2004 – March 2013. We also applied the four-step approach by Ramachandran and Hyndman (2012) to estimate accurately V_p/V_s ratios.

Results of the tomography show that low velocity anomalies ($> 5\%$ in both P and S wave velocities and high V_p/V_s ratio > 1.8) are located in deep low frequency events areas at 30–40 km depths on the Philippine Sea slab and that another strong low velocity anomaly ($> 10\%$ in P wave velocity and low V_p/V_s ratio < 1.6) is widely distributed in the lower crust beneath the northern Wakayama Prefecture where small to micro earthquake activity is very high in the upper crust (Figure 1). The first feature can be due to discharged H_2O from hydrous minerals in the oceanic crust at 30–40 km depths. The second feature can be explained by a mechanism that fluids upwelling from the low velocity anomaly in the lower crust increase the pore pressure in existing cracks in the brittle upper crust. The low V_p/V_s ratio in the low velocity anomaly beneath the northern Wakayama Prefecture might indicate that the low velocity body is deposited silica.

We used waveform data from permanent stations of NIED; JMA; ERI, Univ. of Tokyo; Nagoya Univ. and DPRI, Kyoto Univ.

Keywords: tomography, slab-derived fluids, Kii Peninsula

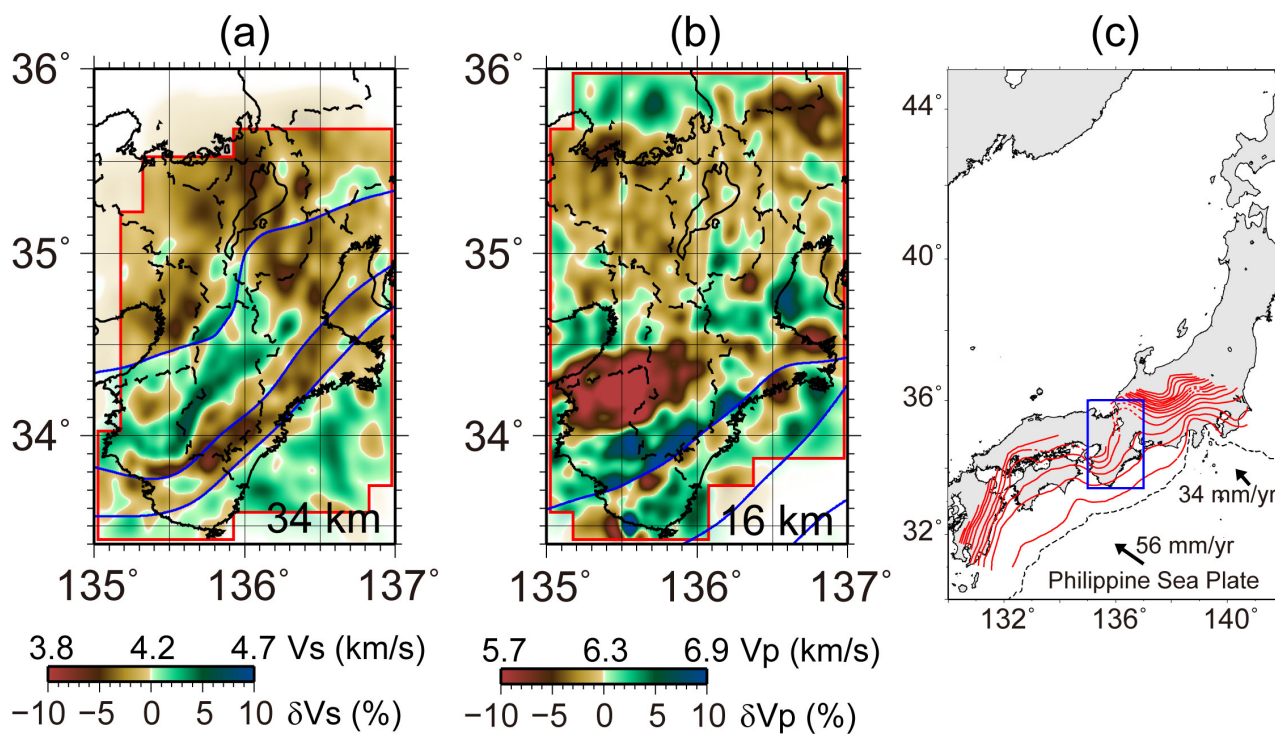


Figure 1

Heterogeneous distribution of seismic wave velocity in and around Kii Peninsula.

(a) Perturbation of S wave velocity at 34 km depth from the reference velocity of 4.23 km/s. The blue lines denote the continental Moho, the slab top and the oceanic Moho from the north to the south. The broken lines indicate prefectures' borders.

(b) Perturbation of P wave velocity at 16 km depth from the reference velocity of 6.28 km/s.

(c) A map showing the location of our study area (blue rectangle). The broken lines indicate Nankai and Sagami troughs. The red lines show contours of the Philippine Sea slab. The arrows indicate velocities of the Philippine Sea plate.

Major components and salinity of slab-derived fluids: insights from fluid inclusions in jadeitites and jadeite-quartz rocks

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Slab-derived fluids play important roles in mass transfer in subduction-zone channels between the subducting slab and the mantle wedge (e.g., Bebout, 2013). High salinity of the slab-fluids probably enhances the mobility of elements such as Pb in subduction-zone channels (Keppler, 1996). Salinity is important to affect solubility and fluid-rock partitioning of elements. Jadeitites and albitites occur as tectonic blocks in serpentinite mélanges intercalated to high-pressure and low-temperature metamorphic rocks. Therefore, fluid inclusions of them are expected to record information of the fluid composition in serpentinized mantle-wedge. Especially, jadeitites have index minerals of metamorphic conditions such as jadeite, quartz, albite and analcime. Jadeitites have been noted on relationships to fluids in subduction-zone channels; they are products of direct precipitation from aqueous fluids (P-type) and/or of fluid-induced metasomatism of a protolith (R-type) (e.g., Harlow et al., 2007, Tsujimori & Harlow, 2012). Albitite-rinds around quartz-bearing jadeitites are developed by metasomatism during retrogression (Shigeno et al., 2012b).

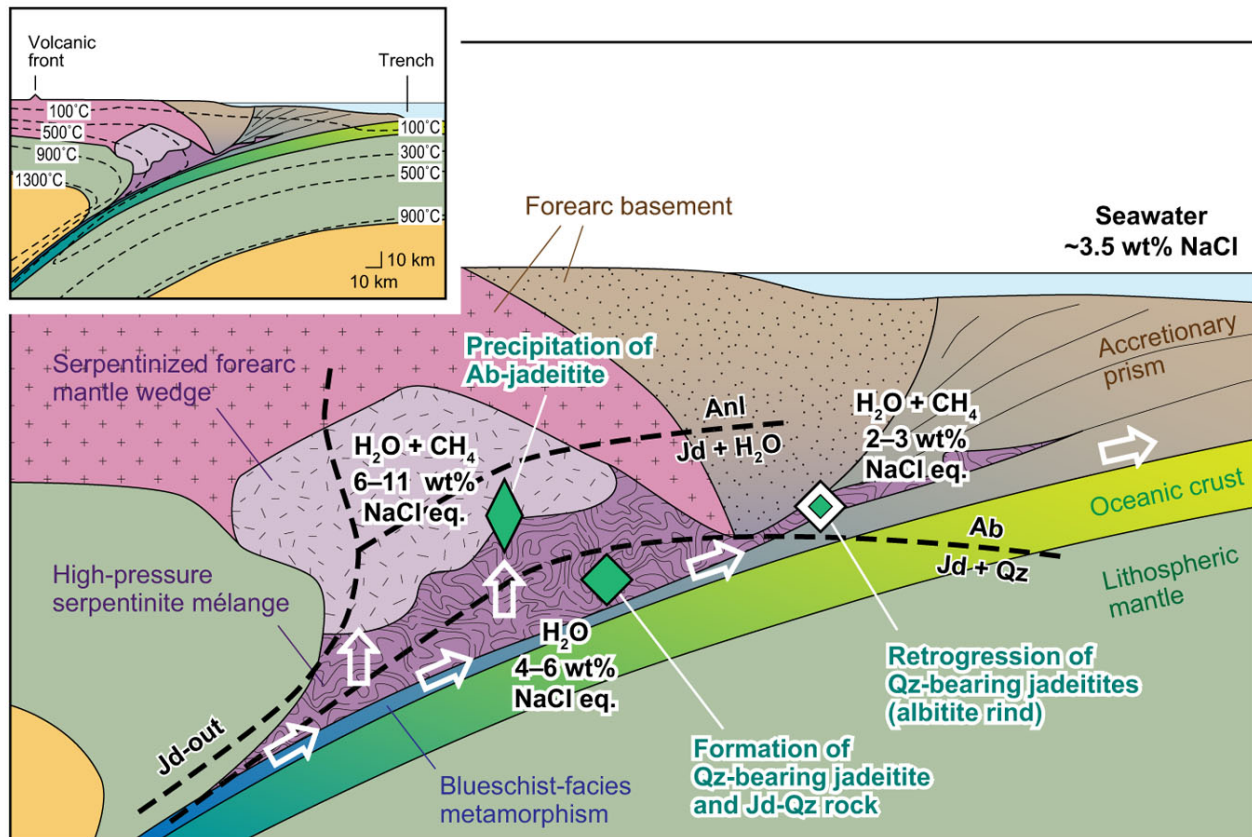
We investigated major components and salinity of fluid inclusions (liquid + gas bubble) in jadeite-quartz rocks (Kamuikotan, Yorii), quartz-bearing jadeitite with albitite rind (Nishisonogi), albite-jadeitites (Itoigawa, Oya) in Japan. The quartz-bearing jadeitite from Nishisonogi is a pale blue-green rock including quartz inclusions in the core of jadeite crystals (Shigeno et al., 2005). Investigation of mineral-inclusions of zircon revealed that the quartz-bearing jadeitite from Nishisonogi and the jadeite-quartz rock from Yorii were R-type (Mori et al., 2011, Yui & Fukuyama, 2015). The jadeite-quartz rocks show green-grey color and consist of subhedral jadeite and quartz. The albite-jadeitites are pale grey rocks, and show signature of P-type jadeitites such as euhedral jadeite crystals and interstice of albite.

Major components and salinity of fluid inclusions were examined by Raman spectrometry and by freezing point depression using heating/freezing stage. Raman spectrometry showed that primary fluid inclusions in jadeite-quartz rocks, quartz-bearing jadeitite and albitite rind of quartz-bearing jadeitite are H₂O liquid and vapor. In albite-jadeitite, primary fluid inclusions are H₂O liquid and vapor with CH₄. The modes of salinity of jadeite-quartz rocks, quartz-bearing jadeitite, albitite rind of quartz-bearing jadeitite are less than 6 wt% NaCl eq. The modes of salinity of fluid inclusions in albite-jadeitites are more than 6 wt% NaCl eq. Many secondary fluid inclusions are H₂O + CH₄ and tend to show higher or lower salinity than each mode.

These results and reaction curves are summarized in Fig.1. These results indicate that salinity distribution of slab-derived fluids and their difference depend on distance from surface of subducting slab. They are possible to explain different appearance, origin and metamorphic conditions (mineral assemblages) of two types of jadeitite as well as contents of fluid inclusions and salinity.

Fig. 1. Schematic model showing the major components and salinity of slab-derived fluids and the formation of jadeite-quartz rocks, quartz-bearing jadeitite with albitite rind, albite-jadeitites in forearc mantle wedge. The figures are not to scale. Modified from Harlow et al. (2015). Mineral abbreviations: Ab = albite, Anl = analcime, Jd = jadeite, Qz = quartz.

Keywords: Slab-derived fluid, Salinity, Fluid inclusion, Jadeitite, Albitite



In situ X-ray diffraction studies of hydrous aluminosilicate at high pressure and temperature

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Water is transported into the deep Earth's interior by hydrous minerals in the descending slabs. Previous studies showed that hydrous aluminosilicate would be stable in the mid-ocean ridge basalt and the sedimentary layer of subducting slab. Discovery of phase egg in the diamond inclusion also supports that hydrous aluminosilicate could exist in the earth's deep interior. Topaz-OH ($\text{Al}_2\text{SiO}_4(\text{OH})_2$) is stable in the pressure range of 8-12 GPa and transforms to Topaz-OH II and Al-phase D under high pressure condition. However, the phase relation of $\text{Al}_2\text{SiO}_4(\text{OH})_2$ has not been clarified yet.

In order to determine the phase relation of hydrous aluminosilicate experimentally, we have conducted an in situ X-ray diffraction study at high pressure and temperature using Kawai multi-anvil high pressure apparatus and intense X-ray of synchrotron radiation at SPring-8. The truncated edge length of the anvil is 3 mm. The pressure medium was made of ZrO_2 and Co-doped MgO. We used a TiB_2 tube heater with a Boron epoxy window for the X-ray path and the W3%Re-W25%Re thermocouple for monitoring temperature of the experiments. Pressure was calculated from the equation of state of gold.

We found that hydrous phase of δ -AlOOH and stishovite were stable in the pressure range of 22-30 GPa and the temperature range of 800-1500 °C. Al-phase D was found at 24 GPa, 1500 °C coexisting with phase egg. Al/Si ratio of Al-phase D was approximately 1.85, which was less than ideal composition.

Keywords: hydrous aluminosilicate, synchrotron X-ray diffraction, lower mantle, subducting slab

In situ observation of wet solidus from xenoliths and its control on rheological structures of lithospheric mantle beneath Ichinomegata, NE Japan

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A fundamental question about lithosphere-asthenosphere boundary (LAB) is what causes the rheological contrast between lithosphere and asthenosphere. Two major proposed solutions for this problem are: (1) abrupt appearance of interstitial melt (e.g. Hirschmann 2010, Green 2010) and of hydroxyls (e.g. Karato 2010, 2012) in the top of asthenosphere. In order to address this issue in the arc environment, where hydrous upper mantle is expected, we investigate depth variations of deformation microstructures and presence or absence of fluid/melt phase in mantle xenoliths from Ichinomegata volcano, where reliable estimates of derivation depths of the xenoliths are available.

Ichinomegata volcano is a 60-80 ka mar (Kitamura 1990) located on Oga peninsula, in a back-arc side of NE Japan. In this area, active subduction of the Pacific Plate beneath the North American Plate has been supplying water to the overlying wedge mantle (e.g. Kumagai et al. 2014). Mantle xenoliths were found in andesitic-dacitic pyroclastic rocks (Katsui et al. 1979). They are either plagioclase- (and/or spinel-pyroxene symplectite after plagioclase) bearing or plagioclase-absent spinel peridotites (Takahashi 1978, 1986). We examined three plagioclase peridotites and six spinel peridotites to identify phases and microstructures along grain boundaries and their distributions.

Interstitial phases were examined with FE-SEM. Fluid phase is identified by the presence of fluid inclusions in olivine and etch pits on the interphase boundaries. Melt phase is identified by the presence of interstitial glass containing vesicles with growth textures of contacting olivine. Two equigranular and tabular granular plagioclase peridotite containing pargasite, one granular spinel peridotite, and one porphyroclastic spinel peridotite are shown to have fluid phases. Two porphyroclastic spinel peridotites, one porphyroclastic spinel peridotites containing amphibole as inclusion in clinopyroxene, and one equigranular spinel peridotites are shown to have melt phase according to above criteria. The chemical compositions of glasses and their petrographic features are consistent with those reported by Takahashi (1986). The samples with interstitial melt recorded a rapid heating event (referred as “preheating” by Takahashi (1986)), and exhibit homogeneous Ca distribution in olivine suggesting persistence (>1000 yrs) of “preheating” forming interstitial melt.

The xenolith samples were compared in terms of the rock textures, depths, and temperatures before xenolith extraction, which are based on pressure-dependent thermometers of T_{BKN} and $T_{\text{Ca-in-Opx}}$ (Brey and Köhler 1990) from chemical compositions of pyroxenes rims (see our companion presentation). There are systematic correlations between the presence of fluid/glass with rock textures, phase assemblage, and pressure and temperature conditions. Fluid phase is found in equigranular samples registering low pressure and temperature (0.7-1.2 GPa and 831-1016 °C), and melt phase in porphyroclastic samples registering high pressure and temperature (1.2-1.6 GPa and 1045-1084 °C). The boundary between the disappearance of the presence/absence of melt and fluid is ca. 1.2 GPa and 1000 °C, which are almost the same as the wet peridotite solidus experimentally determined by Grove et al. (2006). The coincidence of textural transition from equigranular to porphyroclastic and that of intergranular phases from fluid to melt during high temperature “preheating” stage suggests that the appearance of interstitial melt at high-temperature at wet solidus might govern the rheology of hydrous wedge mantle. The wet solidus may have migrated according to the thermal state beneath the LAB, which might represent dynamics of the

LAB region hypothetically assumed above hydrous wedge mantle.

Keywords: wedge upper mantle, petrology, rheological structure, LAB

Effects of temperature, melt, and volatile on polycrystal anelasticity: Toward the application to subduction zone

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Recent progress in the experimental approach to the polycrystal anelasticity shows that the reduction of seismic velocity and Q by partial melting occurs in two stages: reduction just before partial melting and that at the onset of partial melting [Yamauchi and Takei 2016]. This new experimental result significantly affects the interpretation of the upper mantle seismic structures. We present a new anelasticity model derived from these new data, together with some applications to the oceanic mantle. The new model is sensitive to the volatiles, which play important roles in subduction zones.

We measured elasticity, anelasticity, and viscosity of polycrystalline aggregates at near-solidus temperatures ($0.89 \leq T/T_m \leq 1.01$; T_m = solidus temperature), by using organic polycrystals (borneol + diphenylamine binary eutectic system, eutectic temperature $T_m = 316$ K) as partially molten rock analogue [Yamauchi and Takei 2016]. The results showed that the high-frequency part of the attenuation spectrum was significantly enhanced just below the solidus temperature ($0.94 < T/T_m < 1$) in the absence of melt. In this temperature range, viscous deformation was also enhanced. These changes are called subsolidus effects. The onset of melting at $T = T_m$ caused further enhancement of the elastic, anelastic, and viscous deformation. These changes are called direct effects of melt. When the samples can produce very small amounts of melt ($\Phi = 0.4 - 0.5\%$) at $T = T_m$, the direct effects of melt were negligibly small, but the subsolidus effects were large. Therefore, due to the subsolidus effects, a region without melt or with a very small amount of melt can be detected as low V and low Q region. We performed a detailed parameterization of the subsolidus effects and presented a new anelasticity model.

The new model successfully explained the steep reduction of shear wave velocity just below the solidus temperature observed near the Pacific ridge [Priestley and McKenzie 2013]. Because the model includes the nondimensional parameter T/T_m , the solidus depression by volatiles affects the prediction of seismic velocity and attenuation under a given T . So far, the application of this model to the upper mantle is limited to the oceanic mantle, where melt fraction is expected to be very small ($\Phi \ll 1\%$) even beneath the ridge axis. In the subduction zone, melt fraction in the mantle wedge can be larger, and the direct effects of melt may not be negligible. Although the direct effects of melt on elasticity and viscosity are understood well, the direct effect on anelasticity has a large uncertainty. Hence, further experimental study is needed before the application to the subduction zone. Although Yamauchi and Takei [2016] showed that the direct effect of melt on anelasticity is non-negligible for $\Phi > 1\%$, quantitative assessment is difficult, because the samples with $\Phi > 1\%$ used in this previous study had a connected network of solidified melt at $T < T_m$. We are planning an improved experiment to clarify the direct effect of melt on anelasticity, particularly, the effect of melt connection on anelasticity.

Keywords: anelasticity, partial melting, seismic attenuation, seismic low velocity, melt network