

Temperature dependence of seismic velocities in a antigorite serpentinite at 1 GPa

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Serpentines play key roles in subduction zone processes including water transport, seismogenesis, exhumation of high-pressure rocks, etc. Geophysical mapping of serpentized regions in the mantle wedge leads to further understanding of these processes. Seismic properties of serpentized peridotites are critical to interpretation of seismological observations. Antigorite is a major form of serpentine, which is stable to higher temperatures. The single-crystal elastic properties were recently revealed via Brillouin scattering technique (Bezacier et al., 2010; 2013). However, the temperature dependence of elastic properties is still poorly understood. We have measured elastic wave velocities in a antigorite serpentinite at high temperature and pressure conditions.

A black massive antigorite serpentinite was collected from the Nagasaki metamorphic rocks, western Japan. It is composed of antigorite (98.0 vol.%), diopside (1.5 vol.%) and magnetite (0.5 vol.%). Microstructural observation reveals an interpenetrating texture characterized by randomly oriented antigorite blades. Antigorite CPO data shows weak concentration of antigorite axes. Elastic wave velocities measured at 180 MPa shows very weak anisotropy in elasticity. Cylindrical samples (D=L=6mm) were made with ultrasonic machining.

Measurements were made at the pressure of 1 GPa and the temperature of up to 550 C, by using a piston-cylinder type high pressure apparatus at ISEI, Okayama University. The pulse reflection technique was employed for velocity measurement. One LiNbO₃ transducer with the resonant frequency of 5 MHz was used to transmit and receive ultrasonic signals. The length of the sample at high pressure and temperature conditions was estimated from the length of the recovered sample.

Both compressional and shear wave velocities linearly decrease with increasing temperature. The temperature derivatives are -3.6×10^{-4} (km/s/K) and -2.7×10^{-4} (km/s/K) for compressional and shear wave velocities, respectively. The temperature derivative of compressional wave velocity is close to that observed in the direction subparallel to antigorite *c*-axis (Yano et al., in prep.). The temperature dependence of *c*₃₃ might dominate that of the effective elastic constants of a randomly oriented polycrystalline aggregate. Applications to seismological observations will also be discussed in this presentation.

Keywords: seismic velocity, serpentinites, antigorite, subduction zone, fluid

Detection of structured water on quartz interface by Raman-FTIR spectroscopy and its evaluation by molecular dynamics

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Molecular structure of water in thin film shows different characteristics compared with that of free water. Thin film water was observed at mineral grain boundaries, and its structure might be influenced by mineral surface.

High temperature-pressure cell for micro-Raman and Fourier-transform infrared (FT-IR) spectroscopy have been developed to investigate molecular structure of thin film water at high temperature and pressure conditions. As a result of micro-Raman and FT-IR spectroscopic measurements of water, the broad peak around 3400 cm^{-1} , attributed to OH stretching vibration mode of water molecular, was observed at ambient temperature and pressure. The broad peak shifted to higher wavenumber with increasing temperature on metal reflector. Compared with the result of IR properties of water on metal reflector, IR properties of water on artificial quartz surface exhibit different trend: the broad peak contained the peak component of the lower wavenumber (around 3200 cm^{-1}), even at high temperature.

In addition, molecular dynamics simulations were performed under the conditions of the experiment using MXDORTO. In the simulation, the water of a few nanometers of quartz near the surface was structured. The distribution of water density was different from the free water. These properties are discussed in the hydrogen bond between water molecular and silanol (Si-OH) of quartz.

Keywords: Raman spectroscopy, IR spectroscopy, interfacial water, subcritical, quartz, molecular dynamics

Generation process of brecciated marble at Hiraodai karst, Kyushu, Japan

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Geofluid is believed to be closely related to the seismic and volcanic activities. However, the detail relationship of geofluids with seismicity and volcanic activity is not studied properly through geological observations. We have found recently the brecciated marble widely distributed at Hiraodai karst plateau, Fukuoka Pref. This brecciated marble offers unique opportunity to study the relationship between geofluid and seismicity. Here, we shall explore the generation process of this brecciated marble through geological, microstructural and geochemical methods using polarization microscope, SEM, TEM, EPMA, microthermometric and MC-ICP-MS techniques.

The marble in Hiraodai karst plateau was thermally metamorphosed due to Cretaceous Hirao granodiorite intrusion. The brecciated marble occupies about 0.7 km x 1km of area in the central part of the karst. The main results of the present study are as follows.

- 1) The brecciated marble is composed of the rock fragments with variety of sizes ranging from millimeter to meter scale, and having angular to rounded shapes.
- 2) Numerous fluid inclusions are observed in the thin section of the brecciated marble.
- 3) TEM observation shows that the dense tangled dislocations are formed in calcite grains of the brecciated marble.
- 4) The homogenization and freezing temperatures of the fluid inclusions are about 240 deg C and 0 deg C, respectively.
- 5) The whole-rock and mineral separates (biotite and plagioclase) of Hirao granodiorite yields Rb-Sr isochron age of 129.4 +/- 2.4 Ma. Interestingly, Rb-Sr data of the fluid inclusions also lie on the Rb-Sr isochron of Hirao granodiorite.

The above-mentioned results of 1) and 2) suggest that the brecciation occurred by fluid infiltration and that the fragments were moved and rotated at very high speed. The result 3) demonstrates that the calcite grains of the brecciated marble experienced high stress. These three results together indicate that the brecciation process might generate seismic wave. On the other hand, the results of 4) and 5) suggest that the possible origin of the fluid inclusion is the released fluid from the Hirao granodiorite magma. Therefore, the brecciation of marble distributed at Hiraodai karst plateau was probably generated by magmatic fluid from Hirao granodiorite under high stress condition at 129.4 +/- 2.4 Ma ago.

Keywords: Brecciated rock, Hiraodai karst, Hirao granodiorite, Fluid inclusion, Rb-Sr isotope

Equation of state of topaz-OH in the subducted sediment under high pressure and high temperature

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Dehydration reactions of hydrous minerals in the subducted sediment produce a H₂O-rich fluid which causes generations of magma, decreases of melting temperature of sediment, and variations of magma compositions. Topaz-OH [Al₂SiO₄(OH)₂], which is one of hydrous minerals, is considered to be existed in the sediment of the subducting slab. Topaz-OH is the end-member of natural topaz [Al₂SiO₄(OH,F)₂]. The stability field of topaz-OH extends to 1500 degree C at 5-10 GPa (Wunder *et al.*, 1993; Ono, 1998; Schmidt *et al.*, 1998). The equation of state (EoS) for the natural topaz has been also estimated (Komatsu *et al.*, 2003; Gatta *et al.*, 2003). However, the EoS of the end-member topaz-OH has not been performed yet. In this study, we performed *in situ* X-ray diffraction (XRD) experiments under high pressure and high temperature for determining the thermal elastic properties of topaz-OH.

The starting material of topaz-OH was synthesized at 10 GPa and ~1000 degree C from the quench experiment using multi-anvil apparatus. The high pressure (3-8 GPa) and high temperature (up to 800 degree C) *in situ* XRD experiments were carried out using MAX80 installed at beam-line NE5C at PF-AR, KEK, Japan. These XRD patterns were collected by the energy dispersive method. Thermal elastic properties were calculated from EoS fit v5.2 software (Angel, 2000) using 3rd order Birch-Murnaghan EoS.

From *in situ* XRD experiments, we successfully determined thermal elastic properties using all-data for fixed K'=4 as below: V₀=354.7(1) Å³, K₀=169.8(22)GPa, (dK_T/dT)_P=-0.013(7) GPaK⁻¹, a₀=1.61(23)×10⁻⁵K⁻¹, b₀=1.36(41)×10⁻⁸K⁻². From the detailed analysis of compression data, we found the change of the compression properties near 7 GPa. This change was also seen in a- and b-axis. Therefore we re-calculated the thermal elastic properties using two data sets: (I) below 7 GPa (II) above 7 GPa at room temperature. These calculation results from low pressure data show V₀=355.2(1) Å³, K₀=160.1(2)GPa, however those from the high pressure data show V₀=356.5(9) Å³, K₀=153.1(89) GPa (K'=4 fixed). Compared to the natural topaz, topaz-OH shows relatively large volume and bulk modulus. This shows that the volume and bulk modulus increase with increasing OH content. Compared bulk modulus with density, topaz-OH locates near the line for Birch's law and indicates large bulk modulus and density as same as Phase D [Mg₂SiO₄(OH)₂]. We suggest that high density topaz-OH enhances the slab subduction and transports water to deeper earth's interior.

Keywords: topaz-OH, high pressure hydrous phase, subducting slab, equation of state, synchrotron X-ray in-situ experiment

Water content in arc basaltic magma in northeast Japan and Izu-Mariana arc estimated from melt inclusions in olivine and

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Primitive arc basalt magma is generated by partial melting of sub-arc mantle with adding aqueous fluid which was derived from dehydration of subducting slab. Aqueous fluid has profound effects on melting temperature of the mantle, crystallization pathways of generated magmas, and explosivity of magmas. Precise estimation of H₂O content in arc basalt magma is important to evaluate the effect of water on generation, differentiation, and eruption of magmas in subduction zones. We estimated variation of water content of arc basaltic magmas in the northeast Japan arc and the Izu-Mariana arc using a simple plagioclase phenocryst hygrometer and melt inclusion analysis of olivine phenocrysts.

A simple plagioclase phenocryst hygrometer was constructed by high-pressure and high temperature experiments using internally heated pressure vessels: SMC-2000 and SMC-5000 installed at the Magma Factory, Tokyo Tech (Ushioda et al., 2013, VSJ fall meeting). High-pressure and high-temperature experiments were conducted for relatively primitive basalt from Miyakejima volcano under hydrous conditions. OFS (Ofunato scoria: Tsukui et al., 2001; Niihori et al., 2003) is one of the most primitive basalt in the last 10,000 years. All experiments were conducted near the liquidus of plagioclase (\pm magnetite) and therefore the composition of melt is essentially the same as the starting material. H₂O content of melt was calculated by weight ratio of melt using mass balance calculation of all phases assuming that water was concentrated only in melt. Partition coefficient $K_D^{pl-melt}{}_{Ca-Na}$ is proportional to H₂O content in melt. In the experimental conditions, both pressure and temperature effects are negligible.

We then chose geochemical data sets of relatively primitive basaltic rocks (with no evidence of magma mixing) and most frequent Ca-rich plagioclase phenocrysts from 15 arc basaltic volcanoes, which includes both frontal arc volcanoes and rear-arc volcanoes from literature. In 15 volcanoes, plagioclase phenocrysts of high anorthite content (An>90) are commonly observed, whereas plagioclase phenocrysts in rear arc volcanoes usually have lower anorthite content (90>An>80). Estimated H₂O content of basaltic magma is 3 wt.% H₂O or higher.

We also analyzed H₂O content of melt inclusions in olivine phenocrysts using FTIR micro reflectance measurement (Yasuda, 2011) and FTIR micro transmission measurement (absorption coefficient: Yamashita et al., 1996) in order to compare H₂O content between melt inclusion analysis and this simple plagioclase phenocryst hygrometer. For example, melt inclusions of olivine phenocrysts in scoria from Ko-Fuji volcano had up to 3.7 wt.% H₂O which was consistent with estimate from our simple plagioclase phenocrysts hygrometer. In Miyakejima volcano, melt inclusions of olivine phenocrysts from OFS contained up to 3.3wt.% H₂O although H₂O content was 5.2 wt.% estimated from this hygrometer. In either case, basaltic magmas in volcanic front have 3 wt.% H₂O or higher.

Keywords: water in magma, melt inclusion, equilibrium between plagioclase and melt

DEM simulation on fracturing induced by hydration and dehydration reactions

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Dehydration and hydration reactions play significant roles on the global water circulation in the solid Earth, and cause drastic change in the mechanical properties of the subduction zone interface. Progress of both reactions requires an effective transport of water (release or supply) between the reaction sites and outer system, and are commonly characterized by large changes in solid volume, porosity, and fluid pressure. Reaction textures with fracturing are commonly observed both in hydration and dehydration hydration reactions. However, the dynamic relationship among reactions, fluid transport and deformation (fracturing, plastic deformation) is too complicated to be understood solely by observations of natural occurrences.

In the present study, we carried out numerical simulations on fracturing induced by hydration or dehydration reactions by using distinct element method (DEM). At first, we consider a dehydration reaction like a dehydration of serpentine. In the model, the following factors are introduced: (1) pressure dependence of reaction rate, (2) grain boundary as weak and water-saturated region, and that (3) mineral grains become permeable after fracturing or reacted. In this model, reaction rate drastically decreases with progress of dehydration reaction, when fluid cannot escape from the system.

We examined two rock systems; one is composed of reactive minerals (uniform-reactive system) and the other one is composed of reactive minerals embedded in unreactive matrix minerals (reactive minerals in matrix system). In both systems, one is drain-boundary, whereas all the others are undrain-boundary. The spatial variation in fractures and progress of reactions are contrasting between the two systems. In the uniform-reactive system, fracturing does not occur and reactions uniformly occur from the drain-boundary, because fluid effectively escapes through newly-produced pore-network. In contrast, the reactive-mineral-in-matrix-system, the fracture network is produced among the reactive grains, and heterogeneous distributions of reaction progress was produced in the rocks. We will further discuss the key parameters to controls the fracture patterns and difference between hydration and dehydration reactions.

Keywords: hydration, dehydration, fracturing, distinct element method