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.

キーワード：海洋、プレート運動、地球システム変動
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 ~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.

キーワード：流体移動、多孔質粘弾性、沈み込み帯
Keywords: fluid migration, poro-viscoelasticity, subduction zones

前弧マントルの蛇紋岩化における斜方輝石の優先的な反応：地震波速度の解釈への影響

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 $T >$ ~500°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.

キーワード：前弧マントル、蛇紋岩化、斜方輝石、滑石、地震波速度
Keywords: fore-arc mantle, serpentinization, orthopyroxene, talc, seismic velocity

含水フォルステライトの高圧その場IR 測定実験
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.

キーワード：FT-IR、第一原理計算、無水鉱物、その場IR観察実験、上部マントル
Keywords: FT-IR, DFT calculations, nominally anhydrous minerals, in-situ IR observation, upper mantle

Impact of subduction of H_2O on intermediate depth seismicity, slow slip, and mantle wedge hydrology.

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Metamorphic dehydration of H_2O 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, suggestion 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.

キーワード：マントル対流、水輸送、化学進化、リングウッダイトの脱水、含水プルーム、同位体比
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 ($F_{\mathrm{slab\ liq}}$) and the degree of melting of the mantle (F_{perid}) along with the amounts of water in the slab liquid ($XH_2O_{\mathrm{slab\ liq}}$), mantle ($XH_2O_{\mathrm{perid}}$), and magma ($XH_2O_{\mathrm{melt}}$). 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 ($F_{\mathrm{liq}}(AOC)$), sediment ($F_{\mathrm{liq}}(SED)$), and metasomatized mantle peridotite layers ($F_{\mathrm{liq}}(DMM)$); and the degree of depletion of the wedge mantle ($\%MORB_{\mathrm{ext}}$). 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 clinochlore, which contains about 15 wt% H_2O and about 14 wt% Al_2O_3. 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% Al_2O_3, SUB contains 3-8.5 wt% Al_2O_3 and PhD contains 8-18 wt% Al_2O_3 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 ^{1}H 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 (H_2O_{mol}) or hydroxyl (OH^-)] is critical to interpreting water’ s role in magmas[1] in subduction zones. We performed ^{1}H 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 ^{1}H MAS NMR spectra contain information on the speciation of water and the bonding environment of ^{1}H 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 ^{1}H MAS NMR spectra has been demonstrated as a technique to estimate H_2O_{mol}/OH^- in glasses[2], because an increase in the amount structurally-bound H_2O_{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 H_2O_{mol}/OH^- with a slight shift toward larger sidebands suggesting a minor increase in H_2O_{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 H_2O_{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 ^{1}H 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 ^{1}H 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 ^{1}H 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.

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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, = 0, 0.35–0.85) at 900 ℃ and 1.0 GPa for up to 192 hours.
In the end products (from experimental runs under CO_2 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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キーワード：結晶粒成長、流体吐出し、固液二面角、平衡流体量
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 ($T_{\mathrm{tr,\ qtz}}$' s; up to ~781 ºC) 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 ºC). 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 $T_{\mathrm{tr,\ qtz}}$ 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 $T_{\mathrm{tr,\ qtz}}$. 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 ~14 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 ºC) or 60 s (above 700 ºC) with two accumulations per spectrum.

The bulk density of H_2O in the sample chamber for the observed $T_{\mathrm{tr,\ qtz}}$ 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 ºC) and NaCl (800.5 ºC), and the uncertainties in T measurements are ±1.5 ºC. The associated pressures at T_{h} (P_{h}) and $T_{\mathrm{tr,\ qtz}}$ ($P_{\mathrm{tr,\ qtz}}$) 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 ($T_{\mathrm{tr,\ qtz}}$, $P_{\mathrm{tr,\ qtz}}$) 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 ºC using HDAC and Raman spectroscopy.

The α-β quartz phase boundary obtained in this study can be represented by: ($P_{\mathrm{tr,\ qtz}}$) (±8.8 MPa) = 0.0015 $(T_{\mathrm{tr,\ qtz}})^2$ + 1.8268 ($T_{\mathrm{tr,\ qtz}}$) −1544.5, where ($T_{\mathrm{tr,\ qtz}}$) is between 574 and 781 ºC; 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