

Effect of pressure on water solubility in aluminous bridgmanite

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We have conducted a sequence of high pressure experiments to study water solubility in aluminous bridgmanite as a function of pressure at 1900°C. The experimental high pressures were generated using multi-anvil presses at Bayerisches Geoinstitut (BGI) for pressures up to 28 GPa and at Geodynamics Research Center (GRC) for pressures above 30GPa. The starting material for these experiments was a mixture of oxides ( $Mg(OH)_2$ ,  $Al_2O_3$  and  $SiO_2$ ) with equivalent of about 5 mol % of  $Al_2O_3$  and 15 wt % of  $H_2O$ . The structure and composition of the bridgmanite sample after high P/T syntheses were examined using x-ray diffraction (XRD) and electron probe microanalysis (EPMA). Water concentration in the sample was measured using secondary ion mass spectroscopy (SIMS) and Fourier transform infrared spectroscopy (FTIR). The measurements yield that the aluminous bridgmanite with about 2 wt% of  $Al_2O_3$  may take as much as 0.13 wt % of  $H_2O$  at the P/T condition of the top of the Earth's lower mantle and this solubility increases significantly with pressure. At the bottom of Earth's lower mantle, bridgmanite may take nearly a couple of weight percent of water according to simple extrapolation of the experiment result, indicating that the capacity of water reservoir of the lower mantle can be as large as a few to ten oceans of water.

In-situ X-ray diffraction studies of hydrous phases up to ~50 GPa

In-situ X-ray diffraction studies of hydrous phases up to ~50 GPa

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Recent experimental and theoretical studies suggest the high-pressure forms of hydrous minerals, phase H and delta-AlOOH, play important roles in transportation of water into the deep Earth's interior via subduction of oceanic slabs. Phase H forms a solid solution with delta-AlOOH by the substitutions of  $Mg^{2+} + Si^{4+} \leftrightarrow 2Al^{3+}$  because of their similar crystal structure and volume. Since epsilon-FeOOH is also isostructural to  $MgSiO_4H_2$  phase H and delta-AlOOH, delta-AlOOH likely form partial solid solutions with epsilon-FeOOH. However, experimental study shows that FeOOH component in delta-AlOOH is limited (~20 mol%) because of the much larger unit-cell volume of epsilon-FeOOH, in contrast to the complete solid solution between phase H and delta-AlOOH. On the other hand, spin transition of Fe in epsilon-FeOOH at ~50 GPa likely reduce its volume significantly, which may cause the compositional change of hydrous phase in the lower mantle. Thus, the unit-cell volume of hydrous phases at high pressures is important to understand the chemical composition of hydrous phase in the mantle.

Here, we report new experimental results on the X-ray diffraction studies of Phase H, delta-AlOOH, epsilon-FeOOH, and their solid solutions up to 50 GPa. In-situ X-ray diffraction measurements were performed using a multianvil apparatus (SPEED-Mk.II) at BL04B1, SPring-8. The unit-cell volume of  $MgSiO_4H_2$  phase H is ~3% larger than those of pure delta-AlOOH and ~15% smaller than those of epsilon-FeOOH up to 50 GPa. However, the large volume reduction of epsilon FeOOH due to the spin transition of Fe was observed above ~50 GPa, resulting in the similar unit-cell volume with delta-AlOOH and phase H. Based on these experimental results, the chemical composition of hydrous phase in the lower mantle will be discussed.

キーワード : phase H、 mantle、 water

Keywords: phase H, mantle, water

## 下部マントルにおける含水高圧相の生成条件

## Reaction of MORB and water under the lower mantle

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High-pressure hydrous phases are considered to play important role for possible water reservoir in the Earth. The reaction between water and down welling slab into the lower mantle region containing mid-ocean ridge basalt (MORB) and surrounding minerals are important to understand water cycle in the mantle. Among the known hydrous minerals, Phase H has a deepest stability field up to ~60GPa in the MgO-SiO<sub>2</sub>-H<sub>2</sub>O system (Ohtani et al., 2014) and ~128GPa in the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O (MASH) system (Ohira et al., 2014), suggesting possible transportation of water into the deep Earth.

Here we report the results of the direct reaction of the MORB + H<sub>2</sub>O system under high-pressure and high-temperature to investigate the effect of iron and aluminum. We carried out in-situ X-ray diffraction experiments at High Energy Accelerator Research Organization (KEK), Photon factory (PF-AR). High pressure and temperature experiments were conducted using laser-heated diamond anvil cell installed at the station NE1A. Starting materials of glass MORB powder and pure water were confined in rhenium gasket. The pressure was measured using the equation of state of ice VII (Frank et al., 2013). The double-sided heating with Nd:YAG laser to heat, the reaction temperature was estimated from spectroradiometry of the high temperature portion of the sample. X-ray diffraction measurements to identify phases were performed using monochromatic x-ray with about 30keV and imaging plate detector at each step of elevated temperature to about 1000K. We identified the crystalline phases and the reaction products up to 35GPa under laser-heating condition.

Ca-Perovskite, Stishovite and Phase D were observed as the reaction product in all runs. The results indicate an expanding of stability field to high pressure in Phase D than that of MgO-SiO<sub>2</sub>-H<sub>2</sub>O system, we will present further results of SEM-EDS analysis of the recovery sample.

キーワード：MORB、DAC、水

Keywords: MORB, DAC, water

## マントル遷移層における海洋地殻中の含水D相の安定領域

## Stability field of Phase D in hydrous basaltic system at the mantle transition zone

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The distribution of water in the mantle and its effects on mantle dynamics are significant to understand the evolution of the Earth. It's believed that the water is transported from the surface into deep mantle via a variety of hydrous minerals in the subducting oceanic slabs (Ohtani, 2015). However, stability of hydrous mineral(s) in basaltic system at the pressure temperature conditions equivalent to cold slabs in the transition zone, remains unclear.

High-pressure and high-temperature experiments were conducted in a hydrous basalt similar to primitive MORB composition (JB-2 basalt plus brucite, water content=3.5wt.%) at 17-25 GPa, and 800-1200°C using multi-anvil apparatus (SAKURA in Magma Factory) at Tokyo Institute of Technology. We used Au/Pt double capsules as sample containers. In runs below 20 GPa, the sample was loaded into an Au inner capsule and the oxygen fugacity was buffered at ~NNO by NiO + Ni + Ni(OH)<sub>2</sub> powder, which stuffed in the space between Pt outer capsule and Au inner capsule. Simple Au capsule was used in higher pressure runs. The run products were analyzed by FE-EPMA (JEOL-JXA8530F, ELSI Tokyo Institute of Technology). The water contents in hydrous phases were estimated from total deficits in FE-EPMA analyses.

The phase assemblages of the run products include majorite, stishovite, Ca-Ti perovskite, hollandite, silicate melts and hydrous phase(s). The hydrous phase is Fe-Ti hydroxide at pressures lower than 18GPa or Al-bearing phase D at pressures higher than 18GPa. These two hydrous phases coexisted in one experiment (18GPa, 900°C). Our results show that the phase D (containing 46-51 wt.% SiO<sub>2</sub>, 19.1-20.6 wt.% MgO, 7.3-16.0 wt.% Al<sub>2</sub>O<sub>3</sub>, 3.8-5.1 wt.% FeO, 11-14 wt.% H<sub>2</sub>O) is stable in wide pressure ranges of the mantle transition zone at pressures of 18-20 GPa and temperatures of 800-1000°C. In our experiments, the Al<sub>2</sub>O<sub>3</sub> content and (Fe+Mg)/Si ratio of phase D increase with increasing pressure while MgO and FeO content remains constant, relatively. It is important to note that wadsleyite coexisting with Al-bearing phase D seemed to be nearly anhydrous in our experiment suggesting the importance of the subducting basaltic crust as a water carrier in mantle transition zone.

Consequently, we propose that the phase D is one of major water reservoir in cold subducting oceanic crust at the mantle transition zone. Moreover, if the subducting slabs stagnate at the bottom of the transition zone and warmed up, the water would be released from phase D in the subducting crusts, which may be the dominant way to hydrate the transition zone or to cause magmatism in back arc hot spots. Experiments at 25 GPa and 1000°C show coexisting bridgmanite, stishovite, Ca-perovskite, ferropericlasite and very Al-rich phase D indicating that subducting cold MORB crust could be the major carrier of water from transition layer to the lower mantle by the Al-bearing phase D.

キーワード：地球深部への水輸送、沈み込む海洋地殻、含水D相

Keywords: water transportation to deep Earth, subducting oceanic crust, phase D

## マントル遷移層におけるTopaz-OH IIの安定領域

The stability of Topaz-OH II in the mantle transition zone

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Topaz-OH is one of the hydrous phases which would exist in the sedimentary layer of subducting slab. Kanzaki (2010) showed that Topaz-OH transforms to a high-pressure phase, Topaz-OH II, which was reported to be stable at least 13-14 GPa and 1300-1500 °C. However, the stable conditions of Topaz-OH II are not determined well. Here, we report on the results of high-pressure and high-temperature experiments on the stability field of Topaz-OH II.

The starting material was prepared in the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system with the bulk composition of 4.27 wt.% MgO, 52.95 wt.% Al<sub>2</sub>O<sub>3</sub>, 28.47 wt.% SiO<sub>2</sub> and 14.30 wt.% H<sub>2</sub>O. Experiments were carried out using a 1000-ton Kawai type multi-anvil press at Tohoku University. Semisintered zirconia and platinum were used as pressure medium and sample container, respectively. The pressure was calibrated by the β-γ phase boundary of Mg<sub>2</sub>SiO<sub>4</sub>. In order to identify synthesized phases, X-ray diffraction measurements and Micro-Raman spectroscopy measurements were carried out at the Photon Factory in KEK, Tsukuba, Japan and at Tohoku University, respectively. Compositions of the recovered samples were determined using an electron probe microanalyzer (EPMA) at Tohoku University.

We found that hydrous phases of δ-AlOOH and phase egg were stable in the pressure range of 18-20 GPa and the temperature range of 1000-1300 °C. Topaz-OH II was stable at 18 GPa and 1400 °C, which is higher-pressure and -temperature condition than that reported previously. The composition of Topaz-OH II was 2.23(7) wt.% MgO, 55.24(13) wt.% Al<sub>2</sub>O<sub>3</sub> and 31.46(21) wt.% SiO<sub>2</sub>, (88.93(23) wt.% total) and its Al / Si ratio was 2.50(4). The lattice parameters of Topaz-OH II at ambient condition was a= 4.719(9) Å, b= 8.922(23) Å, c= 2.777(6) Å, and V<sub>0</sub>=116.7(5) Å<sup>3</sup>, which is consistent with the parameters reported by Kanzaki (2010).

Our results indicate that Topaz-OH II would be a potential candidate of the water carrier at the middle of the mantle transitions zone.

キーワード：Topaz、放射光X線回折、マントル遷移層、沈み込むスラブ

Keywords: Topaz, synchrotron X-ray diffraction, mantle transition zone, subducting slab

含水カンラン岩中のPhase H  $\delta$ -Al<sub>100</sub>H固溶体の安定性と地球マントルにおける水循環

Stability of Phase H  $\delta$ -Al<sub>100</sub>H solid solution in a hydrous peridotite and water cycle in the Earth's mantle.

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A number of high pressure and temperature (high  $P - T$ ) experiments have been showing that various hydrous minerals can survive in a broad range of  $P - T$  conditions such as the conditions of slabs subducted in the deep mantle. A subducting slab consists of three rock layers; peridotite, oceanic crust (MORB) and sediment. A hydrous peridotite layer includes various dense hydrous magnesium silicates (DHMS), which can carry water as OH<sup>-</sup> or proton in their structures but all of them decompose at the uppermost lower mantle (e.g., Ohtani, 2005). However, the new phase called Phase H (MgSiO<sub>4</sub>H<sub>2</sub>; space group,  $Pn\bar{m}$  (Bindi et al., 2014)) was predicted to be stable at pressures up to 50 GPa and was synthesized by high  $P - T$  experiment (Tsuchiya, 2013; Nishi et al., 2014), suggesting that water stored in Phase H formed in a slab can be transported into the middle region of the lower mantle.

The stability field of Phase H depends strongly on Al content (Nishi et al., 2014, 2015; Ohira et al., 2014; Walter et al., 2015). Ohira et al. (2014) conducted *in-situ* high  $P - T$  experiments using a laser-heated diamond anvil cell (LHDAC) in MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system simplified MORB composition. Their experiments indicated that Phase H  $\delta$ -Al<sub>100</sub>H solid solution coexisted with Al-poor bridgmanite, and water stored in this solid solution may be transported to the lowermost mantle because of the broad stability field of  $\delta$ -Al<sub>100</sub>H (space group,  $Pn\bar{m}$  above 8.2 GPa (Kuribayashi et al., 2014)) extending from the transition zone to the core-mantle boundary (CMB) conditions (Sano et al., 2008).

However, the possible existence of H  $\delta$ -solid solution in realistic complex systems such as hydrous peridotite and MORB compositions has been unknown.

Here, we demonstrate the phase relations in hydrous peridotite system obtained from *in-situ* high  $P - T$  synchrotron X-ray diffraction measurements at BL10XU, SPring-8.

We used the gel-sample having the same composition as hydrous peridotite (bulk water content was 1.0 wt.%). LHDAC and YAG (Nd) or fiber laser were used for generation of high  $P - T$  conditions. In the first run, we only used the gel-sample without laser absorbers and pressure mediums. In the second run, the sample plate was sandwiched between Ir foils, and NaCl plates were put on the outer sides of Ir foils. *In situ* X-ray diffractions were measured at the pressure and temperature ranges of 69-84 GPa and 1910-2260 K in the first run and of 49-53 GPa and 1550-2210 K in the second run. Above 69 GPa, the coexistence of major anhydrous minerals in the lower mantle, bridgmanite (Brg), ferropericlasite (Fp) and CaSiO<sub>3</sub>-perovskite (Ca-Pv), was observed, while none of hydrous phases such as H  $\delta$ -solid solution existed. On the other hand, the diffraction patterns of H  $\delta$ -solid solution together with those of Brg, Fp and Ca-Pv were observed at pressures between 49 and 53 GPa, suggesting that the stability field of H  $\delta$ -solid solution formed in a hydrous peridotite only extends up to the pressure conditions between 53 and 69 GPa. This decomposition boundary was consistent with the stability of pure phase H (Tsuchiya, 2013; Ohtani et al., 2014), implying that

the composition of H- $\delta$  solid solution formed in a hydrous peridotite may be very close to pure-MgSiO<sub>4</sub>H<sub>2</sub> Phase H.

Our results suggest the difference of water transport mechanisms between a peridotite layer and a MORB layer in a hydrous slab subducted in the lower mantle. Al-poor H- $\delta$  solid solution formed in a hydrous peridotite layer may decompose and release H<sub>2</sub>O-rich liquid at the middle of the lower mantle, while Al-rich H- $\delta$  solid solution formed in a hydrous MORB layer can be transported to the lowermost mantle.

キーワード：含水鉱物、水循環、その場X線回折、Phase H、 $\delta$ -AlOOH

Keywords: hydrous minerals, water cycle, in-situ XRD, Phase H,  $\delta$ -AlOOH



## 鉄、アルミニウム含有ブリッジマナイトの生成による含水D相の分解

Decomposition of hydrous phase D by the formation of Fe-bearing aluminous bridgmanite

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It has been considered that a certain amount of water is transported as hydrous minerals into the mantle through subduction of slab. Recent discovery of hydrous ringwoodite inclusion in a diamond suggests that the mantle transition zone is hydrous at least locally (Pearson et al. 2014). Next open question is whether the lower mantle can accommodate water or not. Although the major constituent minerals can host significant amounts of water in the upper mantle, most of the lower mantle minerals (e.g. bridgmanite (Brm) and ferropericlasite (fPc)) can incorporate only a limited amounts of water. Therefore, if water is transported into the lower mantle, water must be hosted by dense hydrous minerals (DHMs) such as hydrous phase D. However, it is not clear whether DHMs can exist in the lower mantle because temperature of slab subducted into the lower mantle is not constrained well. Brm contains significant amounts of Fe<sup>3+</sup> (Fe<sup>3+</sup>/ΣFe > 0.1) even in coexistence with metallic iron (Frost et al. 2004). The amounts of Fe<sup>3+</sup> increase with increasing Al<sub>2</sub>O<sub>3</sub> content in Brm, and the Fe<sup>3+</sup>/ΣFe ratio exceeds 0.5 in the lower-mantle Brm (Frost et al. 2004; Frost and McCammon, 2008). Since the Fe<sup>3+</sup>/ΣFe ratios are only 0.01-0.03 and 0.10-0.14 in the upper-mantle peridotite and MORB, the formation of Brm would extract oxygen from other minerals by the deposition of Fe metal. In other words, Brm should work as a reducing agent against other minerals. Therefore, we expect the breakdown of DHMs by reduction of OH to H<sub>2</sub> through the Brm formation. On the basis of this background, we conducted the following experiment using a Kawai-type multianvil press. A starting materials were used sintered Al-free and aluminous phase D pre-synthesized at 27 GPa and 1100 K, a natural olivine single crystal (Olv) and pyroxene aggregates with bulk composition of pyrolite minus fPc (Pyr-fPc) and (Mg<sub>0.9</sub>Fe<sub>0.1</sub>)(Si<sub>0.9</sub>Al<sub>0.1</sub>)O<sub>3</sub> (FeAl-En) synthesized at 1300 K in a controlled oxygen fugacity (PO<sub>2</sub>≈IW) and ambient pressure. Pyroxene samples were packed in Mo capsule and sintered at 2 GPa and 1500 K. Sintered phase D was directly attached with Olv, sintered Pyr-fPc or FeAl-En in Au sample capsule. The samples were pressurized to 27 GPa and heated at 1100 K for 1 or 10 hours. Analyses of recovered samples were made with FE-SEM and ATEM.

No reaction between Al-free phase D and Brm + fPc aggregate formed from Olv was found in the SEM observation. The existence of 2-4 μm thick SiO<sub>2</sub>-rich fine-grained layers were discovered on the boundary between Al-free / aluminous phase D and Brm formed from Pyr-fPc or FeAl-En. TEM observation indicated amorphous phases with Brm composition in fine SiO<sub>2</sub> stishovite. These observations strongly indicate that the decomposition of phase D accompanied by the formation of Fe-bearing aluminous Brm. The present result suggests that, although water can be transported into the top of the lower mantle due to the formation of phase D through subduction of slab, phase D will decompose by reduction at the depth to 720 km. The produced H<sub>2</sub> should come back to the upper mantle. Thus, water cannot be transported through slab subduction to the majority of the lower mantle.

キーワード：含水D相、下部マントル、ブリッジマナイト、沈み込むスラブ、水輸送、3価鉄

Keywords: hydrous phase D, lower mantle, bridgmanite, subducting slab, water transportation, ferric iron



## Alに富む含水ブリッジマナイトの圧縮特性

## Compressibility of Al-bearing hydrous bridgmanite

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Water is the most important volatile component on the Earth, because it has significant influences on the chemical and physical properties of mantle minerals (e.g., melting temperature, electrical conductivity, and so on). The nominally anhydrous minerals (NAMs) can contain small amount of water. In particular, wadsleyite and ringwoodite which are the major constituent minerals in the mantle transition zone can contain ~2-3 wt% water (e.g., Inoue et al., 1995; Kohlstedt et al., 1996). Recently, hydrous ringwoodite contained ~1.5 wt% water was discovered by Pearson et al. (2014) as inclusion in ultra deep diamond. This observation implies that the mantle transition zone contains some water at least locally. On the other hand, water solubility of bridgmanite which is the most abundant mineral in the lower mantle, is a matter of debate (e.g., Bolfan-Casanova et al., 2000, 2003; Murakami et al., 2002; Litasov et al., 2003). In this situation, Al-bearing hydrous bridgmanite contained ~0.8 wt % water with 4.7 wt% Al<sub>2</sub>O<sub>3</sub> was synthesized by Inoue et al., (in prep). The dominant substitution mechanism was suggested to be Si<sup>4+</sup> → Al<sup>3+</sup> + H<sup>+</sup>. However, the physical properties of Al-bearing hydrous bridgmanite under high pressure are unknown. In this report, the compressibility of Al-bearing bridgmanite is tried to determine.

In situ P-V-T experiments of Al-bearing hydrous bridgmanite were conducted up to 50 GPa and 900 or 1500 K, using multi-anvil high pressure apparatus (SPEED-Mk.II) with sintered diamond 2<sup>nd</sup> stage anvil at SPring-8 BL04B1. Al-bearing hydrous bridgmanite was softer than MgSiO<sub>3</sub> bridgmanite below 27 GPa. Then with increasing pressure up to 40 GPa from 27 GPa, The drastic softening was observed. Above 40 GPa, it become the steady state as below 27 GPa. This phenomenon looked like the symmetrization of hydrogen bond in the case of iceVII - iceX transformation (Sugimura et al., 2008). In this presentation, we will report the compressibility of Al-bearing hydrous bridgmanite in detail.

キーワード：下部マントル、ブリッジマナイト、水、圧縮特性

Keywords: lower mantle, bridgmanite, water, compressibility

Water solution mechanisms in magmas: insights from *ex situ* piston-cylinder and *in situ* hydrothermal diamond anvil cell experiments.

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The global cycle of water on Earth involves different reservoirs in the solid Earth (Earth's crust, mantle, and potentially core) and its surface (atmo-, hydro- and biospheres). Exchanges of water between them occur in specific geological settings, such as subduction zones, mid-ocean ridges or intraplate volcanisms. Each of those settings implies magmatic activity, in which silicate melts play a determining role as they carry water from depth to surface. Furthermore, magmas rheological and thermodynamic properties are strongly affected by dissolved water that, hence, influences transfers of matter and heat in the crust and in superficial volcanic systems. However, the mechanisms of water incorporation in silicate melts are still not well understood, and, in particular, their dependence to melt chemistry, temperature and pressure remain to be fully assessed.

To address those issues, we investigated alkali (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>) silicate, and sodium and calcium aluminosilicate melts containing various quantities of dissolved water. The melts were hydrated with a given amount of water in piston-cylinder apparatus, and studied *ex situ* after quenching using <sup>1</sup>H, <sup>2</sup>H and <sup>29</sup>Si Nuclear Magnetic Resonance, Infrared and Raman spectroscopy. Furthermore, using Raman spectroscopy, we probed *in situ* melts at equilibrium with aqueous fluids in hydrothermal diamond anvil cells (HDACs). While the *ex situ* data allow us to observe the melt structure and water environment at conditions corresponding to the glass transition, *in situ* data allow us to gather knowledge at higher P-T conditions, relevant to the Earth crust and upper mantle.

Results show that the environment of water in quenched melts is deeply affected by the melt composition. For instance, in silicate melts, increasing alkali ionic radius promotes water reaction with the silicate network, while the protons reside in environments with smaller volumes. The comparison of *ex situ* data for two sodium and calcium alumino-silicate melts further substantiates this dependence to melt composition, but also suggest that aluminum might help stabilizing the H<sup>+</sup> local environment. At temperatures much higher than the glass transition, Raman data from HDAC experiments show that the O-H stretching vibration, and hence the O-O distances around H<sup>+</sup>, becomes more similar between the sodium and calcium alumino-silicate melts.

Deconvolution and peak fitting analysis of the Raman peaks assigned to T-O stretching in TO<sub>4</sub> tetrahedral units in the glasses and melts further show a strong depolymerisation of the melts, which depends on melt temperature and initial composition. This complex environment of water in hydrous silicate melts induces non-linear variations of their transport properties as a function of water content, major element composition and temperature. Such knowledge can be integrated in models of magma mobility in the Earth crust, and of possible extrusive mechanisms at the Earth surface.

Keywords: water, magma, silicate melt, diamond anvil cell, NMR spectroscopy, Raman spectroscopy