Japan Geoscience Union Meeting 2014
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SMP06-01 会場:411 時間:4 月 28 日 14:15-14:30

MgSiO2(OH)2-AlOOH 系における含水 H 相および δ 相の固溶体による下部マントル底部への水素の輸送
Hydrogen transport into the bottom of the lower mantle by phase H- phase delta solid solution MgSiO2(OH)2-AlOOH

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Water circulation in a global scale is a key for understanding dynamics and evolution of the Earth. Subducting slabs transport water into the Earth's deep interior. There are many studies on the stability of hydrous phases under the deep mantle conditions, and several hydrous minerals such as phase D and superhydrous phase B have been reported to be stable to the top of the lower mantle. It has been reported that hydrous phase δ-AlOOH is stable up to the bottom of the lower mantle (Ohtani et al., 2005; Sano et al., 2008). Tsuchiya (2013) theoretically predicted that Phase H, $MgSiO_2(OH)_2$, which is the iso-structure with δ-AlOOH, is stable from 45 GPa to 55 GPa. This phase was experimentally confirmed at around 50 GPa (Nishi et al., 2014). Here, we present our recent results on synthesis experiments of hydrous phase H and a solid solution of phase H and phase δ up to the base of the lower mantle along the normal mantle geotherm. The high pressure and high temperature in situ X-ray diffraction experiments were performed by using a double-sided laser heated diamond anvil cell at BL10XU, SPring-8. We observed that the stability field of this new candidate of water reservoir, hydrous phase H, under the lower mantle conditions up to 75 GPa and 2000 K in the MgO-SiO_2-H_2O system, although the previous studies claimed that phase H is broken down at pressures above 55 GPa. Thus, hydrous phase H is a host phase of water in the lower mantle at least up to the depth of 2000 km along both slab and normal mantle geotherms. Our experiments also revealed that the solid solution of phase H and phase δ, AlOOH-$MgSiO_2(OH)_2$, containing 15 mol % of $MgSiO_2(OH)_2$ can coexist with Mg-perovskite and/or Mg-post perovskite up to 135 GPa and 2000 K. If this hydrous phase contacts with the metallic outer core, hydrogen could be dissolved into the core by forming iron hydride, FeH (Terasaki et al., 2012).

キーワード: 水素, 含水 H 相, 含水デルタ相, MgSiO2(OH)2, AlOOH, 下部マントル
Keywords: hydrogen, hydrous phase H, hydrous phase delta, MgSiO2(OH)2, AlOOH, lower mantle

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上部マントル条件において水素が enstatite の相関係に与える影響
Influence of H2 fluid on the stability of MgSiO3 enstatite in the upper mantle condition

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C-O-H 流体はケイ酸塩鉱物の化学組成や融点に大きな影響を与えることから、地球深部でのメルトの生成や化学進化を明らかにする上で重要な物質である。還元的なマントル深部で C-O-H 流体は H_2O だけでなく、H_2 として存在する可能性がある。本研究では、$MgSiO_3$-H_2 系において H_2 流体がケイ酸塩鉱物の相関係に与える影響を明らかにすることを目的として、レーザー加熱ダイヤモンドアンビルセルを用いた高温高圧実験を行った。出発物質には enstatite ($MgSiO_3$) と水素を用いた。加熱、急後の試料の XRD, Raman 測定、回収試料の SEM, TEM を用いた組織観察から高温高圧下で H_2 流体と共存する相の検討を行った。

3.1-13.8 GPa, 1500-2000 K での加熱後の XRD から、enstatite が分解し forsterite と periclase、coesite および sthishovite が観察された。加熱後の Raman スペクトルから水素の分子振動が観察されたことから、この分解反応は水素が共存する条件下で起きたことを示している。enstatite のみの場合には、本研究の温度圧力条件での分解反応は観察されないことから、この反応は水素の影響により起こったと考えられる。回収試料中の coesite や sthishovite は、高温高圧下で水素流体中に溶解した後、再結晶化した組織を示していた。一方で forsterite や periclase は元の enstatite の外形を保ったまま結晶化していることから、高温下で水素と共存する条件で結晶化したと考えられる。本研究の結果から、$MgSiO_3$-H_2 系では、水素流体に SiO_2 成分が溶けて enstatite 相が分解し、periclase+ forsterite 相が生成する事が示された。

キーワード: エンスタタイト, 水素, 上部マントル, レーザー加熱 DAC
Keywords: enstatite, H2 fluid, upper mantle, laser heated diamond anvil cell

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高温高圧下における緑泥石の脱水分解反応境界とその状態方程式
Dehydration boundary and the EoS of chlorite under high pressure and temperature

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1. はじめに
スラブ中の様々な含水鉱物は沈み込みに伴い地球内部へと運搬され、各々の温度圧力条件で分解反応を生じる。含水鉱物が脱水分解反応することで発生する流体は島弧マグマの成因に影響し、また生成される含水相は水をより地球内部へと運搬すると考えられる。

含水ペリドタイト中の主要な含水鉱物の一つとして、蛇紋石（serpentine; $Mg_6Si_4O_{10}(OH)_8$）が挙げられる。この鉱物はマントル中の主要な元素で構成されており、これまで数多くの研究が報告されている。一方実際のマントル中には Al_2O_3 成分がおよそ 4 wt%含まれており、蛇紋石の化学組成に Al を加えた緑泥石（chlorite; $(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$）の存在も重要であると考えられる。しかしながら、これまでの緑泥石単体の脱水分解反応境界は 5 GPa 以下でしか報告されておらず、それ以上の圧力では報告がない。さらに、緑泥石の状態方程式に関する過去の報告の多くは室温・高圧条件のもので、高温・高圧下での報告はわずかにしか存在しない。これらのことを踏まえ、本研究では X 線その場観察を用いて高温高圧下における緑泥石の脱水分解反応境界とその状態方程式の決定を行った。

2. 実験方法
高温高圧下における X 線その場観察実験は高エネルギー加速器研究機構、PF?AR、NE5C 設置の MAX80 を用いて行った。出発物質には天然の緑泥石を用い、反応実験では分解後の流体の放出を防ぐカプセル材として単結晶ダイヤモンドと金のキャップを使用した。緑泥石の分解反応境界は X 線その場観察時分割測定実験によって決定し、得られた回折線と回収試料の組織観察より生成相の同定を行った。状態方程式を求める実験（P-V-T 実験）では同施設の高圧発生装置を用い、試料への差応力の影響を防ぐため試料は NaCl スリーブに封入した。

3. 結果＆考察
緑泥石は 3 GPa 付近では 800 ℃付近まで安定に存在し、4 GPa 以上で脱水分解反応境界は負の dT/dP 勾配となった。7 GPa 以下の圧力下ではフォルステライト、パイロープ、フルイドへの分解が確認された。一方 7 GPa 以上では Mg サーササイトと未知相に分解した。この反応境界は 450 ℃付近に位置し dT/dP=~0 となり、緑泥石の相平衡境界を超えた領域で確認できるカイネティック境界であると考えられる。これまでの相平衡実験では数十時間保持する実験が一般的であったが、本研究結果より 500 ℃以上の条件下では緑泥石は比較的短時間（１時間以内）で平衡状態となるがそれ以下の温度では極めて反応速度が遅くなると考えられる。今回の結果から緑泥石を伴う沈み込むスラブの挙動を考えると、暖かいスラブの場合緑泥石は無水鉱物の組み合わせへと分解するため、それ以深へと水を運搬することができない。しかし、7 GPa 付近で 500 ℃以下の冷たいスラブの場合、緑泥石は Mg サーササイトを含む鉱物組み合わせへと分解し、さらに地球深部へ水を運搬することが可能である。また更に高温高圧力領域では Mg サーササイトは Phase A を含む鉱物組み合わせへと分解することが報告されており、緑泥石は地球深部へと水を運搬する重要な鉱物の一つであると考えられる。発表では状態方程式の結果も報告する。

キーワード: 緑泥石, 含水相, 沈み込むスラブ, 脱水分解反応, 状態方程式, 放射光Ｘ線その場観察
Keywords: chlorite, hydrous phase, subducting slab, dehydration, equation of state, synchrotron X-ray in-situ experiment

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Composition and nature of melts, supercritical fluids and liquids formed by dehydration of subducted oceanic lithosphere

Composition and nature of melts, supercritical fluids and liquids formed by dehydration of subducted oceanic lithosphere

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At crustal pressures, phase relations in natural rock-H_2O systems involve low density aqueous fluids and/or high density hydrous melts. The wide miscibility gap between these two liquid phases leads to a dichotomy of mobile phases with quite distinct major element solubilities and trace element geochemical signatures. With increasing pressure, the fluid-melt miscibility gap closes until the crest of the miscibility gap intersects the fluid-saturated solidus, leaving a single supercritical liquid that has chemical and physical properties continuously evolving with temperature. The question is if the endpoint of the solidus is relevant for natural rock compositions. We have experimentally determined these endpoints in a variety of systems ranging from MOR basalt, to pelitic systems and to the simplified mantle systems MgO-SiO_2-H_2O (MSH) using different experimental techniques in the P-T range from 2.0 GPa/700 ℃ to 13.5 GPa/1300 ℃. Supercriticality occurs over a wide range of P-T conditions ranging from 1 GPa/1100 ℃ for the SiO_2-H_2O system to 12-13 GPa in the SiO_2-poor part of the MSH system.

In the MORB system, major element compositions of the fluid/melt phase evolve from peralkaline, H_2O-rich, granite-like compositions to metaluminous, andesitic to basaltic compositions with increasing temperature. The endpoint of the fluid-saturated solidus occurs around 5 GPa and 1000 ℃; thus, the dichotomy of fluid versus melt ceases to exist in the oceanic crust. Similar conditions were determined for pelitic to greywacke systems representing deep-sea sediments. In the mantle-like system MSH critical endpoints for fluid/melt solvi along the solidus are located between 12 and 13.5 GPa at 1100 ℃. Melt compositions buffered by olivine and opx remain enstatite - olivine normative below the critical endpoint; in contrast, fluids below the endpoint become progressively enriched in MgO and are silica undersaturated (Mg/Si ratios >2) at pressures exceeding 6 GPa. Supercritical liquids coexisting with forsterite and enstatite or dense hydrous silicates are strongly silica undersaturated. The P-T evolution of fluids and liquids in the MSH system allows drawing conclusions regarding the effects of Mg-Si metasomatism in the overlying mantle wedge of a subduction system.

The consequences of the various nature of hydrous mobile phases emanating from hydrated subducted oceanic lithosphere were investigated in the MORB system by determining trace element partitioning between cpx, gar, amphibole, epidote, rutile, titanite, staurolite and phengite and liquid, the latter either being an aqueous fluid, a hydrous melt, or a supercritical liquid. Hydrous melts and supercritical liquids have almost identical trace element pattern. Thus, recycling rates of these elements are not indicative of melting, and in the fast and steep circum-pacific subduction zones, they most likely testify for production of a mobile phase from the subducting crust in the supercritical liquid regime (i.e. at pressure in excess of 4-5 GPa).

Modeling of trace element signatures of fluids, melts and supercritical liquids generated in or passing through eclogitic crustal lithologies during their ascent into the overlying mantle wedge indicate that (1) the mode of fluid advection - porous flow or - focused fluid flow - produces rather contrasting trace element signatures and (2) the presence or absence of accessory phases such as epidote, staurolite, rutile/titanite controls to a large extent the concentrations of high field strength, light REE elements and Th, U. Thus, inversion of geochemical compositions of igneous products in arc settings used to constrain the nature and composition of metasomatizing agents released from the subducted oceanic lithosphere is not straightforward and it is unlikely that an unequivocal solution is obtained.

キーワード: hydrous fluid, supercritical liquid, trace element partitioning, fluid metasomatism, high presssure experiments, subducted oceanic lithosphere
Keywords: hydrous fluid, supercritical liquid, trace element partitioning, fluid metasomatism, high presssure experiments, subducted oceanic lithosphere

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含水かんらん岩の断熱融解における微量元素の挙動：HAMMS1 モデル
Trace element mass balance in hydrous adiabatic mantle melting: The HAMMS1 model

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A numerical mass balance calculation model for the adiabatic melting of a hydrous metasomatized peridotite source was programmed in order to simulate trace element compositions of mid ocean ridge basalt, back arc basin basalt, ocean island basalt, and large igneous province basalt. The Excel spreadsheet-based calculator, Hydrous Adiabatic Mantle Melting Simulator ver.1 (HAMMS1) uses: (1) a thermodynamic adiabatic melting model of mantle peridotite; with (2) experimentally parameterized melting relationships in terms of pressure, temperature, water content, and degree of partial melting. The trace element composition of the model basalt is calculated from the accumulated incremental melts within adiabatic melting, with consideration of source mantle depletion. The mineralogic mode in the mantle in adiabat is calculated using experimental parameterization, and is incorporated into the program. Partition coefficients of the residual mantle minerals are from lattice strain model based parameterization tested by the latest compilations of experimental results. The parameters that control the trace element composition in the model are: (1) mantle potential temperature, (2) water content in the source mantle, (3) depth of termination of adiabatic melting, and (4) source mantle depletion. It is possible to obtain the above controlling parameters by using Monte Carlo fitting calculations and comparing the calculated basalt compositions with primary basalt compositions. Additionally, HAMMS1 compares those melting parameters with its major element model. HAMMS1 provides a unique estimate of the source conditions of basalt genesis using an incompatible trace element mass balance.

キーワード: かんらん岩, 水, 断熱融解, 微量元素, フォワードモデル
Keywords: peridotite, water, adiabatic melting, trace element, forward model

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Very Large Intramolecular D-H Partitioning in Hydrated Silicate Melts Synthesized at Upper Mantle P and T

Very Large Intramolecular D-H Partitioning in Hydrated Silicate Melts Synthesized at Upper Mantle P and T

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Hydrogen isotope fractionation during magnetic processes is key to understanding the deep Earth hydrological cycle and may place constraints on the origin of Earth ' s oceans. It is well established that the D/H content of water in hydrated nominally anhydrous mantle minerals is systematically lower (<-100 ‰) than the standard mean ocean water (SMOW, D/H = 1.5576 x 10^{-4}, defined as 0 ‰). Experiments have revealed significant hydrogen isotope partitioning between melts and fluids or vapors at magmatic temperatures. The origin of such fractionation, given the high temperatures of magmatic processes, is not likely due to classical isotope effects as described by bond energies via statistical mechanics.

It is well known that water has a very high affinity for silicate melts, it both dissolves in the melt as molecular water and hydrolyzes Si-O-Si linkages forming Si-OH. Whereas the molecular forms of water in melts are limited to H_2O and OH, the variety of environments available for water to reside in the melt structure is surprizing large. In order to study water in silicate melts one is restricted to molecular spectroscopy, e.g. Raman spectroscopy in the mid infrared regime, in windowed high pressure devices, e.g. the hydrothermal diamond anvil cell. Alternatively, one can study melts quenched to glass, where the structure of the glass corresponds to the structure of the melt at the glass transition temperature. The advantage of glasses is that one can use Solid State Nuclear Magnetic Resonance (NMR) Spectroscopy. The hydrogen isotopes conveniently provide two stable nuclei with spin, ^{1}H (H) and ^{2}H (D), thus we can use D and H solid state NMR to analyze the nature of water in silicate melts quenched to glass. Given that glass transition temperatures for silicate melts are high (500-600 ◦C), one does not expect H and D to behave differently. D-NMR can, however, be useful in characterizing the molecular dynamics of water in various sites in the glass.

We studied hydrated (with D_2O and H_2O) sodium tetrasilicate glasses, quenched from melts at 1400◦C and 1.5 GPa, using ^{1}H, ^{2}H and ^{29}Si solid state NMR. Whereas D_2O and H_2O depolymerize the silicate melt to similar degrees, as would be expected, we surprisingly find that protium (H) and deuterium (D) intramolecular partitioning between different molecular sites within the glasses is very large and controlled by a strong preferential association of deuterons to sites with short O D O distances. This preference is independent of total water content and D/H ratio. Substantial intramolecular D-H partitioning is also observed in a glass with a model hydrous basalt composition. Such large isotope partitioning cannot result from classic fractionation effects because of the high synthesis temperatures. Potential kinetic isotope effects are excluded via a slow quench experiment. The partitioning is likely governed by density/molar volume isotope effects, where deuterium prefers sites with smaller molar volume. Large intramolecular site partitioning in melts could lead to significant D-H partitioning between water saturated melt and exsolved aqueous fluid (where $D/H_{W,Melt} \neq D/H_{W,Fluid}$) during crystallization of Earth ' s magma ocean, potentially controlling the D/H content of the Earth ' s oceans.

キーワード: Silicate Melt, D-H fractionation, NMR, Magma Ocean
Keywords: Silicate Melt, D-H fractionation, NMR, Magma Ocean

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Chemical dependence of the speciation and structural position of water in silicate melts
Chemical dependence of the speciation and structural position of water in silicate melts

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Water is the main volatile component affecting the thermodynamic, structural and rheological properties of magmatic liquids in the Earth's interior resulting in major influence on past history and present magmatic activity of the Earth. Previous experiments and modelling have shown that water can be dissolved as H_2O molecules (H_2O_{mol}) and OH^- groups, with the OH^- groups bonded to the silicate network to form Si-OH or Al-OH bonds and perhaps alkali-OH and alkaline earth-OH complexes. However, important questions remain as to how bulk chemistry governs the link between the different OH groups and the silicate network, and the global H_2O_{mol}/OH ratio.

It is now widely accepted that dissolved water reacts with the O^{2-} oxygen composing the silicate network following:

$H_2O_{mol} + O^{2-} \Leftrightarrow 2OH^-$. (1)

As O^{2-} from the silicate network is involved in this reaction, its equilibrium constant must depend on the activities of bridging (BO), non-bridging (NBO), and free oxygen species potentially present in silicate melts, and hence on their global chemistry. Even if Al-OH and Si-OH bonding were the only variables (and, therefore, the Al/Si ratio of a melt), reaction (1) implies that the H_2O_{mol}/OH should depend on silicate melt composition. However, as the activity of NBO species is also affected by the ionic field strength of alkali and alkaline earth cations, we expect the equilibrium of reaction (1) to be affected by those cations.

To test and to quantify the occurrence and the impact of chemical effects on the speciation of water in quenched, hydrous silicate melt (glass), we analysed $M_2Si_4O_9$ glasses (M = Li, Na or K) containing different amounts of water (from 3.3 up to 17.6 mol%) with the help of ^{1}H and ^{29}Si MAS NRM, Raman and Infrared spectroscopy. Glasses were formed by temperature quenching (~100 ℃/s) at 1.5 GPa. Raman and infrared spectroscopy show three different bands close to 2300, 2800 and 3600 cm^{-1}. These are assigned to O-H stretching from OH groups bonded to silicate components and from H_2O molecules. Correlation of those frequencies with the O $\cdots$ O distances in minerals suggest that those three bands arise from OH stretching in two main different environments: one with a mean O $\cdots$ O distance close to ~0.26 nm and another one with a ~0.29 nm O $\cdots$ O distance. In the ^{1}H MAS NMR spectra, we retrieved signals near 15 and 5 ppm arising from the ~0.26 and ~0.29 nm environments respectively. Increasing the alkali radius tends to increase the intensities of the 15 ppm ^{1}H MAS NMR peak and of the 2000-2900 cm^{-1} Raman region, indicating an increase of the population of OH groups in the ~0.26 nm environment. In addition, the higher the alkali radius the higher the effect of water on the polymerization degree is, as testified by changes of the ^{29}Si NMR and Raman signals.

Those NMR and Raman observations suggest that the H_2O_{mol}/OH ratio in quenched hydrous silicate melts decreases in the order Li, Na, K. The greater the radius of alkali, the higher the proportion of OH^- the smaller the mean O $\cdots$ O distance in their environment, and hence the more extensive hydrogen bonding. We propose that this structural evolution arises from a combination of steric hindrance and electron distribution around alkali elements that affects both equilibrium reaction (1), which will decrease in the order K >Na >Li, and the local environment of the formed OH^- groups. This interplay between the nature of the alkali modifier, the speciation of water and the polymerization of the silicate network must result in non-negligible differences in viscosity of Li, Na and K silicate melts. Therefore, following this study, variation of the concentration of alkali and alkaline-earth elements in natural hydrous magmas, following their origin, will result in changes of their rheological properties, not only because of the different effects of alkali/alkaline earth elements on Si-O bonds, but also because of differences in the water speciation and OH^- environments.

キーワード: water, silicate glass, Raman spectroscopy, NMR spectroscopy
Keywords: water, silicate glass, Raman spectroscopy, NMR spectroscopy

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塩水による島弧下マントルへのイオン半径の大きな親石元素の移動
Large ion lithophile elements delivered by saline fluids to sub-arc mantle

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Geochemical signatures of arc basalts are explained by addition of aqueous fluids, melts, and/or supercritical fluids from subducting slab to sub-arc mantle. Partitioning of large ion lithophile elements between aqueous fluids and melts is crucial as these two liquid phases are present in the sub-arc pressure-temperature conditions. Using synchrotron x-ray beams, in-situ x-ray fluorescence (XRF) spectra are obtained from aqueous fluids and silicate melts at high-temperature and high-pressure conditions under varied concentrations of (Na, K)Cl (0-25 wt.%). There is a positive correlation between partition coefficients and pressure, as well as partition coefficients and salinity. In the systems with 13-25 wt.% (Na, K)Cl, partition coefficients of Rb, Cs, and Pb are greater than unity, indicating the capacity of such highly saline fluids to effectively transfer those elements. Enrichment of large ion lithophile elements in arc basalts relative to mid oceanic ridge basalts has been attributed to the mantle source fertilization by aqueous fluids from dehydrating oceanic plate. Such aqueous fluids are likely to contain Cl, although their amount remains to be quantified.

キーワード: 沈み込み帯, マグマ, 高温度高圧力, マントルウェッジ, 放射光 X 線, 塩素
Keywords: subduction zone, magma, high temperature and high pressure, mantle wedge, synchrotron X-ray, chlorine

SMP06-09 会場:411 時間:4 月 28 日 16:45-17:00

In-situ characterization of carbon-speciation in silicate-C-O-H fluid and melt with temperature, pressure, and redox con

In-situ characterization of carbon-speciation in silicate-C-O-H fluid and melt with temperature, pressure, and redox con

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Speciation and partitioning of C-bearing volatiles species in and between silicate-saturated C-O-H fluids and (C-O-H)-saturated melts have been determined in-situ with the samples to pressures and temperatures of ~2GPa and 900^{o}C, respectively. Structural characterization was conducted with vibrational spectroscopy of samples contained in externally-heated, hydrothermal diamond anvil cells. The redox conditions were controlled near that of the Fe+H_2O=FeO+H_2 (reducing, RED) and Ni+H_2O=NiO+H_2 (oxidizing, OX) equilibria, respectively. Melts are, therefore saturated in H_2O, H_2, and C-bearing species (redox dependent) and coexisting fluids saturated in silicate components. Solubility of volatile and silicate components depend on both temperature and pressure.

The melt/fluid partition coefficients of the C-bearing species vary with redox conditions and temperature with the $\triangle H_{RED}{}^{melt/fluid}$ = 44(7) kJ/mol and $\triangle H_{OX}{}^{melt/fluid}$ = -70(32) kJ/mol. Pressure is a dependent variable and increases with increasing temperature. It is assumed no pressure effect of the partition coefficients.

The solution equilibria under reducing and oxidizing conditions, respectively, were; (1) $2CH_3{}^-$+H_2O+Q^{n+1}=$2CH_4$+Q^n and (2) $2CO_3{}^{2-}$+H_2O+$2Q^{n+1}$=$HCO_3{}^-$+$2Q^n$, where the superscript, n, in the Q-species denotes number of bridging oxygen in the silicate species (Q-species). In the absence of H_2O equilibrium (1) changes to $CH_3{}^-$+Q^n=CH_4+Q^{n+1}. For oxidized carbon, there is an analogous expression expressing equilibrium between molecular CO_2 and structurally bound $CO_3{}^{2-}$-groups. Under both oxidizing and reducing conditions, the abundance ratios, $CH_4/CH_3{}^-$ and $HCO_3{}^-/CO_3{}^{2-}$ increase with temperature. The enthalpy change associated with the species transformation does, however, differ for fluids and melts and also for oxidized and reduced carbon ($\triangle H_{(1)}{}^{fluid}$ = -16(5) kJ/mol, $\triangle H_{(1)}{}^{melt}$ = -49(5) kJ/mol, $\triangle H_{(2)}{}^{fluid}$=81(14) kJ/mol). For the exchange equilibrium of CH_4 and CH_3 species, the temperature-dependent equilibrium constant yields $\triangle$H=34(3) kJ/mol.

Reactions (1) and (2) involve changes in silicate polymerization where increasing abundance ratios, $CH_4/CH_3{}^-$ and $CO_3{}^{2-}/HCO_3{}^-$lead to increased silicate melt polymerization. As a result of the relations between speciation of C-bearing species and melt and fluid structure, stable isotope (C and H) and element partition coefficients between melts and fluids, which depend on and silicate polymerization and silicate speciation, also vary with speciation of C-bearing species in silicate-C-O-H systems. Pressure, temperature, and redox control on the C-speciation also govern those (and other) properties.

キーワード: COH volatiles, fluid structure, melt structure, high pressure, high temperature, redox conditions
Keywords: COH volatiles, fluid structure, melt structure, high pressure, high temperature, redox conditions

Effect of CO2 content on melting phase relations in kimberlite group I at 6.5 GPa and 1200-1600oC

Effect of CO2 content on melting phase relations in kimberlite group I at 6.5 GPa and 1200-1600oC

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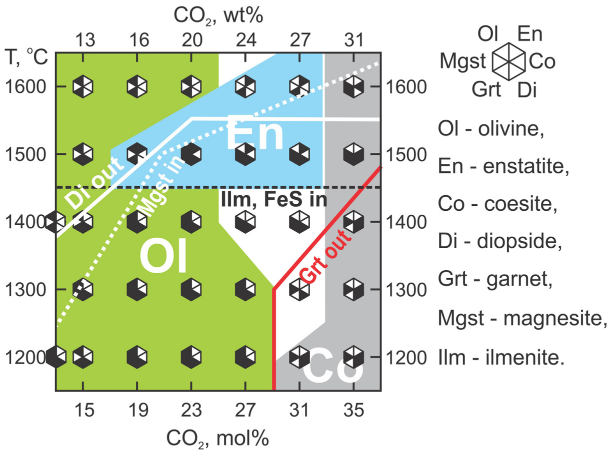
Our understanding of kimberlite petrogenesis is significantly hampered by uncertainty about the compositions of kimberlite magma. It is generally accepted that the last equilibration of kimberlite magma with surrounding mantle (garnet lherzolite) occurred beneath cratons at 6-7 GPa prior its rapid ascent (about 70 km/h) to the surface. This conclusion is based on the following facts. The deepest (170-220 km depths) and hottest (1200-1500^{o}C) xenoliths entrapped by kimberlites are sheared garnet lherzolites originating from the lower part of lithospheric mantle. The preservation of deformation features in sheared lherzolites indicates that the rock was undergoing dynamic recrystallization just before it was picked up by the magma and that it reached the surface after less than a few days or even hours in magma rising by crack propagation (Green and Gueguen, 1983; Meyer, 1985; Sparks et al., 2006). Based on our resent study (Sharygin et al., 2013) of melting phase relations in an exceptionally fresh kimberlite group I from Udachnaya-East kimberlite (UEK) pipe at 3.0-6.5 GPa and 900-1500^{o}C, the kimberlite melt had essentially Na-K-Ca carbonatite composition $<$15 wt.% SiO_2, Na_2O + K_2O = 5-18 wt%, Na/K = 2, Cl $>$1.5 wt%, and Ca/(Ca+Mg) $>$0.5. However, the mineral assemblages obtained in these experiments differ from known mantle parageneses. This may be due to unaccounted CO_2 budget missed at shallow depth as a result of decarbonation reactions at 1.5-2.5 GPa. Therefore, in present study we examined the effect of additional CO_2 on melting phase relations in synthetic UEK kimberlite system at 6.5 GPa and 1200-1600^{o}C.

Based on obtained results mineral assemblage equilibrated with kimberlite partial melt gradually changes from peridotite to eclogite paragenesis with increasing its CO_2 content from 13 to 35 mol %. As can be seen at 6.5 GPa kimberlite partial melt (i.e. Na-K-Ca carbonatite melt) becomes equilibrium with garnet lherzolite (i.e. olivine + enstatite + diopside + garnet + FeS + ilmenite assembly) at 1500^{o}C and 23 mol % (20 wt%) CO_2. This value is 10 mol% more than natural abundance of CO_2 in the Udachnaya-East kimberlite rock (group I kimberlite). In other words, the kimberlite magma lost almost half of the CO_2 budget during the eruption.

We greatly thank the Global Center-of-Excellence program at Tohoku University (Sendai, Japan) for the technical and financial support of this study.

Figure. Melting phase relations in Udachnaya-East kimberlite (kimberlite group I) versus temperature and CO_2 content at 6.5 GPa. 13 mol % CO_2 corresponds to the natural abundance of CO_2 in UEK rock.

キーワード: kimberlite, carbonatite, carbon dioxide, high-pressure experiment, Earth’s mantle, melting
Keywords: kimberlite, carbonatite, carbon dioxide, high-pressure experiment, Earth’s mantle, melting


CO2, wt%
13 16 20 24 27 31
T, °C
1600
1500
1400
1300
1200
15 19 23 27 31 35
CO2, mol%
En
Ol
Co
Di out
Mgst in
Ilm, FeS in
Grt out
Ol En
Mgst Co
Grt Di
Ol - olivine,
En - enstatite,
Co - coesite,
Di - diopside,
Grt - garnet,
Mgst - magnesite,
Ilm - ilmenite.

SMP06-11 会場:411 時間:4 月 28 日 17:15-17:30

Carbon dioxide in granitic magma under lower crustal conditions
Carbon dioxide in granitic magma under lower crustal conditions

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<Introduction>
Carbon dioxide is a major volatile component in the crust and mantle. Its solubility and speciation in silicate melts are important in understanding of mechanisms of magmatism and volcanism. However, they are not well constrained under lower-crustal conditions, especially in granitic magma, which is common in the crustal magmatism. In this study, we carried out equilibrium experiments in the CO_2-H_2O-granitic melt system to investigate the solubility and speciation of CO_2.

<Experimental procedure>
High-PT experiments were performed using a piston cylinder apparatus and a cold-seal pressure vessel. Obsidian flakes of a granitic composition and oxalic acid dehydrate (fluid source) were put in a gold or platinum capsule and run at 1123 and 1473 K and 0.1-1.5 GPa. Oxygen fugacity was estimated to be close to NNO. After quench, volatiles dissolved in the glass were analysed with FTIR spectroscopy. The composition of the coexisting fluid was quantified either by manometric analysis or based on the low-pressure solubility law and volatile contents of the glass.

<Results>
FTIR spectra showed that both CO_2 molecules (CO_{2mol}) and carbonate anions ($CO_3{}^{2-}$) were present in all of the glass samples. The concentrations of CO_{2mol}, $CO_3{}^{2-}$ and total H_2O increased generally with increasing pressure; they were 9200 ppm, 2100 ppm and 6.1 wt%, respectively, at 1.5 GPa and 1473 K. Here, we used new molar absorption coefficients of 2350 cm^{-1} (1192 $\pm$ 130 L cm^{-1} mol^{-1}; CO_{2mol}) and 1410 cm^{-1} (91 $\pm$ 28 L cm^{-1} mol^{-1}; $CO_3{}^{2-}$) determined in this study. The fraction of $CO_3{}^2$ to total CO2 in the granitic melt increased with increasing total CO2 content, from 0.09 (total CO_2 = 260 ppm) to 0.19 (11300 ppm). The molar fractions of CO_2 in the fluids ($X_{CO2}{}^{fluid}$) were 0.25-0.48 for the cold-seal experiments and 0.73-0.79 for the piston cylinder experiments.

<Discussion>
We formulated the solubility law of CO_{2mol} based on a vapour-liquid equilibrium equation. On the basis of the reaction CO_2 (vapour) $\rightleftharpoons$ CO_{2mol} (melt), we calculated the partial molar volume of CO_{2mol} in the granitic melt and the reaction enthalpy to be 24.9 $\pm$ 2.0 cm^3/mol and -22.2 $\pm$ 6.3 kJ/mol, respectively. These values are similar to those in previous experiments carried out at $<$6.6 kbar (Fogel and Rutherford, 1989; Behrens et al., 2004), indicating that the low-pressure solubility law can be extrapolated to 1.5 GPa. As for the formation of $CO_3{}^{2-}$, we assumed a reaction CO_{2mol} + O^{2-} (non-bridging oxygen) $\rightleftharpoons$ $CO_3{}^{2-}$. Possible factors shifting the equilibrium to the right-hand side include the total pressure (e.g., Fine and Stolper, 1985; Guillot and Sator, 2011) and water content (King and Holloway, 1992; Behrens et al., 2004). In this study, it was difficult to evaluate these parameters separately, since the water content increased simultaneously with total pressure. If we assume that the effect of water is small enough to be neglected, the change of the partial molar volume of CO_2 in the melt and the reaction enthalpy can be calculated to be -8.6 $\pm$ 6.0 cm^3/mol and -0.4 $\pm$ 3.1 kJ/mol, respectively.

<Application>
Recently, unusually CO_2-rich rhyolitic melt inclusions (up to 1.7 wt% total CO_2) were reported by Blundy et al. (2010). The saturation pressure of this CO_2 content is estimated to be 1.4 GPa when CO_2 dissolved only as CO_{2mol} ($X_{CO2}{}^{fluid}$ = 1; T=1173 K). If we consider the formation of $CO_3{}^{2-}$, the saturation pressure is estimated to 1.2 GPa.

キーワード: CO2, H2O, solubility, granitic melt
Keywords: CO2, H2O, solubility, granitic melt

SMP06-P01 会場:3 階ポスター会場 時間:4 月 28 日 18:15-19:30

Hydrogen positions in hydrous ringwoodite determined by pulsed neutron powder diffraction

Hydrogen positions in hydrous ringwoodite determined by pulsed neutron powder diffraction

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The transition zone in the Earth's mantle has been considered potentially large water reservoir. It was experimentally evidenced that its main constituent minerals can uptake significant amount of water as hydroxyl groups in their crystal structures. The ringwoodite [(γ-Mg,Fe)$_2$SiO$_4$] is one of the high pressure polymorph of olivine, which is the most major phase in the lower part of the transition zone, between 525 to 660 km in depth. It was reported that ringwoodite can incorporate up to 2.6 wt.% of water (Kohlstedt et al., 1996). The hydration of ringwoodite strongly affects its physical and chemical properties such as electrical conductivity, compressibility and seismic velocities. However, crystallographic sites of hydrogen and its incorporation mechanism are still unclear mainly due to insensitiveness of X-ray probe for hydrogen. The previous studies of its structure refinement by X-ray diffraction demonstrated that hydrous ringwoodite has cubic spinel structure with Fd-3m space group (Kudoh et al., 2000; Smyth et al., 2003). Here we applied neutron diffraction for hydrous ringwoodite for the first time to analyze its hydrogen positions.

Deuterated ringwoodite powder samples were synthesized at 1300 ^{o}C and 18 GPa for 5 minutes using a scaled-up Kawai-type multi anvil apparatus. The run products were evaluated by micro-focused X-ray, Raman spectroscopy and powder X-ray diffractometer to confirm their purity.

Neutron powder diffraction patterns were taken at BL-19 (TAKUMI) at Materials and Life Science Experimental Facility, J-PARC. The two representative deuterated ringwoodite samples were with identical composition mixed and measured together in a sample holder made of TiZr "null" alloy. The obtained diffraction pattern has been analyzed by Rietveld refinement using the "Z-Rietveld" code in order to determine positions and site occupancies of deuterium atoms in the ringwoodite structure.

We can propose two possible models for the deuterium atomic positions, 96g and 192i. These refined models were given with almost identical R factors. They also gave similar site occupancies and temperature factors for the elements except for the deuterium. However, in terms of deuterium temperature factor, the 192i model is more preferable than the 96g model. The refinement results also showed that the (Mg+Fe)/Si ratio is lower than the ideal ratio of dry ringwoodite [(Mg+Fe)/Si = 2.0] while Si in T sites are fully occupied, which demonstrates that deuterium only substitutes Mg and Fe in M sites and Si in T sites is not affected.

References:
[1] Kohlstedt, et al., Contrib. Mineral. Petrol., 123, 345, 1996.
[2] Kudoh, et al., Phys.Chem.Minerals., 27, 474, 2000.
[3] Smyth, et al., Am Mineral., 88, 1402, 2003.

キーワード: ringwoodite, neutron diffraction, Rietveld refinement
Keywords: ringwoodite, neutron diffraction, Rietveld refinement

SMP06-P02 会場:3 階ポスター会場 時間:4 月 28 日 18:15-19:30

Stability of Hydrous phase H MgSiO2(OH)2 in the lower mantle
Stability of Hydrous phase H MgSiO2(OH)2 in the lower mantle

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Subducting slabs transport water to Earth's deep interior and its circulation on a global scale is the key to understanding the evolution of the planet. However, it is still a matter of debate how deep water can be transported. Therefore, there are many studies on phase relationships in hydrous minerals or MORB-H2O systems. Most dense hydrous magnesium silicates (DHMS) are stable up to 50 GPa (e.g., Komabayashi et al., 2004). Recently, the synthesis of Mg- and Si- bearing δ-AlOOH, which is a solid solution between 2AlOOH-MgSiO2(OH)2, was reported and it might be transported with Mg-perovskite or Mg-post perovskite up to 135 GPa (Ohira et al., 2012, AGU). Tsuchiya (2013) theoretically reported Phase H, the end member of the system, was stable above 45 GPa and up to 55 GPa. And also it was experimentally synthesized at 50 GPa (Nishi et al., 2014). Although the previous studies claimed that Phase H was broken down above 55 GPa, it may be a host phase of water in the deep Earth interior. Here, we report the stability field of a new candidate phase of water reservoir at the lower mantle conditions by investigating the MgO-SiO2-H2O system up to 75 GPa and 2000 K.

A mixture of quartz and brucite (molar ratio 1：1) powders were used as starting materials. The high pressure and high temperature experiments were performed by using a double-sided Laser heated diamond anvil cell. A pellet with thickness of about 15 μm was made by a cold compression technique. In situ XRD experiments in the MgO-SiO2-H2O system were performed at BL10XU, SPring-8. In this study we confirmed that hydrous phase H does exist in the MgO-SiO2-H2O system and its stability fields expands at least up to 75 GPa and above 2000 K in contrary with previous reports (Tsuchiya, 2013; Nishi et al., 2014).

If Phase H exists under high pressure conditions corresponding to the pressure of CMB, it may transport water to CMB and thus the core may contains hydrogen as a light element.

キーワード: hydrous phase, lower mantle, subduction
Keywords: hydrous phase, hydrous phase, subduction

Japan Geoscience Union Meeting 2014
(28 April - 02 May 2014 at Pacifico YOKOHAMA, Kanagawa, Japan)

SMP06-P03 会場:3 階ポスター会場 時間:4 月 28 日 18:15-19:30

Partitioning of carbon between metallic- and silicate-liquids in carbonaceous chondrite compositions at high pressure

Partitioning of carbon between metallic- and silicate-liquids in carbonaceous chondrite compositions at high pressure

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Major volatile elements in the terrestrial planets are oxygen, sulfur, carbon, hydrogen, and nitrogen. They are also candidates for light components in the earth's core which were incorporated into the core at terrestrial magmaocean stage. Partitioning behavior of carbon has not been determined well though it is one of the strong candidates for light elements in the earth's core. We investigated partitioning of carbon with sulfur and oxygen between metallic- and silicate liquids at 6 GPa and 2073 K in carbonaceous chondrite composition (Allende meteorite; CV3). Effect of nitrogen and water as accessory components were also examined. High pressure experiments were conducted with multi-anvil high pressure apparatus. Graphite was used as capsule material. Composition of coexisting metallic- and silicate liquids were measured by electron microprobe with wavelength dispersion type spectrometer except for carbon in silicate liquid. Carbon concentration of bulk recovered sample was measured by elemental analyzer. Then, carbon concentration in silicate liquid was obtained by subtraction of carbon amounts in metallic phase which obtained by electron microprobe and SEM image analyses. Present result suggests that in oxidized carbonaceous chondrite composition, partitioning coefficient of carbon [$D^{Metallicliquid/Silicateliquid} = C^{Metallicliquid}/C^{Silicateliquid}$; C is concentration of carbon in wt.%] is close to 1, and it may increase with increasing the Fe^{metal}/Fe^{oxide} ratio in the carbonaceous chondrite composition.

Microanalysis of H2O and CO2 in silicate melt using laser Raman spectroscopy
Microanalysis of H2O and CO2 in silicate melt using laser Raman spectroscopy

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<Introduction>

Water and carbon dioxide are the major volatile components in the crust and mantle. Development of microanalytical techniques of these volatiles has made it possible to investigate mechanisms of igneous and volcanic processes. FTIR has been used as a fundamental tool for this purpose, but its spatial resolution is too large ($\sim$30 μm) to analyse small melt inclusions and micro-scale volatile distribution within a high-pressure experimental sample. In this study, we developed a new technique for volatile analysis in silicate glasses with $\sim$1 μm spatial resolution using laser Raman spectroscopy.

<Experimental and analytical procedure>

Standard glasses were synthesized by using a piston-cylinder apparatus in M. Nakamura's laboratory. Basaltic glass power was loaded into a platinum-sleeved nickel capsule together with oxalic acid and run at 1473 K and 0.5-1.2 GPa. After quench, the H_2O and CO_2 (dissolved as ${CO_3}^{2-}$) contents of the glasses were measured by using FTIR. The same glasses were then analysed with a Thermofisher DXR laser-Raman spectrometer. Wave length, power and diameter of the laser beam were 532 nm, 10 mw and 0.7 μm, respectively. We normalized the Raman spectra by the intensity of a peak at 500 cm^{-1} (T-O-T bond) and subtracted the spectrum of the volatile-free glass. The intensities of peaks at 3550 cm^{-1} (H_2O) and 1080 cm^{-1} (${CO_3}^{2-}$) in the resulting spectra were compared with the H_2O and CO_2 contents determined by FTIR spectroscopy.

<Results>

The H_2O and CO_2 contents were determined to be 0.7-2.1 wt% and 0.05-0.82 wt%, respectively. Raman spectroscopy showed that the intensities of peaks at 3550 and 1080 cm^{-1} increased with increasing H_2O and CO_2 contents, respectively. We fitted a linear equation to the data and obtained H_2O (wt%) = $(3.58\pm0.14)\times I_{3550}$ and CO_2(wt%) = $(4.61\pm0.21)\times I_{1080}$.

<Application>

We applied this technique to volatile analysis of an experimentally-produced bubble-bearing basaltic glass. In the experiment, basaltic melt was first equilibrated with H_2O-CO_2 mixture fluid at 1473 K and 1 GPa, and then decompressed to 0.5 GPa and kept for 10 minutes. After quench, the H_2O and CO_2 contents around bubbles were measured along the radial direction at 2-μm intervals for a total of 50 μm. The CO_2 contents decreased on moving towards the bubble, indicating that CO_2 was diffusing into the bubble. Fitting the diffusion equation to this profile, we estimated the diffusivity of CO_2 to be 1.2×10^{-12} m^2/s. This value is consistent with that reported by Zhang et al. (2007). In contrast to CO_2, H_2O showed a flat profile, suggesting that H_2O was already equilibrated with the fluid in the bubble. This is because the diffusivity of H_2O is one order of magnitude greater than that of CO_2. Such a diffusive fractionation was observed also in rhyolitic melt (Yoshimura and Nakamura, 2010).

キーワード: CO2, H2O, glass, Raman
Keywords: CO2, H2O, glass, Raman

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地球内部の炭素含有鉱物相の循環過程
Dynamic and cyclic process of carbon-bearing phases of the terrestrial interior

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本研究は次のようにまとめられる。

１）地球内部の炭素含有鉱物相は、物質状態の動的変化（気体、液体、固体）を活動的な地球惑星上で解明するために議論する。

２）本研究で用いた試料は、ダイヤモンド（コンゴ、アフリカ)、石灰岩（秋吉等、日本）、カーボナタイト（レンガイ-タンザニア-アフリカ、ヨーロッパ、北米） とシンガイト （シュンガ、ロシア）そして炭酸塩粒子を有するリビアガラス（アフリカ）などで、それらを FE 分析型 SEM などで炭素含有物質のマイクロ状ナノ結晶粒等を観察している。

３）本件の研究データでは、マイクロ炭素含有粒子が容易に三状態の物質相変化し、地表から内部における高圧衝撃波現象（地震、火山と衝突）で固化したガラス相等の存在を示す。

４）局地的な炭素を含む流体相を含む堆積が、不規則表面および動的な地球の内部に分布するのは、原始地球の地球外衝突の動的プロセスにより物質状態を変化し、さらに進化した地球の海底衝突で固化した混合物が地球内部の動的な混合形成したことによります。

５）創成期の衝突過程で形成された不均質な地表面と内部は、マクロ生命活動を安定的な動的な炭素を含む三物質状態（空気、液体や固体）を生成し、その後継続的地表や内部の変化過程で複雑で局地的な分布を示している。

キーワード: 炭素, 地球内部, 循環過程, 衝撃波現象, 不規則分布, 局部形成
Keywords: carbon, interior, cyclic process, shock wave event, irregular distribution, local deposit