圧力 1GPa におけるアンチゴライト蛇紋岩弾性波速度の温度依存性
Temperature dependence of seismic velocities in a antigorite serpentinite at 1 GPa

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

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

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

Both compressional and shear wave velocities linearly decrease with increasing temperature. The temperature derivatives are -3.6×10^{-4} (km/s/K) and -2.7×10^{-4} (km/s/K) for compressional and shear wave velocities, respectively. The temperature derivative of compressional wave velocity is close to that observed in the direction subparallel to antigorite c-axis (Yano et al., in prep.). The temperature dependence of c33 might dominate that of the effective elastic constants of a randomly oriented polycrystalline aggregate. Applications to seismological observations will also be discussed in this presentation.

キーワード: 地震波速度, 蛇紋岩, アンチゴライト, 沈み込み帯, 流体
Keywords: seismic velocity, serpentinites, antigorite, subduction zone, fluid

ラマン・赤外分光計測による石英表面の水の構造化の検出とその分子動力学的評価
Detection of structured water on quartz interface by Raman-FTIR spectroscopy and its evaluation by molecular dynamics

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　地殻中では含水鉱物や流体包有物中の水、間隙中の水など、様々な形で水が存在しており、プレートの沈み込み帯も、海洋由来の水やマントル由来の水などが存在する環境である。沈み込み帯における地震発生帯の温度は 150〜350 ℃程度であり、水は亜臨界-超臨界で存在する熱水である。また、この領域の水は鉱物粒界に非常に薄い薄膜状の形で存在しており、この薄膜水はバルクの水（自由水）とは違った性質を持つことが知られている。

　本研究では、高温高圧の薄膜水が観察可能なダイヤモンドセルと顕微ラマン-赤外分光計を用いて、様々な温度圧力における金属反射板上および石英基板上の水を観察した。

　ラマンスペクトルおよび赤外吸収スペクトルの観察結果より、3400cm^{-1} 付近に現れる水の OH 伸縮振動ピークが温度圧力によって変化することが観察された。このピークは高温では水素結合の影響は弱まり 3700cm^{-1} 付近にシフトするが、石英基板上の水について、高温であっても水素結合の影響を強く受けた 3200cm^{-1} 付近の振動の存在が確認された。

　また本研究では、分子動力学プログラム MXDORTO を用いて実験を模擬した条件でシミュレーションを行い、石英基板上の水の構造化を再現した。シミュレーションでは、石英表面近傍の数ナノメートルの範囲において、通常の水には見られない水の密度の分布が見られた。

　以上のような分光観察、分子シミュレーションを用いて得られた石英表面の水分子の構造および性質の変化を、水分子と石英表面のシラノール基（Si-OH）の水素結合に着目して考察する。

キーワード: ラマン分光, 赤外分光, 界面水, 亜臨界, 石英, 分子動力学
Keywords: Raman spectroscopy, IR spectroscopy, interfacial water, subcritical, quartz, molecular dynamics

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地質学的証拠に基づいた地殻流体が関与する岩石破壊過程の解明
Generation process of brecciated marble at Hiraodai karst, Kyushu, Japan

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

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

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

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

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

沈み込む堆積岩層中の含水相 topaz-OH の高温高圧下における状態方程式の決定
Equation of state of topaz-OH in the subducted sediment under high pressure and high temperature

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沈み込むスラブ中の含水鉱物の脱水分解反応によって H_2O に富んだ流体が生成され、その流体はマグマの生成や溶融温度の低下、マグマ組成の変化を引き起こすと考えられている。topaz-OH [$Al_2SiO_4(OH)_2$] は沈み込むスラブの堆積岩層中に存在すると考えられる含水鉱物であり、天然の topaz [$Al_2SiO_4(OH,F)_2$] の端成分である。安定領域については topaz-OH は 5-10 GPa、1500 ℃まで安定に存在すると報告されている (Wunder *et al*,. 1993; Ono. 1998; Schmidt *et al*,. 1998)。状態方程式の研究は天然の topaz (Komatsu *et al*,. 2003; Gatta *et al*,. 2003) では行われているが topaz-OH においては未だに報告されておらず、また高温及び高圧下での実験も行われていない。従って、本研究では topaz-OH の状態方程式すなわち熱弾性的性質を明らかにするために高温高圧下での X 線その場観察実験を行った。

出発物質の topaz-OH はマルチアンビル型高圧発生装置を用いた急冷回収実験によって 10 GPa、~1000 ℃の条件下で合成した。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 の高圧発生装置 MAX80 を使用し、エネルギー分散法により X 線回折パターンの収集を 3-10 GPa,800 ℃までの範囲で行った。熱弾性物性値は Angel（2000）による EosFit v5.2 の計算ソフトを用いて計算し、フィッティングには 3 次のバーチマーナハンの状態方程式を用いた。

高温高圧条件下で得られた全データを 3 次のバーチマーナハン状態方程式によってフィッティングしたところ (K'=4 で固定)、V_0=354.7(1) Å^3、K_0=169.8(22)GPa、$(dK_T/dT)_P$=-0.013(7) GPaK^{-1}、a_0=1.61(23) × 10^{-5}K^{-1}、b_0=1.36(41) × 10^{-8}K^{-2} という値が得られた。一方、今回得られた圧縮データを詳しく解析すると、7 GPa 付近で圧縮特性の変化が示唆された。この現象は a 軸と b 軸の圧縮特性の変化として現れている。従って、7 GPa 付近を境界に低圧側、高圧側で状態方程式の計算を試みた (K'=4 で fix)。結果、低圧側で V_0=355.2(1) Å^3、K_0=160.1(2)GPa、高圧側で V_0=356.5(9) Å^3、K_0=153.1(89) GPa と異なる値をとる結果が得られた。天然の topaz を用いた先行研究との比較を行うと本研究によって得られた topaz-OH の体積、体積弾性率はともに先行研究より大きい値となった。これは OH の含有量の増加に伴う体積弾性率の増加が原因であると考えられる。体積弾性率に対する密度の比較を行うと、topaz-OH はバーチの法則に従う直線近くに位置し、高圧含水相である Ph D [$Mg_2SiO_4(OH)_2$] と並んで体積弾性率が大きく、密度が大きい鉱物であることが明らかとなった。そのため、topaz-OH は堆積岩層中の安定な領域ではスラブの沈み込みを促進させ、より深部へ水を運搬することができると考えられる。

キーワード: topaz-OH, 高圧含水相, 沈み込むスラブ, 状態方程式, 放射光 X 線その場観察
Keywords: topaz-OH, high pressure hydrous phase, subducting slab, equation of state, synchrotron X-ray in-situ experiment

メルト包有物と斜長石の Anorthite 成分から見積もる東北日本・伊豆弧の玄武岩質マグマの含水量
Water content in arc basaltic magma in northeast Japan and Izu-Mariana arc estimated from melt inclusions in olivine and

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Primitive arc basalt magma is generated by partial melting of sub-arc mantle with adding aqueous fluid which was derived from dehydration of subducting slab. Aqueous fluid has profound effects on melting temperature of the mantle, crystallization pathways of generated magmas, and explosivity of magmas. Precise estimation of H_2O content in arc basalt magma is important to evaluate the effect of water on generation, differentiation, and eruption of magmas in subduction zones. We estimated variation of water content of arc basaltic magmas in the northeast Japan arc and the Izu-Mariana arc using a simple plagaioclase phenocryst hygrometer and melt inclusion analysis of olivine phenocrysts.

A simple plagaioclase phenocryst hygrometer was constructed by high-pressure and high temperature experiments using internally heated pressure vessels: SMC-2000 and SMC-5000 installed at the Magma Factory, Tokyo Tech (Ushioda et al., 2013, VSJ fall meeting). High-pressure and high-temperature experiments were conducted for relatively primitive basalt from Miyakejima volcano under hydrous conditions. OFS (Ofunato scoria: Tsukui et al., 2001; Niihori et al., 2003) is one of the most primitive basalt in the last 10,000 years. All experiments were conducted near the liquidus of plagioclase ($\pm$magnetite) and therefore the composition of melt is essentially the same as the starting material. H_2O content of melt was calculated by weight ratio of melt using mass balance calculation of all phases assuming that water was concentrated only in melt. Partition coefficient $K_D{}^{pl-melt}{}_{Ca-Na}$ is proportional to H_2O content in melt. In the experimental conditions, both pressure and temperature effects are negligible.

We then chose geochemical data sets of relatively primitive basaltic rocks (with no evidence of magma mixing) and most frequent Ca-rich plagioclase phenocrysts from 15 arc basaltic volcanoes, which includes both frontal arc volcanoes and rear-arc volcanoes from literature. In 15 volcanoes, plagioclase phenocrysts of high anorthite content (An>90) are commonly observed, whereas plagioclase phenocrysts in rear arc volcanoes usually have lower anorthite content (90>An>80). Estimated H_2O content of basaltic magma is 3 wt.% H_2O or higher.

We also analyzed H_2O content of melt inclusions in olivine phenocrysts using FTIR micro reflectance measurement (Yasuda, 2011) and FTIR micro transmission measurement (absorption coefficient: Yamashita et al., 1996) in order to compare H_2O content between melt inclusion analysis and this simple plagioclase phenocryst hygrometer. For example, melt inclusions of olivine phenocrysts in scoria from Ko-Fuji volcano had up to 3.7 wt.% H_2O which was consistent with estimate from our simple plagioclase phenocrysts hygrometer. In Miyakejima volcano, melt inclusions of olivine phenocrysts from OFS contained up to 3.3wt.% H_2O although H_2O content was 5.2 wt.% estimated from this hygrometer. In either case, basaltic magmas in volcanic front have 3 wt.% H_2O or higher.

キーワード: マグマ中の水, メルト包有物, 斜長石メルト間平衡
Keywords: water in magma, melt inclusion, equilibrium between plagioclase and melt

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加水・脱水反応に起因するフラクチャーパターン：個別要素法によるアプローチ
DEM simulation on fracturing induced by hydration and dehydration reactions

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

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

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

Keywords: hydration, dehydration, fracturing, distinct element method