

What control the position of volcanic arc?

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To understand physical and chemical processes in subduction zones, I use 2D numerical model that include the dehydration of subducting slab, hydration of mantle wedge, water fluxed melting of mantle wedge, change in peridotite composition through melt extraction and addition, solid flow of mantle wedge with temperature, pressure, stress and water content dependent rheology and migration of aqueous fluid and melt through permeable flow. I present the calculation results for five subduction zones that span normal ranges in subducting slab age, convergence velocity, and slab dip angle. The model shows the following general features. A hydrous layer saturated with water in NAMs and rich in aqueous fluid is developed just above the subducting slab surface due to the dehydration of the slab. This layer consists of harzburgite formed by the melt extraction from lehrzomite. The high solidus temperature of the harzburgite suppresses melting of the mantle wedge just above the slab surface and results in melt distribution nearly parallel to and separated at some distance from the subducting slab surface. The depth for slab dehydration and the melt distribution in mantle wedge show general agreement with the seismological observations. The comparison between the results of present model and the geophysical and geological observations indicates variable melting mode for the formation of volcanic front: the flux melting caused by the dehydration of oceanic crust for NE Japan and N Chile, the flux melting caused by the dehydration of mostly slab mantle for Nicaragua and Bonin, and slab melting (slab-melt flux mantle melting) for SW Japan. This variation may be a cause for the wide range of depth to the slab surface below the volcanic front.

Keywords: Subduction zones, Numerical model

Along-arc variation in the slab-mantle coupling due to a thin, low viscosity layer just above the slab

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In order to understand how seismic and volcanic activities occur in the subduction zone, it is critical to better understand the thermal structure there. Previous studies have shown that many factors affect the thermal structure including slab velocity, plate age, temperature dependence of viscosity, viscous anisotropy, complex slab geometry, and slab-mantle coupling. Among these factors, I focus on slab-mantle coupling in this presentation. It is well known mainly based on the observed low surface heat flow and low seismic attenuation that the forearc mantle is cold and rigid. To explain such a "cold corner", the movement of slab and mantle need to be decoupled down to a certain depth by a thin, low viscosity layer (LVL) just above the slab so that hot material does not reach the corner of the mantle wedge. Many numerical studies have investigated the effects of slab-mantle coupling so far, although very few of them focus on its along-arc change. In this presentation, I will show how LVL at the plate interface affects the along-arc change in the degree of slab-mantle coupling.

I construct 3D finite element models to investigate a possible role of LVL in the subduction zone. The model domain is divided into crust, slab, and mantle wedge that includes LVL just above the slab. The flow is computed only in the mantle wedge and temperature is computed for the whole model domain. Buoyancy force is not considered and viscosity is assumed to be temperature and strain rate dependent except for LVL where it is constant. The model setting is exactly the same in the along-arc direction.

I find that when the viscosity of LVL is sufficiently low, the degree of slab-mantle coupling starts to change in the along-arc direction at some point and 3D flow and thermal structure develop. Temperature dependence of viscosity may be a key factor in producing such a feature. I also find that a thicker LVL leads to a longer wavelength of the 3D flow, and a deeper down-dip limit of LVL leads to a delayed onset of the 3D flow. In order to explain the spatial distribution of Quaternary volcanoes in Northeast Japan with this model, the viscosity and thickness of LVL need to be $<5 \times 10^{18}$ Pa.s and ~6 km, respectively. These results show that a detailed understanding of LVL including its formation process and spatial extent is essential to constrain the thermal structure in the subduction zone.

Keywords: subduction zone, slab-mantle coupling, distribution of volcanoes

Characteristics of slab-derived fluids beneath Kii Peninsula inferred from seismic traveltimes tomography (2)

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1. Introduction

In order to investigate behavior and nature of slab-derived fluids discharged from the Philippine Sea plate subducting beneath Kii Peninsula, we have carried out seismic observations, receiver function analyses and seismic travel time tomography mentioned below. We estimated the geometry of the slab and the seismic velocity structure beneath the Kii Peninsula, and discussed the behavior of the fluids with the distribution of low velocity anomalies. We are now understanding relations between the fluids and deep low frequency events (DLFEs) and active micro seismicity beneath the northern Wakayama Prefecture.

2. Previous results

We carried out linear array seismic observations in the Kii Peninsula from 2004 to 2013. We deployed seismometers along profile lines with an average spacing of ~ 5 km. We applied a receiver function analysis and obtained images of S wave velocity discontinuities. We estimated 3D configurations of the continental Moho, the slab top and the oceanic Moho from receiver function images for four profile lines in the NNW-SSE direction which is the dip direction of the Philippine Sea plate and for two profile lines in the NNW-SSE direction that is almost perpendicular to the dip direction. A new knowledge obtained by the analysis is that the continental Moho dips upward in the southeast direction above the Philippine Sea slab.

We carried out the tomography with FMTOMO (Rawlinson et al., 2006) in which a robust wavefront tracking (de Kool et al., 2006) is implemented for the theoretical travel time calculation and the ray tracing. We used a velocity model with the 3D geometries of the three discontinuities derived from the receiver function analysis. We also used observed travel times at temporary stations in the dense linear arrays in addition to permanent stations. A dense distribution of the temporary stations contributed to higher resolutions of tomographic images. By analyzing travel time data for 74 months from May 2004 to the middle of 2010 we found that (1) DLFE areas show low velocity anomaly of ~5 % and (2) another strong low velocity anomaly (> 10 %) is widely distributed in the lower crust beneath the northern Wakayama Prefecture.

3. New attempts

Automatic picking of P and S times was carried out for the remaining waveform data in and after 2010. Travel time data for 33 months were added. They almost doubled the numbers of earthquakes and travel times utilized in the tomography. The result showed the similar features to (1) and (2) above. The result of checkerboard tests was improved in 22 -34 km depths. (1) can be due to discharged H₂O from hydrous minerals in the oceanic crust at 30 -40 km depths. (2) can be explained by a mechanism that fluids upwelling from the low velocity anomaly in the lower crust increase the pore pressure in existing cracks in the brittle upper crust. The Vp/Vs ratio of the low velocity anomaly beneath the northern Wakayama Prefecture has small values near 1.6. This might be due to silica-saturated fluids (Manning, 1996). The Vp/Vs ratio in the DLFE areas should be re-examined. We will contrive ways to estimate the Vp/Vs ratio by referring to Ramachandran and Hyndman (2012, Solid Earth).

We used waveform data from permanent stations of NIED; JMA; ERI, Univ. of Tokyo; Nagoya Univ. and DPRI, Kyoto Univ.

Keywords: tomography, slab-derived fluids, Kii Peninsula

Experimental constraints on the serpentinization rate of fore-arc peridotites:
implications for the welling condition of the "Arima-type" hydrothermal fluids

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In order to place a constraint on the water circulation in subduction zones, hydration rates of peridotites have been investigated experimentally in fore-arc mantle conditions. Experiments were conducted at 400–580°C and 1.3 and 1.8 GPa, where antigorite was expected to form as a stable serpentine phase. Crushed powders of olivine + orthopyroxene and orthopyroxene + clinopyroxene were reacted with 15 wt% distilled water for 4–19 days. The synthesized serpentine was lizardite in all experimental conditions except that of 1.8 GPa and 580°C in the olivine + orthopyroxene system, in which antigorite was formed. In the olivine + orthopyroxene system, the reactions were interface-controlled except for the reaction at 400°C, which was diffusion-controlled. Corresponding reaction rates were 7.0×10^{-12} – $1.5 \times 10^{-11} \text{ m}\cdot\text{s}^{-1}$ at 500–580°C and $7.5 \times 10^{-16} \text{ m}^2\cdot\text{s}^{-1}$ at 400°C for the interface- and diffusion-controlled reactions, respectively. Based on a simple reaction-transport model with these hydration rates, we infer that leakage of the slab-derived fluid from an water-unsaturated fore-arc mantle is allowed only when focused flow occurs with a spacing larger than 77–229 km in hot subduction zones like Nankai and Cascadia, whereas the necessary spacing is just 2.3–4.6 m in intermediate-temperature subduction zones like Kyushu and Costa Rica. These calculations suggest that fluid leakage in hot subduction zones may occur after the fore-arc mantle is totally hydrated, while in intermediate-temperature subduction zones, leakage through a water-unsaturated fore-arc mantle may be facilitated.

Keywords: hydration reaction, slab-fluid, serpentine, fore-arc mantle

Feedback among reaction, mass transport and fracturing during metamorphism: controls and pattern formation

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Analyses of equilibrium phase relations with recently-developed thermodynamic dataset of rock-forming minerals has provided us significant information on distributions of stable mineral assemblage and water content within the Earth's interiors. However, based on the petrological observations of metamorphic rocks and serpentinites, thermodynamic equilibrium is not always attained during metamorphism at individual P-T conditions, and unreacted parts often remain. To understand the dynamic behavior of the Earth's interior, it is important to investigate essential controls on the progress of metamorphic reactions. We have developed a novel model for the coupled processes of surface reaction, fluid transport and fracturing during metamorphic reactions by a distinct element method (DEM) (Okamoto and Shimizu, 2015). This model considers a reaction rate as a function of fluid pressure, and revealed that contrasting fracture patterns are produced between volume-decreasing dehydration (typical in prograde metamorphism) and volume-increasing hydration reactions (retrograde metamorphism, or serpentinization).

In this contribution, we focus on the relative rate of fluid transport and surface reaction on the fracture pattern during the volume-increasing hydration reaction. The new DEM model treats transport of water in two ways; flow along the fractures and flow through matrix. The latter has the similar effects to diffusion. For evaluate the system, we introduce two nondimensional parameters; the ratios of the rates of fracture flow (Y_F) and diffusion (Y_D) to the surface reaction rate. We found systematic changes in fracture pattern and system evolution as a function of Y_D and Y_F . In the first case that reaction is faster than water transports ($Y_D < 1$ and low $Y_F < 1$), the reaction proceeds from the boundaries and forms fine fractures layer-by-layer. In the second case that reaction is faster than diffusive transport of water but much slower than flow along the fracture (low $Y_D < 1$ and high $Y_F > 1000$), the reaction proceeds inward effectively to form hierarchical fracture networks. In the third case with high diffusion rate ($Y_D > 10$), the reaction tends to proceed from the boundaries without fracturing. The dependence of the fracture pattern on Y_F and Y_D suggests the importance of the rates of water transport relative to the surface reaction rate in studying the mechanism and overall rate of water-rock reactions. The fracture pattern generated in the second case is similar to mesh texture found in the partly serpentinized peridotite in oceanic peridotites. We also discuss the effects of grain boundaries and will develop the model to more realistic reaction system which incorporate element diffusion such as silica.

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Keywords: reaction-transport-fracturing feedback, distinct element method, serpentinization

Influence of pore size distribution on elastic wave velocities during evaporative drying

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Elastic wave velocities (V_p, V_s) in porous rocks are known to be sensitive to the water saturation (S), the size and shape of pores, the distribution of fluids in pores, and the incident wave frequency. Various studies have tried to understand these dependences on the basis of Biot's theory (Biot, 1956). The method for accurately predicting the quantitative relationship between S and V_p, V_s for the entire range of S (from $S = 1$ (saturated) to $S = 0$ (dry)) still remains to be fully elucidated. In this study, we measured the changes of V_p and V_s during drying for two Berea sandstones (permeabilities: 300 mD, 20 mD; hereafter described as Berea300 and Berea20, respectively) and Shirahama sandstone (permeability: <0.6 mD). P-wave and S-wave frequencies used in the measurements were 200 kHz and 100 kHz, respectively. The measured pore size distributions (aperture radius) showed that the predominant pore radii were ~5-100 μm for Berea300, ~1-10 μm for Berea20, and less than 0.4 μm for Shirahama. The change of V_p with S for Berea300 can be classified into the following 4 stages: [(1) $S=1 \rightarrow 0.5$: decrease of V_p ; (2) $S=0.5 \rightarrow 0.3$: increase of V_p ; (3) $S=0.3 \rightarrow 0.1$: decrease of V_p ; (4) $S=0.1 \rightarrow 0$: increase of V_p]. The change of V_s with S for Berea300 can be separated to 2 stages: [(1) $S=1 \rightarrow 0.15$: gradual increase of V_s ; (2) $S=0.15 \rightarrow 0$: rapid increase of V_s]. For Berea20, the V_p change trend appeared to correspond to part of stage 1 plus the entire range of stages 2, 3, 4 observed in Berea300, and the V_s change trend was approximately equal to that in Berea300. For Shirahama, the V_p change trend seemed to be equivalent to the stages 3 and 4 in Berea300, whereas V_s decreased first and then increased, unlike in the case of Berea sandstones. When the drying proceeds, it is known that water is lost first in the larger pores, and later in the smaller ones (Nishiyama et al., 2012). Therefore, the size of pores containing water at a given S can be determined on the basis of the pore size distribution of each rock. By incorporating the information of pore size distribution and the frequency dependence of bulk modulus into previously reported models, we tried to precisely predict the change of V_p and V_s during drying.

Keywords: Elastic wave, Water saturation, Pore size distribution, Sandstone

Effect of pore fluid on seismic velocity of serpentinite and the origin of high V_p/V_s in mantle wedge

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Serpentine is one of the candidates to explain low-velocity anomaly and high V_p/V_s in mantle wedge. However, extremely high V_p/V_s found beneath Kanto and southwest Japan requires the presence of aqueous fluid in addition to the serpentinites. In this study, we investigated the effect of pore fluid on elastic-wave velocity of antigorite during triaxial deformation using intra-vessel apparatus at $P_c = 10\text{-}20$ MPa, $P_p = 5\text{-}10$ MPa and room temperature. Compressional and shear-wave velocities decrease during deformation, possibly due to the formation of micro-cracks in the specimen. Since shear-wave velocity changes more drastically than compressional-wave velocity, V_p/V_s increases during deformation, which is consistent with the crack model by O'Connell and Budiansky (1974). In future, we are going to monitor volume change of pore fluid during deformation, and discuss the amounts of pore fluid to explain the observation of high V_p/V_s in mantle wedge.

Keywords: serpentinite, seismic velocity, pore fluid

Elastic constants of single-crystal topaz and their temperature dependence studied via sphere-resonance method

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Transport of ocean floor sediments by plate motions might play an important role in the circulation of materials within the Earth. Imaging subducted sediments through seismological observations requires a thorough understanding of elastic properties of sediment origin hydrous minerals. Topaz is a hydrous mineral, which can be formed from subducted sediment at high pressures. We have studied elastic constants of single-crystal topaz and their temperature dependence by the sphere-resonance method.

A sphere sample ($D=6.483(1)$ mm) was made from a topaz single-crystal ($\text{Al}_{1.97}\text{SiO}_4(\text{F}_{1.56}, \text{OH}_{0.42})$) collected from Nakatsugawa, Gifu Pref. by the two-pipe method. The uniformity of crystallographic orientation was confirmed with SEM-EBSD (Shizuoka Univ.) measurement. Resonant frequencies were measured at frequencies from 600 kHz to 1.5 MHz with different specimen-holding forces. Extrapolating to the specimen-holding force of zero, we obtained frequencies of "free" oscillation. The temperature was changed from 0 to 400°C. Elastic constants were determined by comparing measured and calculated resonant frequencies. The xyz algorithm (Visscher et al., 1991) was employed to calculate resonant frequencies of the sphere sample. At room temperature (18.7°C), $C_{11}=281.3$, $C_{22}=346.3$, $C_{33}=294.8$, $C_{44}=108.5$, $C_{55}=132.5$, $C_{66}=130.3$, $C_{12}=121.5$, $C_{13}=80.90$, $C_{23}=81.73$ (GPa). Using determined elastic constants, compressional- and shear-wave velocities were estimated for an isotropic polycrystalline aggregate of topaz at high temperature. Compressional- and shear-wave velocities at 800°C are 9.32 km/s and 5.57 km/s, respectively. These values are significantly higher than those in minerals like olivine or garnet.

Keywords: elastic constants, resonance method, hydrous mineral, topaz

A new mechanism to produce chemical heterogeneity of Earth's mantle: Slab dehydration at 660-km phase boundary

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Introduction

Dehydration-hydration processes are thought to be essential for creating chemical heterogeneity in the Earth's mantle: e.g., the mantle geochemical end-member "HIMU" likely represents recycling of an extremely dehydrated oceanic crust, and mantle geochemical hemispheres (Iwamori and Nakamura, 2012) seem to be originated from dehydration-hydration reactions in subduction zones. We investigate behaviors of hydrophilic components during mantle convection and water transport using a self-consistent numerical model in order to reveal the chemical evolution of Earth's mantle with geophysical validity.

Methods

A 2-D fluid mechanical simulation with following characteristics is conducted.

- (1) Free convection of whole-mantle scale without synthetic forces (Tagawa et al., 2007).
- (2) Phase diagrams of hydrous peridotite and hydrous basalt (Iwamori, 2007) to introduce hydration and dehydration reactions.
- (3) Realistic constitutive and state equations for the hydrous rocks to make (1) and (2) interactive.
- (4) Transport of multiple elements that can be partitioned between mantle rocks and aqueous fluid using a Marker-in-Cell technique.

Results and Discussion

During slab subduction, dehydration reactions occur at specific p-T conditions. Then instantaneous aqueous fluid enriched in hydrophilic components and less-hydrated residue minerals depleted in the components are produced. The aqueous fluid is assumed to be immediately incorporated into dry rocks through which the fluid percolates. The transported hydrophile elements are assumed to precipitate with the fluid. In each run, three major dehydration and fractionation processes are reproduced as follows.

[Process 1] (Depth < 200 km; under-arc process) Associated with dehydration of the subducted slab, discharge of highly hydrophilic elements results in depletion of the slab subducting into deeper mantle. The hydrophilic elements are deposited into the overlying lithosphere. This process does not contribute to global redistribution of hydrophile elements, because of high viscosity in the cold region. The depleted layer is fixed along the subducting slab for a long time.

[Process 2] (Depth = 660 km; slab penetration process) When the slab penetrates into the lower mantle, the hydrophiles are continuously emitted depending on their partition coefficients during dehydration associated with wet-Rw → Pv + MgO + Aq transition. This process helps heterogeneity in terms of the hydrophile elements to horizontally expand. During the slab penetration process, the depleted rock as a product of 660-km dehydration is produced just below the phase boundary, and descends into the deeper mantle.

[Process 3] (Depth = 410 km; upwelling wet plume process) If the water-saturated layer is formed just above the 660-km phase boundary, wet plumes enriched in the hydrophiles ascend due to their buoyancy. After plumes reach the 410-km phase boundary, dehydration by Wd → Ol transition and the corresponding fractionation of the hydrophiles occur. However, the depleted plume tails are not

well separated from the enriched plume head.

Among them, [Process 2] is the most efficient process for creating and distributing the geochemical heterogeneity. [Process 2] with wet plumes and aqueous porous flows from the 660-km phase boundary involves a possible mechanism to produce the observed geochemical hemispheres representing a hydrophile-rich part (eastern hemisphere) and a depleted part (western hemisphere) (Iwamori and Nakamura, 2012).

Keywords: hydrophilic trace elements, water transportation, mantle convection, 660-km phase boundary, chemical heterogeneity of mantle, element partition

Iron-titanium oxyhydroxides as a water transporter into the Earth's mantle transition zone

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We experimentally discovered a new hydrous phases, iron-titanium oxyhydroxides, in the system basalt + H₂O at pressure of 12 GPa and temperature of 1000°C which corresponds to condition of the deep upper mantle in the slab (Matsukage et al. submitted). These new hydrous phases have chemical compositions in the system FeOOH-TiO₂. However, their small grain sizes in basalt + H₂O system has hindered efforts to determine their crystal structures and to confirm the presence of water. We synthesized single phase in the system FeOOH-TiO₂ at pressures of 8-16 GPa and temperatures of 900-1600°C which corresponds to conditions of the deep upper mantle and the mantle transition zone (Nishihara and Matsukage, 2016). Seven different compositions in the FeOOH-TiO₂ system having molar ratios of $x = \text{Ti}/(\text{Fe} + \text{Ti}) = 0, 0.125, 0.25, 0.375, 0.5, 0.75$ were used as starting materials. High-pressure and high-temperature experiments were carried out using Kawai-type multi-anvil apparatus (Orange-1000 at Ehime University, SPI-1000 and SAKURA at Tokyo Institute of Technology). In this system, we identified two stable iron-titanium oxyhydroxide phases whose estimated composition is expressed by (FeH)_{1-x}Ti_xO₂. One is the Fe-rich solid solution ($x < 0.23$) with e-FeOOH type crystal structure (e-phase, orthorhombic, *P2₁nm*) that was described by the previous studies (e.g., Suzuki 2010), and the other is the more Ti-rich solid solution ($x > 0.35$) with a-PbO₂ type structure (a-phase, orthorhombic, *Pbcn*). The a-phase is stable up to 1500°C for a composition of $x = 0.5$ and at least to 1600°C for $x = 0.75$. Our result means that this phase is stable at average mantle temperature in the Earth's mantle transition zone. We also found that the hydrous phase with a-PbO₂ type structure was stable in basalt + H₂O system at wide pressure range at deep upper mantle and mantle transition zone (8-17 GPa), and it dehydrate at pressure of ~17 GPa. Above 17 GPa, CaTi perovskite was formed as a Ti-bearing phase. After dehydration of FeTi oxyhydroxide, Al-bearing phase D, which is one of major water carriers in deep mantle, was stable (Liu et al., this meeting). Therefore our findings suggest that water transport in the Earth's deep interior by basaltic crust is probably much more efficient than had been previously thought.

Keywords: deep upper mantle, mantle transition zone, water, titanium, hydrous phase, basaltic crust

Prediction of elemental partition between fluid and melt by bond valence method

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Matsui, Onuma and others (Bull. Soc. fr. Mineral. Crystallogr., 1977) revealed that elemental partition between minerals and magma is mostly governed by local structure of ion sites in crystalline phases, and accordingly elemental partition has been predicted by Nagasawa model or similar models. However, these models can not be applied to partition between fluid and melt, as these models do not explicitly treat these phases. Recently, the author found that "bond valence" method can be applied to predict partition behavior. Initial tests to crystalline phases are promising. So, I'm currently trying to extend this method to fluid and melt.

Bond valence method is an extension of Pauling's original idea, that valence of central cation can be divided into each bond in ionic crystals. I.D. Brown extended this by including bond distance dependence to bond valence; longer bond has lower bond valence. In ionic crystals, bond valence sum on central atom coincides with its valence or very close to it. If deviation is large, something wrong with the structure. To date, several authors compiled bond valence parameters using databases of crystal structures for almost all elements except rare gases. Therefore, if crystal structure (or at least local structure) is known, bond valence sum (bvsum) can be calculated. For example, if we put Sr in M2 site of forsterite, we will have bvsum larger than 2, as Sr ion is too large for M2 site. This difference is related to "strain" energy, as bond valence equation ($\exp((R_0 - r_{ij})/B)$) is identical to repulsive term of two-body inter-ionic potentials. So, I defined misfit parameter; $\text{misfit} = \text{abs}(\text{bvsum} - Q)$ where Q is valence of central cation. If we take difference of misfits between two distinct crystallographic sites (e.g., M1 and M2 sites of forsterite), it can be related to partition coefficient. In this way, "partition coefficient" of intra- and inter-crystalline phases are calculated, and they can compare well with experimental data. This calculation is very simple, and only bond distances and bond valence parameters are necessary. Prediction of partition behavior such as perovskite/postperovskite is now possible. It was found that bond valence method can be used to quantitatively predict elemental partition, however, there are several unsolved issues, such as how to quantitatively relate difference of misfits to partition coefficients, and how to treat different valences consistently etc.

If we know the local structures of fluid and melt, partition behavior can be qualitatively predicted using present method. However, this is not the case at moment. Therefore, single virtual site for each fluid and melt was assumed, then partition behavior between two sites was evaluated by changing size of the sites. Based on Pearce et al. (doi:10.1029/2004GC000895), Ba, Cs, K, Pb and Sr prefer fluid, whereas REE, Nb, Ta, Zr, Hf etc. prefer melt. Such behavior was reproduced when the size of the site for fluid is about 3.2 Å, and that of melt is 2.5 Å. Using this local structure model, partition behaviors of other elements can be predicted. Alternatively, local structures of fluid and melt could be estimated by comparing precisely determined partition data with present model.

Keywords: bond valence method, elemental partition, fluid, melt, local structure

Is the non-destructive analysis of carbon isotope ratio useful?

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Carbon is an important volatile element that has had a great influence on the environment of the Earth's surface through the history. Carbon dioxide has a greenhouse effect gas and this gas exhausted by our production activities is regarded as a cause of modern global warming.

Carbon dioxide is observed as the fluid inclusions in the mantle xenolith that is derived from deep earth. A paper reports that the integral exhaust amount of carbon from the deep earth is equal to the amount of the carbon that exists on the Earth's surface in present. Therefore it is important for the discussion of environmental issues to understand the origin of the deep earth carbon and the cycle of carbon using mantle xenolith.

The modern sampling method of carbon dioxide fluids (Crushing method) has two problems, the destruction of the samples and the shortage of the spatial resolution. The measurement of carbon isotope ratio using Raman spectroscopy has a possibility to break through those problems. However, this method hasn't had the precision to be able to discuss the origin of carbon dioxide fluids yet. In this study, we tried to improve the precision of the measurement of carbon isotope ratio using Raman spectroscopy using a micro-Raman spectrometer with high spectral resolution. Moreover, we discuss the cause of uncertainty depends on the result of measurement and the prospects for the future.

As a result of measurement, the uncertainty of this method is revealed $\pm 26\%$ (1σ) at 1500 sec. A reason of this bad uncertainty is the shortage of sensitivity of the Raman spectrometer. The lowness of signal noise ratio (S/N) with the low sensitivity causes a lack of precision of the peak fitting. We can estimate the ultimate precision of this method by assuming an infinite peak count using regression line. For the analytical system of this study, the limit value is $\pm 11\%$ (1σ), which is still worse than the precision to be able to discuss the origin of carbon in mantle xenolith.

The factor of this error is revealed the apparent Raman shift depends on the changing of room temperature. If it does not exist, the precision can improve to discuss the origin of deep carbon.

Keywords: carbon dioxide, fluid inclusion, Raman spectroscopy, mantle xenolith, carbon isotope ratio

