### Origin of geochemical mantle components: Role of spreading ridges and thermal evolution of mantle

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We explore the element redistribution at mid-ocean ridges (MOR) using a numerical model to evaluate the role of the decompression mantle melting process in the Earth' s geochemical cycle, particularly in the formation of the depleted mantle component. Our model uses a trace element mass balance based on an internally consistent thermodynamic-petrologic computation to explain the composition of MOR basalt (MORB) and residual peridotite. Model results for MORB-like basalts from 3.5 to 0 Ga indicate a high mantle potential temperature ( $T_n$ ) of 1650–1500°C during 3.5–1.5 Ga before decreasing gradually to 1320°C today. The source mantle composition changed from primitive (PM) to depleted as  $T_{\rm p}$  decreased, but this source mantle is variable with an early depleted reservoir (EDR) mantle periodically present. We examine two-stage Sr-Nd-Hf-Pb isotopic evolution of the mantle residues from melting of PM or EDR at MOR that formed ancient MORB-like basalts. Formation of depleted MORB source mantle (DMM) is also examined using modern MORBs. At high- $T_p$  (3.5–1.5 Ga), the MOR process formed extremely depleted DMM. This coincided with formation of the majority of the continental crust, the sub-continental lithospheric mantle, and the enriched mantle components formed at subduction zones. During cooler- $T_{\rm p}$ mantle conditions (1.5–0 Ga), the MOR process formed most of the modern ocean basin DMM. Changes in the mode of mantle convection from vigorous deep mantle recharge before ~1.5 Ga to less vigorous afterwards is suggested to explain the thermochemical mantle evolution.

Keywords: Depleted mantle, Thermal evolution, Chemical evolution

### Towards constitutive equations for the deep Earth

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Currently a full treatment of both bulk- and shear properties at conditions of high pressure is only available for the Birch-Murnaghan formulation based on power series expansion of the strain energy. This representation is most suitable for extrapolation to mid-mantle conditions. Fits to experimental data for high pressures frequently favour the Vinet or Keane equations of state for bulk-modulus, but in neither case is there any connection to shear.

However, by working with invariants of the stretch tensor suitable isotropic constitutive equations can be found that add-in shear properties in a consistent way via local representations about a pre-stressed state. Such constitutive relations are particularly useful for high-pressure phases in the deep Earth, and make only slight modifications to popular representations for the bulk modulus.

Keywords: Deep Earth physical properties, Bulk modulus, Shear modulus

# Rheology of $CaGeO_3$ (perovskite)±MgO: Implications for multiphase flow in the lower mantle

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With a thickness of well over 2000 km, the lower mantle is the largest rocky layer in Earth and plays a critical role in controlling dynamics of deep earth. Mineralogical mantle models suggest that the lower mantle is dominated by (Mg,Fe)SiO<sub>3</sub> bridgmanite (SiBr) and (Mg,Fe)O ferropariclase (Fp). In addition to rheological properties of these individual minerals, knowledge of stress/strain partitioning among the phases and texture evolution during deformation is critical in understanding dynamic processes of the deep Earth. Currently, there is a lack of experimental studies on lower mantle rheological properties, because of the difficulties in conducting quantitative experimental studies under lower mantle pressure and temperature conditions. Here we examine rheological properties of a two-phase polycrystalline assembladge consisting of CaGeO<sub>3</sub> perovskite (GePv) and MgO, deformed in the D-DIA with strain rates of  $^{-1}$  - 3×10 $^{-5}$  s $^{-1}$ ) at high pressures and temperatures (up to 10 GPa and 1200 K, respectively), with bulk axial strains up to ~40%. Stresses within individual phases are measured directly using in-situ monochromatic x-ray diffraction. GePv is found to have a strength 3 - 4 times that of MgO, a ratio similar to that between SiBr and Fp. Thus strain is expected to partition primarily into MgO. Elasto-ViscoPlastic Self-Consistent modeling (EVPSC) is used to reproduce experimentally measured lattice strain and texture of the two phase aggregate. Recovered samples are examined using electron back scattered diffraction (EBSD) and scanning electron microscopy (SEM), to extract final microstructural information. These results are compared with deformation of single-phase CaGeO<sub>3</sub> perovskite polycrystals. Active slip systems of the two phases, partitioning of stress and strain in the composite aggregate, and textural development will be discussed, with potential implications to the lower mantle. We find that texture development, which depends primarily on the level of shear strain, has a fundamental influence on the bulk rheology of multi-phase assemblages. A texture-induced rheological transition is likely to occur in certain regions of the lower mantle, profoundly affecting convection patterns in the Earth.

Keywords: multi-phase rheology, lower mantle, convection, mantle dynamics

### First principles investigation of high pressure behavior of FeOOH

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It has been believed that water is carried into the deep Earth' s interior by hydrous minerals such as the dense hydrous magnesium silicates (DHMSs) in the descending cold plate. A numbers of researches have been conducted so far about the high pressure behaviors of DHMSs. In recent years, we found new DHMS, phase H, at lower mantle pressure condition and the solid solution between phase H and d-AlOOH has been proposed as the most important carrier of water in the deepest part of Earth' s mantle (Tsuchiya 2013, Nishi et al. 2014, Ohira et al. 2014). However, those hydrous minerals are actually not denser than surrounding (dry) mantle minerals (Tsuchiya and Mookherjee 2015) and the gravitational stability in deeper part of the Earth is questionable. Therefore, the effects of denser element such as Fe on the stability of DHMS are intimately connected to the ability of transportation of water into Earth' s deep interiors. In order to assess the effect of Fe on the phase relation of phase H and d-AlOOH, we first investigated the high pressure behavior of the end-member composition of this system, the e-FeOOH. We have found the new high pressure transformation of FeOOH in the lower mantle conditions both theoretically and experimentally. Here, I show high pressure structures and the physical properties of these phases.

## Experimental investigation of high-pressure phase transitions in AIOOH and FeOOH

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Hydrogen is transported into deep Earth' s mantle regions as a form of hydrous minerals via subduction of oceanic plates. Recently discovered  $CaCl_2$ -type hydroxides such as (Mg,Si)OOH phase H, delta-AlOOH, and their solid solutions were reported to have large P–T stability fields that encompass conditions representative of the lower mantle, implying the possibility that surface water may be transported as far as the core-mantle boundary. However, although Epsilon-FeOOH has  $CaCl_2$ -type structure as well, the solid solution of FeOOH component in  $CaCl_2$ -type structure has not been studied. Since FeOOH was recently reported to decompose under the lower-mantle conditions to form FeO<sub>2</sub> releasing H<sub>2</sub>, FeOOH could be a key component that strongly affect the stability of  $CaCl_2$ -type hydroxide. Here, we report the results of in-situ X-ray diffraction and theoretical studies on AlOOH and FeOOH using a laser-heated diamond anvil cell technique at up to ~200 GPa. In contrast to the previous work suggesting the dehydration of FeOOH in the middle of the lower mantle, we report the formation of a pyrite-type FeOOH that is significantly denser than the surrounding mantle and stable to conditions representative of its base. Furthermore, delta-AlOOH and CaCl<sub>2</sub>-type (Al,Fe)OOH also transform to a pyrite-type structure at higher pressures. Based on these experimental and theoretical results, the stability of hydrous phase in the lower mantle and deep interiors of icy planets will be discussed.

キーワード:含水鉱物、高圧 Keywords: hydrous mineral, high pressure

### ニュートリノ振動を用いた核・下部マントル中の水素の探索 Search for hydrogen in the Earth's core and lower mantle using neutrino oscillations

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近年、下部マントルはこれまで想定されていたよりも多くの水を含みうることが報告された。また、外核中 に含まれる軽元素として、水素が着目されている。しかし、下部マントルや外核のサンプリングすることは現 状では困難であることから、地球深部の水素量についての情報を直接得ることはできない。

一方、近年の高圧実験の目覚ましい進歩により、地球深部の温度圧力条件を実験室中で再現することが可能 となり、地球深部の化学組成に制限を与えている。しかし、地球深部と同じ温度圧力条件下で、地球深部と同 じ弾性波速度を再現する化学組成モデルは複数存在しうるため、高圧実験だけから地球深部の化学組成を決定 するのは困難である。

上述のように、地球外核の化学組成、特に水素量を知る手掛かりは限られているのが現状であ る。我々は、これまで、大気ニュートリノを用いた外核の組成測定についての研究を行ってきた。この研究は 下部マントル中の水分量の測定にも応用可能である。また、太陽ニュートリノを用いることで、さらに感度を 向上させることが可能であることを新たに発見した。

ニュートリノとは素粒子の一種である。ニュートリノは反応断面積が小さい、言い換えると物質貫通能力が 高いため、地球を容易に貫通することができる。ニュートリノには3つの種類があり、それぞれ電子 型、ミュー型、タウ型と名付けられている。ニュートリノは大気中や、太陽中で絶えず生成されており、光を 除くと、地表面で最も数の多い素粒子である。

ニュートリノは、ニュートリノ振動という、他の素粒子に無い特異な性質を持っている。ニュートリノ振動 とは、ニュートリノの種類が時間と共に別の種類のニュートリノに変化する現象のことを指す。例えば、生成 された際はミュー型ニュートリノであったものが、電子型ニュートリノとして検出される、等である。変化す る確率は、ニュートリノの混合角、質量、そして周囲の電子数密度によって一意に決まり、混合角や質量は他 の実験から測定できるため、ニュートリノ振動を精度よく測定することによって、物体の電子数密度を測定す ることができる。

従って、大気中や太陽中で生成され、地球を貫通したニュートリノを測定することで、地球深部の電子数密 度分布を測定することが可能となる。地球内部の物質密度は、地震波や地球の自由振動の測定等から、精度よ く決まっている。物質密度と電子数密度の比は、質量数と原子番号の比(Z/A)に等しいため、ニュートリノ振動 の測定から、地球深部の平均化学組成を得ることができる。岩石のZ/Aはおよそ0.5、鉄のZ/Aはおよそ0.47で あるのに対し、水素のZ/Aは1であるため、ニュートリノ振動は特に水素に感度が高い。この性質を用い て、地球深部での水素の探索を行うことが可能である。

ニュートリノは既に多くの実験によって測定がなされている。我が国が誇るスーパーカミオカンデやカムランド、南極にあるlceCube等が有名であるが、既存の実験では、地球深部の化学組成を十分な精度で測定する ことはできない。スーパーカミオカンデでは統計精度が足りないため、カムランドやlceCubeでは感度のある エネルギー領域が異なるためである。地球深部の化学組成測定に必要となるのは、10億電子ボルトから100億 電子ボルトの間の、大気中で生成されたニュートリノ、または数百万電子ボルトから数千万電子ボルトの間 の、太陽中で生成されたニュートリノを、十分な感度で測定することのできる装置である。現在、ハイパーカ ミオカンデ、IceCube Gen2 Phase-1、ORCA等、次世代のニュートリノ観測実験が複数計画されており、そ れらを用いることで、近い将来に地球深部の平均化学組成を測定することが可能となる。

本講演では、ニュートリノ振動を用いた地球深部の水素量の探索について、特に下部マントル中の水分量の 測定について述べる。

キーワード:化学組成、下部マントル、外核、ニュートリノ Keywords: chemical composition, lower mantle, outer core, neutrino



## Waveform inversion for the 3D elastic and anelastic structure of the lowermost mantle beneath the western Pacific

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We invert seismic waveforms data for the 3D shear velocity ( $V_s$ ) and attenuation (measured by the quality factor, Q) structure of the lowermost mantle beneath the western tip of the Pacific low shear velocity province (LLSVP). Our dataset consists of seismic waveforms from F-net for 31 deep earthquakes beneath Tonga and Fiji, and shows regional variations of S and ScS arrival times and amplitude ratios. Residuals between arrival times and amplitude ratios of peak-to-peak amplitude of S and ScS vary from west to east in the target region, as illustrated by inversion of our dataset for radial models of VS and Q in three subregions. The model explains lateral variations in those values. However, while the distribution of the travel time for the obtained 1D model (shown in the left) seems homogeneous, the other still shows lateral variation from west to east, that is we can see large values around 165 E. 10 N. In this study, in order to extract more information on the 3D structure from our dataset, in particular using waveform, we extend our 1D approach by dividing our region of interest in a larger number of subregions, which, when assembled together, provide a 3D elastic and anelastic model of the region. We show distribution of resolution for 3D structures and improvement of waveforms in several ways (not only peak-to-peak times and amplitudes but waveform variance, peak sharpness). We further discuss about the possibility to build models using stochastic inversion methods. Finally, we establish preliminary 3D joint models of V<sub>s</sub> and Q for the western tip of the Pacific LLSVP.

キーワード:波形インバージョン、最下部マントル Keywords: Waveform inversion, lowermost mantle



## Correction of ScS–S travel times for 3D mantle structure to reveal shear wave azimuthal anisotropy in the lower mantle

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ScS–S differential travel times have contributed to reveal heterogeneity in the lower mantle. However, azimuthal anisotropy has not been fully considered probably due to insufficient azimuthal coverage. Recent increase of large scale seismic arrays and networks improves the coverage. Here we collected the seismograms from NECESSArray (Northeastern China), F-net (Japan), INDEPTH (Tibet), a seismic network in Thailand, whose ScS bounce points are located beneath Philippine with various azimuths. Observed ScS–S differential travel time residuals with respect to PREM show a large scattering with a standard deviation of about 2.6 s and significant apparent azimuthal variation. When a cos 2*a* (*a* is a propagation azimuth of the seismic ray) curve is fitted by least squares, we find that the fastest azimuth is about 103° measured from the north in clockwise and the amplitude of the azimuthal variation is about  $\pm$  1.4 s. However, it is quite difficult to recognize that the azimuthal variation truly reflects the anisotropy in the lower mantle due to the large scatter of the travel time residuals.

To reduce the scattering of the data, we corrected for 3D mantle S-wave velocity structure models (e.g., S16U6L8, SB4L18, SH18CEX, S40RTS, SEMUCB-WM1). Unfortunately, the large scattering is not fully improved by using any models probably due to a poor resolution in the upper and uppermost lower mantle. However, if we use the 3D P-wave velocity model GAP-P4 (Obayashi et al., 2013) with an assumption of dlnVs/dlnVp=1.7, the scattering is significantly reduced (the standard deviation is about 1.3 s). After this mantle correction, the amplitude of the cos 2*a* function becomes  $\pm 0.4$  s. However, the fastest direction is about 105°, which is almost same as in the case of the original data.

キーワード:下部マントル、異方性 Keywords: lower mantle, anisotropy

## *Ab initio* anharmonic lattice dynamics calculation for Fe-bearing lower mantle minerals

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Determination of lattice thermal conductivity ( $\kappa_{lat}$ ) of lower mantle minerals is key to understanding the dynamics of the Earth's interior. Although it was impractical in the deep Earth pressure (*P*) and temperature (*T*) condition for a long time, recent experimental and computational developments have been extending the accessible *P* and *T* ranges. We recently succeeded in developing an *ab initio* technique to calculate  $\kappa_{lat}$  at any *P* and *T* condition based on the density-functional theory (DFT) combined with anharmonic lattice dynamics theory. The technique was then applied to major end-members of lower mantle minerals, MgSiO<sub>3</sub> bridgmanite (Dekura,Tsuchiya,Zo13,PRL) and MgO periclase (Dekura,Tsuchiya,2017,under review). Next we extend our technique to more realistic Fe-bearing minerals in conjunction with the internally consistent LSDA+*U* technique (Wang,Tsuchiya,Hase,2015,Nature geoscience) to deal with such strongly-correlated systems. In this presentation, we introduce the current situation of our research on  $\kappa_{lat}$ .

キーワード:下部マントル鉱物、格子熱伝導率、コンピュータシミュレーション、フォノン-フォノン相互作 用、密度汎関数理論

Keywords: Lower mantle minerals, Lattice thermal conductivity , Computer simulation , Phonon-phonon interaction , Density-functional theory

# Constraints on lowermost mantle structure from core-mantle boundary dynamic topography

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Mantle flow induces dynamic topography at the core-mantle boundary (CMB), with distribution and amplitude that depend on details of the flow. To assess whether CMB topography can bring constraints on the deep mantle structure, we calculate the CMB dynamic topography associated with different models of mantle convection, including thermo-chemical and purely thermal models. We investigate the influence of key controlling parameters, more specifically the thermal viscosity ratio ( $\delta \eta_{\tau}$ ) and, for thermo-chemical models, the chemical density contrast (  $\delta \rho_{c}$ ) and viscosity ratio (  $\delta \eta_{c}$ ) between primordial and regular materials. In purely thermal models, plume clusters induce positive topography with an amplitude that decreases with increasing  $\delta \eta_{T}$ . In thermo-chemical models with  $\delta \rho_{C}$  around 100 kg/m<sup>3</sup> or more, reservoirs of dense material induce depression in CMB topography, surrounded by a ridge of positive topography. The average depression depth and ridge height increase with increasing  $\delta 
ho$ <sub>c</sub> and  $\delta \eta_{c'}$  but decrease with increasing  $\delta \eta_{\tau}$ . We find that for purely thermal models or thermo-chemical models with low  $\delta \rho_{c}$ , 90 kg/m<sup>3</sup> and less, the long-wavelength (spherical harmonic degrees up to I = 4) dynamic topography and shear-wave velocity anomalies predicted by thermo-chemical distributions anti-correlate. By contrast, for models with  $\delta \rho_{c}$  100 kg/m<sup>3</sup> and  $\delta \eta_{c} > 1$ , long-wavelength dynamic topography and shear-wave velocity anomalies correlate well. This potentially provides a test to infer the nature, thermal or thermo-chemical, of low shear-wave velocity provinces (LLVSP) observed by global tomographic images. The presence of post-perovskite (pPv), provided that the viscosity of this phase is similar to that of bridgmanite, does not alter these conclusions. If the viscosity of pPv is lower than that of bridgmanite by 2 or 3 orders of magnitude, however, more substantial changes may arise.

Keywords: Mantle convection, Core-mantle-boundary topography, Mantle structure

## Waveform inversion for whole mantle 1-D S-velocity and Q structure beneath Central America and the Caribbean

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We simultaneously infer the 1-D S-velocity and anelastic (Q) structure in the whole mantle beneath Central America using waveform inversion. Our dataset consists of ~8000 transverse components recorded at USArray broadband stations from ~40 intermediate- and deep-focus events in South America. We use waveforms in time windows cut around the minor arc arrivals which include body-wave arrivals (e.g. Sn, sSn) as well as multiple reverberations at the core-mantle boundary (ScSn, sScSn). These data provide constraints on the difference in Q structure between the upper- and lower-mantle. We use the Born approximation to compute partial derivatives for 1-D shell perturbations at depth increments of 20 km in the whole mantle. Our model is parametrized in radial splines formed by linear combination of those 20 km-increment perturbations. Synthetic tests suggest that our dataset and method can simultaneously resolve the 1-D S-velocity and Q structure in the whole mantle. Knowledge of both the S-velocity and Q structure can help to provide constraints on the origin of the S-velocity anomalies, i.e., whether they are of thermal or chemical origin.

Keywords: Waveform inversion, Earth's mantle, Anelastic structure

### 地球史を通じたマントルダイナミクスの歴史 Mantle dynamics of the Earth through time

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1990年代に太平洋中央部におけるスーパープルームの存在が明らかになって以来、プルームやスーパープ ルームの原理が長く議論されてきた。また、プルームやスーパープルームの駆動力についても議論が進み、特 に、中心核のみを熱源としてこれらの現象を説明できるかという議論がある。おそらく、核は熱源としては不 十分で、重要な熱源としての役割を果たしたのは、放射性源元素(主にウラン、カリウム、トリウム)を豊富 に含む花崗岩(TTG)だと考えられる。これらの岩石は、地球内部のD"層やマントル遷移層(深さ410-660km)に滞留しており、プレートテクトニクスによって沈み込み帯から地球深部に運ばれたものである。特 に、冥王代の地球表層に存在したと考えられる原初大陸はCMBに存在しているはずである。こうした原初大陸 の分布は、表層地質の記録にっ基づくマントルダイナミクスモデルによってすでに明らかにされている (Kawai et al., 2008, Tsuchiya and Maruyama, 2012, Maruyama et al., 2015; Zhao et al., 2017). D"層に蓄積した原 初大陸の物質は、放射性元素の崩壊熱によって発熱し、固体核を溶融させ、液体核を作った。そして、そのこ とによって、地球磁場を形成することになった。

地球史におけるマントルダイナミクスを議論するためには、揮発性物質、特に水の存在とその役割を理解す ることが最も重要で、含水プルームを地下410kmで発生させる最も重要な要素である。したがって、含水鉱 物の安定領域やベニオフ面にそった温度勾配とその地球史を通じた変化の理解が必要不可欠である。

キーワード:水の関与、含水プルーム、スーパープルーム、冥王代の原初大陸 Keywords: presence of water, hydrous plume, superplume, Hadean primordial continent

### Chemical exchange between core-forming metal and magma ocean in the early differentiating Earth

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The differentiation of the Earth into its metallic core and silicate mantle and crust was among the most profound events shaping the planet in its early history, and the geochemical consequences of this event remain today, recorded in the composition of minor and trace elements in the core and mantle. Inferences can be made on the nature of the physical and chemical aspects of planetary differentiation by experimentally investigating metal-silicate partitioning of these elements under the range of thermodynamic conditions that are appropriate to the core-forming event. We report metal silicate partitioning of several key elements at high pressure, high temperature conditions. The experiments were performed using laser heated diamond anvil cells, and the samples were recovered and analyzed using focused ion beam / high resolution electron microscopy (FIB/SEM). Heat producing elements such as uranium partition into the metallic melt at high P,T conditions to a higher degree than previously observed, but still only produce <2 TW of heat in the core 4.5 Gyr ago. Partitioning of tungsten, a moderately siderophile element, places additional constraints on the range of P,T conditions that best describe the trace element composition of the modern mantle. Light lithophile elements including magnesium can dissolve into a metallic core-forming melt at sufficiently high temperature, and their exsolution can contribute to buoyant energy release as the early core cooled. These observations contribute to models of the early thermal and chemical evolution of the Earth's deep interior.

Keywords: planetary differentiation, metal-silicate partitioning, experimental petrology

# Light elements in the core based on elemental partitioning experiments between Fe-S melts and silicate magma

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The compositions of Earth's core are important research topics to understand the Earth's deep interior and evolution. Seismological observations provided density and sound velocity data of the Earth's interior. Comparing with experimental studies on density of Fe under the core conditions, the observed Earth's core densities are smaller than those of pure Fe. These results implied an existence of light elements in the core and the species and amount of light elements have remained still unknown. The terrestrial magma ocean was formed in the early Earth. During the core separation from the magma ocean, elements are assumed to be partitioned between molten iron and silicates melts at the base of the magma ocean. Therefore, clarification of partitioning behavior of the Earth materials at high pressure and temperature is important for understanding characteristics of the Earth's core.

In this study, partitioning experiments between silicate (garnet) melts and metallic liquids (Fe-8wt%Sulfur) were conducted by using a diamond anvil cell combined with a fiber laser heating system. The experiments were carried out at the pressures between 52 and 76 GPa and the temperatures between 3140 and 5140 K. Recovered samples were cut and polished by FIB. Chemical analyses were performed using FE-SEM/EDS and metal/silicate partitioning coefficients ( $D_{Si}$ ) and exchange partitioning coefficients ( $K_{D}$ ) of silicon were determined.

The results demonstrated a strong oxygen fugacity dependence of  $D_{Si}$  to be negative and a positive temperature dependency of  $K_{DSi}$ . In this study, Si was less partitioned in the metal phase than previous studies of partitioning using Sulfur-free iron as a metal, suggesting less Si in the metal phase which S is included in. The present result suggests that the existence of S in the metal phase might affect the partitioning behavior of Si during the magma ocean. Assuming the values of Si content in the core and oxygen fugacity from geochemical constraints, 2.3<sup>°</sup>6.1 wt% of S in the core can explain the partition between the core and mantle at 4200 K. When the estimated temperature of the bottom of the magma ocean was lower, the abundance of S would be smaller.

キーワード:軽元素、核、マントル Keywords: Light elements, core, mantle

# Reconciling Magma-Ocean Crystallization Models with the present-day Structure of the Earth's mantle

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Terrestrial planets are thought to experience episode(s) of large-scale melting early in their history. Studying the crystallization and fractionation of terrestrial magma oceans (MO) can provide constraints for the initial condition and thermochemical evolution of solid-state mantle convection. MO fractionation leads to unstable stratification within the cumulate layer due to progressive iron enrichment upwards, but the effects of incremental cumulate overturn that may occur during MO crystallization remain to be quantitatively explored. Here, we use geodynamic models with a moving-boundary approach to study convection and mixing within the growing cumulate layer, and thereafter within the resulting, fully-crystallized mantle. For fractional crystallization, pronounced stratification leads to incremental cumulate overturns during MO freezing and hence efficient cumulate mixing, except for the most iron-enriched final-stage cumulates, which remain unmixed and persist for billions of years near the base of the mantle. Less extreme crystallization scenarios can lead to somewhat more subtle stratification and more pervasive mixing. However, MO cooling models indicate that fractional crystallization should have been dominant at least during the slow final stages of MO freezing. The long-term preservation of strongly iron-enriched cumulates at the base of the Earth' s mantle as predicted by MO fractional-crystallization models is inconsistent with seismic constraints. Based on scaling relationships, however, we infer that final-stage Fe-rich MO cumulates should thermally equilibrate during overturn and sinking, and hence undergo melting and reaction with the host rock. The resulting moderately iron-enriched hybrid rock assemblages should be preserved in the deep mantle through the present day. In contrast to the original strongly-enriched final-stage cumulates, moderately iron-enriched hybrid rock assemblages can much better reconcile the physical properties of the large low shear-wave velocity provinces in the present-day lower mantle. Thus, we reveal Hadean melting and rock-reaction processes by integrating simplified MO crystallization models with the present-day seismic snapshot.

Keywords: Magma Ocean, Large-Low Shear Wave Velocity Province, Lower Mantle

### The sound velocity measurements of FeO at high pressure and temperature: Implications for the low velocity anomaly around the core-mantle boundary

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Wustite,  $Fe_{1-x}O$ , is one of the most important oxides in the Earth because it is an endmember of ferropericlase, (Mg,Fe)O, which is one of main phases in the Earth' s lower mantle. In addition, it is also significant for understanding the composition of planetary cores. Seismological data reveal physical properties of the Earth' s interior, such as velocities ( $V_p$ ,  $V_s$ ) and density. Although the seismological velocity profile of the Earth' s interior can provide us an important knowledge about structure and chemical compositions, there are few experimental reports about the sound velocity of Fe-light elements system including FeO at high pressure and temperature.

Here, we report  $V_P$  of FeO up to 86 GPa and 2500 K based on a combination of the laser-heated diamond anvil cell and inelastic X-ray scattering measurements at BL35XU of SPring-8. In this experimental condition, FeO shows B1 phase and rhombohedral one, which has a distorted B1 structure. We find difference in velocity between them.

Based on our results, we could obtain the Birch's law for FeO. This relation is extrapolated to the inner core condition. Combining with Birch's law of Fe, we compared the density-velocity linear relation of Fe-FeO system to PREM. This relation is inconsistent with the seismic data of the inner core. In other words, oxygen is not suitable in the inner core as a major light element.

Seismological observations indicate a chemical heterogeneity in the deep lower mantle, and FeO can play an important role to cause the heterogeneity. Several processes have been proposed to account for formation of the enriched FeO region around the core-mantle boundary.

We can find that the velocity of FeO is smaller than that of lower mantle minerals. That is, an addition of FeO to the lower mantle can make a low velocity anomaly, such as ULVZs (ultra-low velocity zones).

キーワード:FeO、弾性波速度、密度、非弾性X線散乱、X線回折 Keywords: FeO, Sound velocity, Density, Inelastic X-ray scattering, X-ray diffraction

# Can the Earth's core be the source of primordial noble gases in the mantle?

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It has been suggested a number of times that the Earth's core could be the source of primordial noble gases (He, Ne, Ar, etc) observed in OIBs. The core is an attractive option for storing noble gases since it has remained mostly isolated from the convecting mantle since its formation 4.5 Ga. This view is supported by experiments show that He partitioning into Fe during core formation at elevated pressures (>10 GPa) is higher than previously thought. However, even if the core does contain primordial noble gases, there has to be a mechanism for incorportating them into OIBs. Small amounts of background degassing from the core into the mantle does not work since the noble gases will simply mix into the convecting mantle and the primordial signal will appear to be the same in both OIBs and MORBs.

We propose an alternative model whereby noble gases diffuse from the core into the base of the large low shear velocity provinces (LLSVPs), where they are stored and concentrated until sampled by plumes. To assess the viability of this model, we have determined the diffusion coefficients of He, Ne and Ar in lower mantle minerals by first-principles methods. We show that diffusion of these noble gases is sufficiently fast that they can concentrate into LLSVPs. However, diffusion is not fast enough to concentrate noble gases throughout LLSVPs and some sort of mixing within LLSVPs is needed. Assuming that LLSVPs are internally convecting, and assuming a range of reasonable mixing times for LLSVPs, we show that LLSVPs can act as a staging post for noble gases and allow them to build up in concentration over time. If LLSVPs are then periodically sampled by plumes, this provides an attractive method for sampling primordial noble gases originally residing in the core.

Keywords: Core, Mantle, Noble gases, Diffusion, Ab initio, First principles

#### Light element isotope fractionation processes in the deep Earth

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Partitioning of light elements and the distribution of isotopes between silicates in the mantle and metallic melts in the core during the early Earth differentiation and accretion process have governed the present day elemental and isotopic composition of the bulk silicate Earth. However, little is known till date about the factors that controll these processes in the deep Earth, especially in the core-mantle boundary, since we are unable to gather informaion from natural samples and yet to clearly reproduce the equillibrium conditions at high-pressure and high-temperature experiments. Especially, the role of light elements in the melting phase relations of mantle rocks, metal-silicate partitioning, and mass transfer between core and mantle are key in understanding the processes going on in deep Earth. Stable isotopic compositon is widely and efficiently used tool to understand the mobility of light elements in the deep Earth environments. Here I present a review of experimental determination of partitioning of light element isotopes at high-pressure and high-temperature conditions, in systems analogous to magma ocean environment where aggregation of core has happened and in the mantle conditions where recycling occurred thereafter.

A review of the previous experimental studies in the Fe-C and Mg-Si-C-O systems suggest that large carbon isotope fractionation occur between graphite/diamond and iron carbide melt. The results indicate that the iron carbide melt will preferentially gather <sup>12</sup>C than <sup>13</sup>C, and has a strong temperature dependence. Factionation is also observed between graphite/diamond and carbonate melt at temperatures and pressures corresponding to upper mantle conditions. The pressure dependence on carbon isotope fractionation is also being tested at higher pressure conditions. Preliminary results indicate that carbon isotopes also fractionate at high pressures corresponding to the deep Earth. Recent results in the sulfur, nitorgen and hydrogen sytem are consistent with the carbon-bearing system, that lighter isotopes generally fractionate to the metallic melt and heavier isotopes to the silicate melt. In order to understand the factionation process in detail, it is essential to have accurate measurement of isotopic composition for the run products at high-pressures. The difficulty arises from the smaller volume of samples, separation of phases and confirmation of equilibration between the phases. Ongoing studies on microvolume isotope measurements using laser ablation and curie point pyrolyser gave encouraging results with good accuracy.

It is anticipated that the combined high-pressure and high-temperature dependent fractionation of light element isotopes in the deep Earth is an effective mechanism that can create a "lighter core" with large scale differences in the distribution of the isotopes between the metallic core and bulk silicate Earth during the accretion and differentiation of early Earth. Our findings also have implications on the light element cycling at the core-mantle interface.

Keywords: Isotope fractionation, Deep Earth, Metallic melt-silicate fractionation

# Effects of Fe and Al incorporations on ${\rm MgSiO}_3$ postperovskite phase boundary

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MgSiO<sub>3</sub> bridgmanite (Br) will undergoes a post-perovskite (PPv) phase transition[1,2,3] in the pressure (*P*) and temperature (*T*) conditions corresponding to the Earth's D" layer. Therefore, The phase change is recognized as the key for understanding the seismological observations in the D" layer. However, to date, it is still a challenging subject to determine the phase transition boundary preciously in the geophysically relevant Fe and Al-bearing compositions. Based on the first-principles methods combined with the internally consistent LSDA+*U* method and the lattice dynamics approach, the high-*P*,*T* thermodynamics of the MgSiO<sub>3</sub> phases are directly calculated with incorporation of 6.25 mol% of Fe<sup>2+</sup>, Fe<sup>3+</sup>Fe<sup>3+</sup>, Fe<sup>3+</sup>Al<sup>3+</sup>, and Al<sup>3+</sup>Al<sup>3+</sup> [4,5]. Using calculated free energies, we determine the PPv phase boundaries for Fe and Al-bearing compositions. Our results show that at 2500 K, incorporations of Fe<sup>3+</sup>Fe<sup>3+</sup> and Fe<sup>3+</sup>Al<sup>3+</sup> span coexisting domains between Br and PPv significantly with lowering the transition pressure, in contrast to the Fe<sup>2+</sup> and Al<sup>3+</sup>Al<sup>3+</sup>-bearing cases.

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Keywords: First-principles method, internally consistent LSDA+U, MgSiO3, postperovskite

# Experimental study on chemical interaction at the core-mantle boundary

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The core-mantle boundary (CMB) is the biggest physicochemical discontinuity in the Earth's interior. Abundance of siderophile elements in the Earth's mantle is much higher than that predicted from the partitioning study at low pressure. Chemical interaction across the CMB after core formation is one of candidates to realize the observed geochemical affinity as well as late veneer hypothesis. Hayden and Watson (2007) suggested that the diffusivities were high enough to allow transport of a number of siderophile elements over geologically significant length scales (tens of kilometres) over the age of the Earth based on grain-boundary diffusion of siderophile elements through polycrystalline MgO. On the other hand, enrichment of iron may occur at the bottom of the mantle, leading to low seismic-wave velocities and high electrical conductivity. Otsuka and Karato (2012) suggested that iron-rich melt could be transported 50 to 100 kilometres away from the core-mantle boundary by a morphological instability, providing an explanation for the iron-rich regions in the mantle. Thus there are potential fast pathways for chemical communication at the CMB. However, the dominant lower mantle mineral is not periclase but silicate minerals such as bridgmanite. In this study, validity of these processes in bridgmanite or post spinel experimentally investigated.

A study on the metal infiltration to bridgmanite, postspinel and ferropericlase was also performed using a Kawai-type multianvil press at 25 GPa and temperatures of 1600-2000 °C. Although significant penetration of metallic phase through the grain boundary was observed in only ferropericlase aggregates, iron alloy penetration to bridgmanite and postspinel was not observed. This result indicates that capillary force and morphological instability to enrichment does not contribute to the enrichment of iron and siderophile elements in the Earth' s silicate mantle.

A study on the grain boundary diffusion of siderophile elements (W and Re) in bridgmanite and postspinel was performed using a Kawai-type multianvil press at 25 GPa and above 1600 °C. The grain boundary diffusion of W in post spinel is faster than that in bridgmanite, and is only effective under highly oxidized condition. Such oxidized state at the core-mantle region is realized by accumulation of the sinking slab. Although the core-mantle interaction after the core formation can change W isotope in the mantle through the convection, it would be limited.

キーワード:核ーマントル境界、浸透、拡散 Keywords: core-mantle boundary, infiltration, diffusion

### Thermo-chemical evolution of Earth's core in a coupled core-mantle evolution –Stably stratification or light element precipitation

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Two possible resources for thermo-chemical convection of Earth's core occurred in the core-mantle boundary region have been proposed, which are dissolution of light element working for the negative feedback of cooling rate and age of the inner core [O' Rourke and Stevenson, 2016; Badro et al., 2016] and diffusive processes for reactant caused by core-mantle chemical reaction [Buffett and Seagle, 2010; Gubbins and Davies, 2012]. In this investigation, we make an assessment for those two mechanisms in a coupled core-mantle evolution model based on numerical mantle convection simulations plus core energy balance model based on formulations provided from Labrosse [2015] as a function of melting temperature of iron alloy, initial CMB temperature and thermal conductivity of Earth' s core such that several constraints of evolution of Earth' s core can be satisfied (Continuous generation of magnetic field for instance). With diffusive processes caused by core-mantel chemical reactions, the initial CMB temperature should not be quite high plus high CMB heat flow because the heat transfer system is dominated by the isentropic effects. Whereas, with dissolution of light elements, the initial CMB temperature should not be quite high either but the heat flow across the CMB would be quite low. On the thermal conductivity of Earth' s core, for the best-fit parameter set found in both processes, it would not be quite high value that would not be consistent with thermal conductivity measurements based on electrical resistivity [Gomi et al., 2013; Ohta et al., 2016]. Further discussions will be done in the presentation.

キーワード:熱化学進化、コアーマントル化学結合 Keywords: thermo-chemical evolution, core-mantle chemical coupling

### Ab initio prediction of potassium partitioning into the Earth's core

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Silicate earth is depleted in potassium compared with chondrites [Wasserburg et al., 1964, Science]. Barely varying ratios of potassium isotope in chondrite, lunar and earth samples suggesting evaporation cannot be responsible for the missing of potassium [Humayun and Clayton, 1995, GCA]. The finding of a change in electronic structure of potassium from alkaline- to transition metal-like at high pressure highlighted the possibility of its incorporation into the core [Parker, 1996, Science]. If potassium is present, even ~ppm, the radiogenic heat produced by <sup>40</sup>K could be an important energy source for geodynamics [Labrosse, 2001, EPSL]. The potassium content in the core is determined by its partitioning behavior between silicate and metal system, which could be affected by many factors such as temperature, pressure, compositions of the metal (the type and content of light elements) and silicate systems (nbo/t: the ratio of non-bridging oxygen to tetrahedral cations) [Bouhifd etal., 2007, EPSL; Muthy etal., 2002, Nature]. However, previous experimental studies provided contradictory results of potassium incorporation into the core uncertain.

Ab-initio free energy simulations based on molecular dynamics conbined with thermodynamics integration[Taniuchi, 2014] are performed to investigate whether and how much potassium can enter the metal system. Potassium partition coefficient( $D_k$ =Kwt%<sub>metal</sub>/Kwt%<sub>silicate</sub>) is determined as a function of pressure, temperature and composition by calculating the Gibbs free energy changes of its exchange reactions in different conditions. Helmholtz free energy is estimated with "thermodynamic integration" by computing the difference between two systems with different potential energy functions[Kirkwood, JCP, 1990].

Calculations performed from 3000 K to 5000 K suggest that temperature has no distinct effect in potassium incorporation into Fe-alloys. Results of  $D_k$  obtained from 20 GPa to 135 GPa at constant temperature and composition reveal that potassium partitioning behavior has a negligible pressure dependence. Besides, the potassium partial density of states (pDOS) shows its electronic structure remains to be alkaline metallic even at 135 GPa. Simulations show a limited effect of Al concentration in silicate composition to potassium solubility into metal system.

Influences of the light elements (O and S) proposed to be responsible for the density deficits of the core to potassium partitioning are also investigated in this study. Potassium solubility seems unchanged when the S content of the metal system increases. Simulations with oxygen free metal composition suggest that potassium will completely sequester into silicate system. However, with the presence of oxygen in metal, potassium will start its incorporation into metal system. Our results suggest that effects of temperature, pressure, silicate composition and S content are insignificant, while oxygen controls potassium partitioning between silicate and metal system.

Keywords: Ab initio, Potassium, Earth's core

### An Introduction to Using Neutrinos for Understanding Geodynamics

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Neutrinos from radioactive decays deep in the earth reveal the location of the heating that drives most geodynamics. We will present a sketch of the physics and of the neutrino production, largely from U and Th decay, the neutrino propagation and detection. Only two experiments so far have detected these "geoneutrinos" coming out of the earth, but there are long term plans to study the distribution of the sources. We will discuss current plans and these prospects.

Keywords: neutrino, Uranium, Thorium, Mantle Heating

### 日本島弧地殻のウラン・トリウム濃度:マントル由来地球ニュートリノフ ラックスの制約に向けて

### U and Th abundances of crustal rocks in the Japan Arc: Towards better constraints on the geoneutrino flux from the mantle

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It has been widely assumed that the bulk silicate Earth (BSE) has chondritic relative abundances of refractory-lithophile elements. The validity of this long-standing paradigm can be potentially addressed using electron antineutrinos produced within the Earth, the so-called geoneutrinos. The geoneutrinos have been measured with two liquid scintillator detectors at KamLAND in Japan and Borexino in Italy. Once the crustal contribution to the measured total geoneutrino fluxes are well established by determining U and Th distributions around the detectors, the data allow us to determine the absolute U and Th abundances in the mantle with sufficient precision to evaluate the chondritic BSE model, in particular whether highly incompatible refractory-lithophile elements are significantly (~50%) depleted as inferred from an impact-erosion model. Yet, the U and Th distributions in the Japan Arc crust, in particular deep crust, are still poorly constrained.

For better understanding of U-Th distributions in the Japan Arc, we have compiled previously reported U-Th abundance data for crustal rocks in the Japan Arc and further conducted petrology and geochemistry on mafic-ultramafic xenoliths from Oki Dogo. The equilibrium temperatures of two-pyroxenes indicate their derivation from the depth of 25-35 km. By combining the compiled data and newly obtained data, we found that the relative abundances of U and Th of the Japanese deep crust are distinctive from those of the deep crust in cratonic regions. The discrepancy may reflect that the Japan Arc crust was formed under more oxidized conditions as compared to the cratonic deep crust. In the presentation, we will further discuss about a methodology for combining these rock data with seismic data to estimate the U and Th distributions within the deep crust over the wide area.

キーワード:ニュートリノ、コンドライト質地球、全ケイ酸塩地球 Keywords: neutrino, chondritic Earth, bulk silicate Earth

# Application of nano-polycrystalline diamond to novel ultrahigh-pressure technology

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Nano-polycrystalline diamond (NPD) developed at GRC, Ehime Univ., is known to be harder than conventional sintered polycrystalline diamond (SD) and single crystal diamond, and is potentially important as anvil material for various types of high-pressure apparatus. Some successful applications of NPD to both diamond anvil cell (DAC) and Kawai-type multianvil apparatus (KMA) have been achieved, including higher pressure generation in these apparatus and some mineral physics applications in deep Earth sciences. For DAC, the following progress has been made in the last couple of years; generation of pressures exceeding 500 GPa in a double-stage DAC (Sakai, Yagi, et al.), invention of rotational DAC for rheological studies in Mbar regime (Nomura, Azuma et al.), and successful applications to large DAC for high-pressure neutron (Komatsu et al.), X-ray absorption (Ishimatsu et al.; Pascarelli et al.) and X-ray Raman (Fukui et al.) studies. Some attempts have also been made using NPD anvils for Mbar generation (Kunimoto & Irifune) in KMA, demonstrating its potential importance as the third-generation anvil material, after tungsten carbide and sintered polycrystalline diamond. The current status of applications of NPD in these techniques will be reviewed with some future perspectives.

キーワード:ナノ多結晶ダイヤモンド、超高圧技術、高温高圧実験、鉱物物性、超高圧発生

Keywords: nano-polycrystalline diamond, high pressure technology, high pressure and high temperature experiment, mineral physics, ultrahigh-pressure generation

### Newly developed internal-resistive heated diamond-anvil cell with boron-doped diamond: Toward deep lower-mantle petrology

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The development of the diamond-anvil cell (DAC) technique combined with laser heating enabled easy access to the entire lower-mantle pressure and temperature regime at laboratory. However, a number of major issues remain highly controversial, including the location of the post-perovskite phase boundary, solid–liquid iron partitioning, Fe–Mg partitioning among mantle minerals, and melting temperatures of mantle rocks. Although the discrepancies between previous experimental studies on these issues have likely arisen from multiple sources, they could more or less have originated from possible problems in the laser-heated diamond-anvil cell (LHDAC) experiment: inherited temperature gradient in the heated area and temperature fluctuation during heating.

In this study, we developed an internal-resistive heated diamond-anvil cell with a new resistance heater—boron-doped diamond (BDD)—along with an optimized design of the cell assembly, including a composite gasket. We find this heating technique to demonstrate clear advantages over the conventional LHDAC technique, such as (1) ultrahigh temperature generation (>3500 K), (2) long-term stability (>1 h at 2500 K), (3) uniform radial temperature distribution ( $\pm$ 35 K at 2500 K across a 40- $\mu$ m area), (4) chemical inertness (no boron diffusion into the silicate sample), and (5) weak X-ray diffraction intensity from the BDD heater. This newly developed IHDAC with a BDD heater can determine the phase diagrams of silicate/oxide materials with high precision and can be used in deep lower-mantle petrology.

キーワード:ダイアモンドアンビルセル、下部マントル Keywords: DAC, lower mantle

## Constrains on light elements in Earth's core via sound velocity measurements of liquid Fe alloys

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The Earth's core consists mainly of iron alloying with some lighter elements. The nature of the lighter elements is the key to understand the building blocks of the bulk Earth, the core formation process, and the chemical and thermal history of the core. Seismological observations give fundamental information of the physical properties of the core. The density and sound velocity of liquid outer core based on seismological observations are about 10 % less and about 4 % faster than pure Fe under the corresponding pressure and temperature conditions (Anderson and Ahrens, 1994 JGR). The effects of possible lighter elements on those properties of liquid iron are therefore important to constrain the core composition. We have measured the sound wave velocity of liquid Fe alloying with several candidates of the light elements such as carbon (C), silicon (Si), and sulfur (S) to 50-70 GPa, using the inelastic X-ray scattering method combined with a laser-heated diamond anvil cell technique. Based on obtained sound velocity data we constructed equations of state for liquid Fe-C (Nakajima et al., 2015 Nat.Commun.), Fe-Ni-S (Kawaguchi et al., submitted), and Fe-Si (Nakajima et al., in prep.). We found that both carbon and silicon increase significantly the P-wave velocity of liquid Fe, whereas sulfur has negligibly small effect. The abundances of C and Si in liquid Fe are only less than 1 wt.% and 2 wt.%, respectively, so as to explain the P-wave velocity of the outer core. However, such a small amount of C and Si cannot take into account for the 10 % core density deficit. On the other hands, the presence of 5.8-7.5 wt.% S can mutually explain seismological sound velocity and density of the outer core. Therefore, sulfur can be the most abundant among the light elements in the outer core.

#### キーワード:地球コアの軽元素、液体外核、音速、高圧実験

Keywords: Light elements in the Earth's core, Liquid outer core, Sound velocity, High pressure experiments

### Effects of light-element impurities on transport properties of liquid Fe-Ni alloy at Earth's core conditions

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It is widely believed that the Earth's outer core consists of liqud iron (or liquid-nickel alloy) with light element impurities. Therefore, electrical and thermal conductivities of liquid iron-nickel alloys are important to understand magnetic and thermal behaviors of Earth.

Several experimental studies investigated the electrical conductivity or resistivity for iron under high pressure (Keeler, 1969 : Bi ,2002 : Ohta, 2016). Also, by using first principles calculations, electrical conductivity for liquid iron and mixtures with silicon and oxygen under high pressure has been investigated. (Pozzo, 2012, 2013 : de Koker, 2012)

Although first principles studies for liquid iron-oxygen and -silicon mixtures have been conducted so far, mixtures with other light elements such as hydrogen and carbon have not been investigated yet. Under this circumstance, in this study, we perform ab initio molecular dynamics simulations for liquid Fe-Ni alloy with H, C, O, S and Si. We calculate electronic and thermal conductivities at Earth's core conditions with using Kubo-Greenwood formulation. By comparing against results of pure system, we discuss effects of light element impurities on transport properties of liquid Fe-Ni alloy.

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キーワード:第一原理分子動力学シミュレーション、輸送特性、液体鉄ーニッケル混合系 Keywords: Ab initio molecular dynamics simulation, Transport properties, Liquid Fe-Ni mixtures

#### Eddy viscosity of core flow estimated from geomagnetic field data

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The molecular diffusivities of the Earth's core are very small, so that large-scale fields are diffused much more effectively by small-scale turbulence than by molecular processes. Therefore, geodynamo simulations have replaced the molecular diffusivities by the eddy diffusivities, of which values should appropriately adopted. It should be noted, however, that the eddy viscous diffusion, or the eddy viscosity, is not a property of the core fluid but of the core flow. Hence estimating the eddy viscosity from core flow models is very significant.

Fluid motions near the core-mantle boundary (CMB) cause the secular variation of the geomagnetic field observed above the Earth' s surface. As an inverse problem, core flows can be inferred from geomagnetic field data, or spatial distributions and temporal variations of the geomagnetic field. Most of core surface flows are estimated by use of the diffusionless induction equation; that is, the frozen-flux approximation (Roberts and Scott, 1965) is adopted. The magnetic diffusion term in the induction equation can be neglected for a large-scale magnetic field with time scales much shorter than magnetic diffusion time. At the CMB, however, there exists a viscous boundary layer, where the magnetic diffusion cannot be neglected in temporal variations of geomagnetic field. Hence, Matsushima (2015) has devised a new approach to estimation of core surface flow; that is, the magnetic diffusion is explicitly incorporated within the boundary layer, whereas it is neglected below the boundary layer. Furthermore, core flows are assumed to obey a geostrophic balance or a magnetostrophic balance below the boundary layer.

To investigate relation between core surface flow and core-mantle coupling, a geomagnetic field model, COV-OBS.x1 (Gillet et al., 2015), from 1840 to 2015, has been used to derive a core surface flow model, which would contain any information on phenomena in relation with core-mantle coupling, such as the length-of-day (LOD), and spin-up/spin-down of core flows. A possible correlation between time series of the LOD and the axial component of global vorticity suggests any core-mantle coupling. The phase shift leading to the maximum correlation coefficient between the LOD and the axial vorticity is found to be about 18 years, from which the eddy viscosity can be estimated. Since other core-mantle coupling is not taken into account, such as electromagnetic coupling, the value could be a maximum one.

キーワード:渦粘性、コア表面流、永年変化、地球磁場 Keywords: eddy viscosity, core surface flow, secular variation, geomagnetic field

## Seismological evidence for heterogeneous lowermost outer core (F-layer) of the Earth

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We present seismic evidence for heterogeneous structure in the layer directly above the inner core (F-layer), which suggests a localized concentration of light elements.

In this study, we examined the F-layer structure beneath Australia using core phases on vertical-component seismograms of Hi-net in Japan for earthquakes near the South Sandwich Islands. We analyzed the waveforms using the method developed by Ohtaki and Kaneshima (2015). The method uses two observations that are particularly sensitive to the layer structure and are relatively insensitive to the structure of the other parts of the Earth. The first observation is the frequency dispersion in P-waves that graze or are diffracted at the inner core boundary (PKPbc); the second observation is differential travel times between the P-waves reflected from the inner core boundary (PKiKP) and those that turn above the boundary (PKPbc). The dispersion is sensitive to the velocity gradient just above the inner core boundary, but insensitive to the velocity values between the PKPbc turning depth and the inner core boundary, but insensitive to the velocity gradient in the F-layer. The observed PKPbc dispersion requires nearly constant velocity on the inner core boundary in this region. The observed CD-BC necessitates that cumulative velocity in the F-layer is close to that of PREM. The velocity model which satisfies both the observations has nearly constant and smaller velocities than PREM on the boundary and faster ones above.

This feature is in contrast to the F-layer velocity model for the region beneath the northeast Pacific (FVW) (Ohtaki and Kaneshima, 2015), which has a somewhat gentler velocity gradient and smaller velocities than PREM in the whole F-layer. Velocity in the liquid core has a little dependence on temperature (Ichikawa et al., 2014). Thus the difference in velocities between the two regions is ascribed to the relative abundance of light elements. The reduced velocity gradient on the inner core boundary beneath Australia signifies chemically unmixed materials there. The higher velocities than FVW and also PREM indicate a localized higher concentration of light elements in the F-layer.

#### キーワード:外核最下部(F層)、地震波速度構造、局在高濃度軽元素

Keywords: lowermost outer core (F-layer), Seismic velocity structure, localized light-element enrichment

### Generation of MAC Waves by Convection in Earth's Core

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Convection in Earth' s core generates long-period magnetic waves when the top of the core is thermally stratified. These waves can be detected in magnetic-field observations and the wave properties are used to recover quantitative estimates for the stratification. A description of the waves and wave generation is similar to the problem of acoustic-wave generation in stars, although the largest source of excitation is probably due to buoyant parcels rising into the stratified layer. The influence of inertial and magnetic forces are expected to be much smaller. Numerical dynamo models suggest that convection preferentially excites symmetric waves about the equator, which is compatible with the observations. Estimates of the strength and thickness of thermal stratification imposes tight constraints on the thermal evolution of the core.

Keywords: Secular Variation, Thermal Evolution, Dynamics of Planetary Interiors



### 地球外核の上部安定成層に対する組成対流の貫入 Penetration of compositional convection into the upper stably stratified layer in the Earth's outer core

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近年の第一原理計算ならびに高圧実験から, 惑星中心核条件下での熱伝導率が, これまでに議論されていた値 よりも大きいことが示唆されている(Pozzo et al. 2012, 2014; Gomi et al. 2013). この新しい熱伝導率を用い た1次元熱バランスモデルを用いて, 外核内での安定成層の生成が議論されている(Gomi et al. 2013, Labrosse 2015). そこでは, 核マントル境界(CMB)における熱流量 Q\_{cmb} が小さい場合に安定成層が数 1000 km の暑さに及ぶ結果が示されている.

かれらは安定成層の存在を判定するのに熱フラックスが下向きであることを用いている.この条件は,外核内 の流体運動が熱によってのみ引き起こされている場合には適切であるが,内核の成長に伴い外核下部に放出さ れる軽成分の浮力により駆動される,いわゆる組成対流も同時に生じている状況では正しくない.組成対流が熱 的な安定性に打ち勝てる程度に激しければ

熱的に生成された安定成層は混合され,中立状態になってしまうだろう.

熱組成対流がどこで発生できるかを定量的に判断するひとつの基準として,われわれは熱的および組成のど ちらにも起因する浮力による仕事率(運動エネルギー生成)を提案する.仕事率は熱フラックスに比例する項と組 成フラックスに比例する項から成っている.仕事率が正である領域は浮力により運動エネルギーが生成できる ので対流が発生可能であると判断できる.逆に仕事率が負の領域では運動エネルギーが生成できないため,安定 成層が形成される可能性があると判断できる.

新しい熱伝導率を用いた地球外核の 1 次元熱および組成収支モデルを構築し, 仕事率の動径分布をさまざま な Q<sub>cmb</sub> に対して計算したところ, Q<sub>cmb</sub> > 9.3 TW の場合には安定成層が形成されず全層対流が発生する結果と なった. 一方 Q<sub>cmb</sub>< 4.8 TW の場合には, CMB 直下に数 10km 程度の安定成層ができる可能性があることが示 された.

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キーワード:熱伝導率、熱フラックス、組成フラックス、運動エネルギー生成 Keywords: Thermal conductivity, heat flux, compositional flux, production of kinetic energy

### Effects of a thin stably stratified layer below the core mantle boundary on the dynamo action in the core

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By seismic and geomagnetic field observations, a stably stratified layer below the core-mantle boundary (CMB) has been detected. Chemical or thermal origin of the stable stratification is suggested (Helffrich and Kaneshima, 2010; Buffett and Seagle, 2010; Pozzo et al. 2012; Ohta et al. 2016). The geomagnetic field is generated by thermally and chemically driven convection, that is, dynamo action. Assuming the turbulent diffusivity in the core, the co-density has been preferred modeling thermo-chemically driven dynamo. However, the origin of stable stratification cannot be distinguished with the co-density approach. Therefore, thermal and compositional buoyancy must be treated separately. In this study effects of a stable layer of either origin below the CMB are examined, adopting thermochemical double diffusive convection. We have found in a suite of runs that the morphology of dynamos is strongly affected by a thick stably stratified layer (~400 km according to seismic observations) regardless its origin. Then, we focus on the effects of a stable layer, of which thickness is about 150 km close to that detected by geomagnetic observations. We will show results of our dynamo modeling with a thin stably stratified layer of either origin, and discuss its effects on the observed magnetic field and implications for the origin of the stable layer.

キーワード:安定成層、ダイナモ、二重拡散対流

Keywords: stably stratified layer, dynamo, double diffusive convection
# Crystallization of $SiO_2$ from the outer core: A possible means of stratification

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The PREM seismic wavespeed model in the outermost core is in near-uniform self-compression. Slight deviations from self-compression constitute evidence for a radial compositional gradient there, and possibly for stable stratification. Based on melting experiments in the Fe-Si-O system in the diamond anvil at outer core pressures and temperatures that show crystallization of  $SiO_2$ , we developed a thermodynamic model of  $SiO_2$  saturation in liquid Fe at high pressure and temperature conditions suitable for modeling magma ocean and outer core processes. Conditions in a magma ocean between 30-50 GPa allow for significant incorporation of Si + O in the metal, which, after the core evolves to its present temperature (3500-4500 K at the CMB), leads to exsolution of SiO<sub>2</sub>. Using a transition-element hard-sphere model for seismic wavespeeds, we show that the continuous crystallization of SiO<sub>2</sub> at the top of the core produces denser, iron-enriched liquid that mixes downward into the core. The net effects of the density and mean atomic weight change in the mixed region leads to reduced wavespeeds in the top of the outer core that require only a small change in concentration of the SiO<sub>2</sub> component in the liquid, about 0.15 wt%.

Keywords: core, stratification, SiO2 saturation, seismology

# Lateral temperature variation through ICB to CMB in geodynamo simulations

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Resent seismic observations suggests that inner core has a seismic anisotropy. This seismic anisotropy suggests aspherical growth of the inner core, and slow viscous deformation of the inner core and latent heat distribution by flow motion are expected to be the origin of the aspherical growth of the inner core. To explain inner core anisotropy and aspherical growth of the inner core, a number of dynamo simulations has been performed with prescribed boundary conditions at ICB to take into account the inner core heterogeneity. To represent thermal structure of the ICB self-consistently, geodynamo simulations are performed with considering the heat equation throughout the inner and outer core.

In the present model, we assume that the inner core is electrically insulated and co-rotate with mantle to compare the results with the simulation without considering the inner core. To compare simulations with the boundary condition at ICB, we assume no heat sources in the outer core. For the thermal boundary condition at CMB, a homogeneous heat flux is applied. To simplify the model, we assume that the same thermal diffusivity for the inner core and outer core. To sustain the average temperature in the outer core, a constant heat source is introduced in the inner core. We compare the simulations results with the simulations results using fixed heat flux or temperature condition at ICB. We performed four cases of the simulations with changing Rayleigh number to investigate dependency of the thermal structure on the Rayleigh number.

The results show that the time averaged thermal structure at ICB is likely to the simulation results with homogeneous heat flux boundary conditions. The time averaged lateral temperature variation is approximately 26% of the average temperature difference between ICB and CMB, while lateral heat flux variation is only 6% of the average heat flux at the ICB. We also observe small scale temperature and heat flux variations; however, these components vary with time. In addition, the length scale of the heat flux variation is smaller than the temperature variation at ICB. Furthermore, There is small dependence of the  $Y_2^{0}$  component of the temperature variation on the Rayleigh number. This lateral temperature variation also generate intense lateral variation at CMB. We observe that temperature inside of the tangent cylinder is higher than the other area. This variation increasing with the Rayleigh number, while the temperature variation is not observed in the simulations without magnetic field, and meridional circulation inside of the tangent cylinder in the dynamo case is stronger than the non-magnetic cases. we conclude that the Lorentz force near the ICB sustains the meridional circulation and lateral temperature variation at ICB and ICB.

キーワード:地球ダイナモシミュレーション、内核一外核境界、核ーマントル境界 Keywords: Geodynamo simulation, ICB, CMB

## Has Earth's Plate Tectonics Led to Rapid Core Cooling?

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Earth' s mantle and core are convecting planetary heat engines. The mantle convects to lose heat from secular cooling, internal radioactivity, and core heatflow across its base. Its convection generates plate tectonics, volcanism, and the loss of ~35 TW of mantle heat through Earth' s surface. The core convects to lose heat from secular cooling, small amounts of internal radioactivity, and the freezing-induced growth of a compositionally denser inner core. Until recently, the geodynamo was thought to be powered by ~4 TW of heatloss across the core-mantle boundary. More recent determinations of the outer core' s thermal conductivity (Pozzo et al., 2012; Gomi et al., 2013) would imply that >15 TW of power should conduct down its adiabat. Secular core cooling has been previously thought to be too slow for this, based on estimates for the Clapeyron Slope for high-pressure freezing of an idealized pure-iron core (cf. Nimmo, 2007).

The ~500-1000 kg m<sup>-3</sup> seismically-inferred jump in density between the liquid outer core and solid inner core allows a direct estimate of the Clapeyron Slope for the outer core's actual composition which contains ~0.08±0.02 lighter elements (S,Si,O,Al, H,···) mixed into a Fe-Ni alloy. A PREM-like 600 kg m<sup>-(-3)</sup> density jump yields a Clapeyron Slope for which there has been ~774K of core cooling during the freezing and growth of the inner core, cooling that has been releasing an average of ~21 TW of power during the past ~3 Ga. If so, core cooling could easily have powered Earth's long-lived geodynamo. Another implication is that the present-day mantle is strongly 'bottom-heated', and diapiric mantle plumes should dominate deep mantle upwelling. This mode of core and mantle convection is consistent with slow, ~37.5K/Ga secular cooling of Earth's mantle linked to more rapid secular cooling of the core (cf. Morgan, Rüpke, and White, Frontiers, 2016). Efficient plate subduction, hence plate tectonics, is a key ingredient for such rapid secular core cooling.

We also show how a more complete thermodynamic version of Birch's accretional energy calculation predicts that accretion with FeNi-sinking-linked differentiation between an Earth-like mantle and core could naturally generate a core that, post-accretion, was both hotter than overlying mantle and ~1000K hotter than today.

Keywords: core heat loss, mantle convection, plate tectonics, subduction, accretion energetics

# Iron-carbonate interaction in the lower mantle and at the core-mantle boundary

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The presence of carbonates in the deep Earth strongly depends on the oxygen fugacity, controlled by oxidation state of iron in minerals and melts. A large part of the lower mantle can be significantly reduced with detectable amount of Fe<sup>0</sup>. Therefore, subducted carbonates would interact with Fe<sup>0</sup> dispersed in the ambient mantle. However, the mechanism of this interaction remains controversial. We investigated the MgCO<sub>3</sub>-Fe<sup>0</sup> system at 70-145 GPa and 800-2600K using *in situ* X-ray diffraction in a diamond anvil cell. MgCO<sub>3</sub> crystals and Fe foil (99,9%) were used as the starting materials. Formation of wustite (FeO), ferropericlase ( $Mg_{0.6}Fe_{0.4}$ )O, carbide ( $Fe_7C_3$ ) and diamond was observed. Three different modifications of FeO were detected: B1 at T = 1100-2600K and 70-145 GPa, rB1 at T<1100 K and P<136GPa; and B8 at P = 143-145 GPa. Interestingly, we observed coexistence of wüstite and ferropericlase, which may suggest an existence of immiscibility gap in FeO-MgO system at P > 70 GPa. Mg-carbonate reduction can be presented by following reaction:  $6MgCO_3 + 19Fe = 8FeO + 10(Mg_{0.6}Fe_{0.4})O + Fe_7C_3 + 3C$ . The formation of diamond was confirmed by TEM study of run products at 100-145 GPa. The studied carbonate-iron reaction supports formation of the (Fe,Mg)O, carbide and diamond in the lower mantle and at the Earth' s core-mantle boundary indicating that subducted carbonates transported to the core-mantle boundary would be reduced to carbide or diamond. Similar reaction may occur in the Fe-CaMg-carbonate systems. Using these data we propose that core-mantle boundary is important to produce diamond and Fe-carbide.

Keywords: Mg-carbonate, carbide, diamond, lower mantle, core-mantle boundary

# Composition of the core: Geochemical and mineral physics constraints

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The Earth' s core is believed to contain certain amount of light elements based on seismological observations and mineral physics data. The major potential candidates of the light elements of the core are considered to be S, Si and O. Recent studies on the Fe-Si-O system revealed that Si and O have mutual avoidable nature in metallic liquid (1,2), and precipitation of silicates such as  $SiO_2$  or  $FeSiO_3$  occurred during cooling of the liquid core (e.g., (3)). Therefore, the composition of the inner core coexisting with metallic liquid outer core should be ether Fe-O-S or Fe-Si-S alloy, i.e., coexistence of Si and O are prohibited to occur in the core crystallizing metallic solid inner core.

Our sound velocity measurements of FeO revealed that O is not likely to be the major light element of the inner core (4). Thus the most plausible candidates of the light elements in the core are likely to be S and Si, without O.

Based on our measurements of the sound velocity of iron (5), iron-silicon alloy (6), and Fe<sub>3</sub>S (7), and the solid-liquid partitioning in the Fe-Si-S system at high pressure and temperature, we constrained the composition of the inner and outer cores. The present experiments on the solid-liquid partitioning of S and Si revealed that the major element of the inner core is silicon whereas that in the outer core is sulfur. The present results on sound velocity measurements and solid-liquid partitioning of iron alloy indicate that an iron alloy with about 5 wt.% of Si and 0.1 wt. % of S can explain the physical properties of the PREM inner core at the ICB condition, whereas the outer core contains both S and Si (about 7 wt.% S and 3 wt% Si) without O.

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#### キーワード:内核、外核、組成、軽元素、音速

Keywords: Inner Core, Outer core, composition, light elements, sound velocity

## High-P,T Elasticity of Iron-Light Element Alloys

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Earth' s inner core (329~364 GPa and 5000~6000 K) is thought to be composed of solid Fe-Ni alloy with some light elements. Thermoelasticity of iron and iron-light element alloys is therefore a key to interpreting seismological information of the inner core: density, seismic wave velocities, and their anisotropy. However, several studies reported that pure hcp iron has a shear modulus distinctly larger than that of the inner core (e.g., Mao et al., 1998; Vocadlo et al., 2009). This large Poisson ratio of the inner core is one of the remaining inexplicable features of the deep Earth, and some studies recently proposed this be explained by alloyed with light elements such as carbon (e.g., Chen et al., 2014). In this study, we perform ab initio molecular dynamics simulations of iron-light element alloys with potential candidates of Si, C, and H and examine their high-P,T elasticity to identify the viability of iron alloys in the inner core.

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キーワード : 鉄軽元素合金、第一原理計算、内核 Keywords: Iron-light element alloy, Ab intio computation, Inner core

# Constraint on composition and size of lunar Fe-Ni-S core Constraint on composition and size of lunar Fe-Ni-S core

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In order to constrain S content in the lunar core and to estimate the structure of lunar interior, we compared measured  $V_p$  and r data of liquid Fe-alloys at the lunar core condition with observed geophysical data. We have measured sound velocity and density of liquid Fe-Ni-S using ultrasonic pulse-echo and X-ray absorption methods combined with multianvil apparatus up to 14 GPa. The obtained sound velocity and bulk modulus significantly decreased with increasing S content at the lunar core condition (5 GPa, 1800 K). Estimated Fe-Ni-S lunar core model from the present elastic properties will be compared with the previous interior models of Moon (Garcia et al. 2011 and Weber et al. 2011).

キーワード : 核、月、音速 Keywords: Core, Moon, Sound velocity

## 高圧下における鉄ー炭素合金メルトの熱弾性的性質:月内部における炭素 への応用

Thermoelastic properties of iron-carbide melts under high pressure: implication for carbon in the lunar interior

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Carbon is one of the possible light elements in lunar interior. Thus, it is important to understanding the effect of density and sound velocity of liquid Fe at high pressure in order to evaluate the presence of carbon in lunar core. Simultaneous measurements of P-wave velocity and the density of liquid Fe-C have been conducted up to 3.4 GPa and 1850 K. Addition of carbon decreased the V<sub>p</sub> of liquid Fe by about 2% at 3 GPa and 1700 K and reduced Fe density by about 2% at 2 GPa and 1700 K. The V<sub>p</sub> of liquid Fe-3.5 wt% C decreased linearly with increasing temperature at constant pressure. The bulk modulus of liquid Fe-C and its pressure (P) and temperature (T) effects were precisely determined from directly measured r and V<sub>p</sub> data to be K<sub>0,1700K</sub> = 83.9 GPa,  $dK_T/dP = 5.9(2)$ , and  $dK_T/dT = -0.063(8)$  GPa/K. The effect of carbon in the Birch (r-V<sub>p</sub>) plot decreases with increasing pressure. Based on the directly measured V<sub>p</sub> and r of liquid Fe-C, elastic properties, such as K, dK/dT, and dK/dP, were determined precisely. These properties can explain differences in  $dV_p/dT$  of Fe-C, Fe, and Fe-S.

キーワード:月、外核、液体、音速、密度、弾性率 Keywords: Moon, Outer core, liquid, sound velocity, density, bulk modulus

# A textural and chemical view of melting of the Sahara 97072 (EH3) meteorite at 5 GPa and different temperatures

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Melting interval of (Fe, Ni)-sulfide and silicate was studied with heating experiments on the Sahara 97072 (EH3) meteorite at 5 GPa and 1000-1700°C using multi-anvil apparatus. Results from our experiments show that: (1) (Fe, Ni)-bearing sulfide is completely molten at 1200°C; (2) partial melting of silicate begins at 1400°C; and (3) the Sahara 97072 meteorite is completely melted at 1600°C. At 5 GPa, both pyroxene and olivine appear to be stable near the liquidus as the first liquidus phase, indicating that 1600°C and 5 GPa is very close to the pyroxene-olivine cotectic.

Overheating the Sahara 97072 meteorite sample to 1650 and 1700°C causes (Fe, Ni)-alloy exsolved from (Fe, Ni)-sulfide, and the spherical shape of the (Fe, Ni)-alloy indicating that the exsolution happened during heating rather than quenching. The coexisting of (Fe, Ni)-alloy and S-rich metallic phase at higher heating temperature could be results of the decrease of portioning coefficient of S between metallic liquid and silicate liquid with temperature or the volatility loss of S at overheating conditions. The silicate liquid in these two experiments shows smaller Mg<sup>#</sup> than the completely melt condition, indicating a relatively larger Fe content in the silicate liquid, which is consistent with the decreased bulk content of metallic liquid. Results from these experiments suggest that the relatively small planetary bodies with elevated sulfur content would have likely experienced sizable core stratification during early melting event as a result of the segregation of (Fe, Ni)-alloy from (Fe, Ni)-sulfide.

Keywords: enstatite chondrite, partial melting, core formation



# 高圧下中性子回折実験のためのナノ多結晶ダイヤモンドアンビルセルの開 発

# Development of nano-polycrystalline diamond anvil cells for neutron diffraction experiments under high-pressure

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Neutron diffraction requires significantly larger sample volume than the case of x-ray diffraction because of the relatively small scattering cross section, so that crystallographic studies by neutron diffraction have long been limited to 30 GPa by using the Paris-Edinburgh press (Klotz, 2012), which enables to load larger volume of samples than conventional diamond anvil cells (DACs). Recently, conically shaped single crystal diamond anvils were applied for high-P neutron diffraction for ice VII, and the highest pressure record of 94 GPa was established by Boehler et al. (2013). On the other hand, we have noted that nano-polycrystalline diamond (NPD) rather than single crystal diamond could have a great potential for neutron diffraction (e.g., Okuchi et al., 2010), because of its orientaion-independent hardness owing to the absence of cleavage. Here we report on the development of originally designed anvil cells by using NPD specifically for neutron diffraction studies. Cylinders of NPD with 6 mm diameter and 6 mm height were supplied from GRC, Ehime Univ. and cut and polished to single beveled anvils with 1 mm culet diameter by Syntek co., ltd. Stainless steel (SUS301) drilled with 0.5 mm hole were used as gaskets. Load was applied by the Paris-Edinburgh press (VX2), which was placed on the gonio stage of the beamline PLANET (BL11) in J-PARC. We managed to obtain neutron diffraction from iron oxide up to at least 40 GPa without any damage of anvils, but the diffraction peaks were broadened when deuterated glycerol was used as pressure transmitting medium. We are now developing a gas-loadable cell and it will be tested near future.

キーワード:中性子回折、技術開発、ナノ多結晶ダイヤモンド Keywords: Neutron diffraction, Technical development, Nano-polycrystalline diamond

## 核の圧力までの変形実験を目指した回転ダイアモンドアンビルセルの開発 Development of rotational diamond anvil cell for deformation experiments under ultra-high pressure corresponding to Earth's core

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近年の高圧実験装置の開発はめざましく、今ではダイアモンドアンビルセル(DAC)によって地球の内核の圧 カ(~360GPa)まで再現できるに至った(Tateno et al., 2010)。その一方で、変形実験に特化した装置については 技術的困難により再現できる圧力は限定的である。地球内部とその進化は動的過程によって支配されてお り、それを理解するためには超高圧下での変形実験から鉱物のレオロジー特性を明らかにすることが必要不可 欠である。それゆえ変形実験装置が再現できる圧力範囲を拡大することは我々の地球深部ダイナミクスの理解 を大きく前進させてくれることが期待される。そこで本研究の目的は、内核までの圧力を再現でき、大歪の変 形実験を実現できる回転ダイアモンドアンビルセル(R-DAC)を開発し、実用化することである。

本研究では既存のダイアモンドアンビルセルを改良し、超高圧下においてねじり変形をサンプルに与えられ るようにした。この改良されたR-DACでは、下部アンビルは固定し、上部アンビルが回転する。この回転する 上部アンビルは開発した回転DAC専用のギアボックス(made by *PRETECH*)に取り付けられ、定速度( $10^{-6}-10^{-3}$  rpm)で回転する。テスト実験としてサンプルには下部マントルを構成しているPericlase(MgO)の(1相)と Bridgmanite((Mg,Fe)SiO<sub>3</sub>)とFerropericlase((Mg,Fe)O)のmixture (2相)を用いて変形実験を行った。これらの サンプルはFIBによって溝を作り、溝の側面にPtを蒸着することでStrain markerとする。変形実験後は回収試 料のStrain markerを観察し歪を決定できる。実験条件として温度は室温、圧力35–150 GPa、歪速度5.6×10<sup>-5</sup> -1.7×10<sup>-4</sup> s<sup>-1</sup>である。さらに本実験はSPring-8において、新しく開発された技術であるX線ラミノグラ フィー(Nomura and Uesugi, 2016)と組み合わせることでStrain markerのその場観察も行い、実験中の歪と歪 速度を評価した。

Strain markerの評価によって せん断歪に対する圧縮軸方向の歪の影響を評価したところ、最大でも10%以 下であり、ほぼsimple shear(or general shear)を実現できていると考えられる。本実験はねじり変形であるた め、サンプル内の歪分布は一様ではない。回転軸からの距離が増加するにしたがって、歪は大きくなる。上部 アンビルを80-120°回した場合、歪が最も大きいところで~4-10に達する。しかし上部アンビルの回転角度か ら予想されるサンプルの歪、歪速度と実際のサンプルのStrain markerから決定されたそれらとは差があること から、上部アンビルとサンプルの間でスリップが起きていることが予想される。それゆえ、歪、歪速度をその 場観察できるX線ラミノグラフィーとR-DACの組み合わせは非常に有用であると言える。回収された試料につ いてはFE-SEMによって観察した。その結果、BridgmaniteとFerropericlase2相系での変形実験で は、Ferropericlaeが大きく変形し、連結した微細組織が観察された。本発表では開発、改良されたR-DACに よってメガバールの圧力下において行われた変形実験の結果とR-DACの実用性について予察的ではあるが報告 を行う。

キーワード:変形実験、ダイアモンドアンビルセル、下部マントル、核 Keywords: Deformation experiment, Diamond anvil cell (DAC), Lower mantle, Core

## X線ラミノグラフィをダイヤモンドアンビルセルに用いた、高温高圧その 場三次元構造解析

# *In situ* 3D textural observations at high pressure and high temperature using X-ray laminography technique in diamond anvil cell

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High-pressure and -temperature experiments have been widely conducted using diamond anvil cells to understand the structure and evolution of the Earth's interior. Nowadays, 3D visualization technique has been developed to observe internal structure of the sample recovered from high pressures (Shi et al., 2013; Nomura et al., 2014). In addition, *in situ* high-pressure X-ray computed tomography techniques have been developed by transmitting X-rays through a light metal gasket such as Be (Liu et al., 2008; Wang et al., 2012). Using these techniques, geometric information such as the changes of the volume or shape of the sample with pressure is obtained. However, it is difficult to generate high-pressure and -temperature of the Earth's lowermost mantle or the core with keeping sufficient sample thickness when light metal is used as a gasket.

To overcome this problem, Nomura and Uesugi (2016) introduced X-ray laminography technique (Gondrom et al., 1999) to diamond anvil cell. In X-ray laminography, the rotational axis of the sample is inclined to the direction of the incident X-ray beam. Therefore, the incident X-ray beam can avoid the metal gasket surrounding the sample; it is no longer necessary to use a light metal as a gasket. However, it is still challenging to combine such measurements with heating technique in the diamond anvil cell. Here, to carry out in situ high pressure and "high temperature" X-ray imaging, we have introduced the internally resistive heating method by using boron-doped diamond as a heater material. Boron-doped diamond has high X-ray transmissivity and can generate high temperatures more than 3000 K with high stability (Yamada et al., 2008; Shatskiy et al., 2009; Yoneda et al., 2014; Xie et al., 2016). We performed X-ray laminography experiments at BL47XU, SPring-8. The sample was Au foil, heater was boron-doped diamond and pressure medium and heat insulator was Al<sub>2</sub>O<sub>3</sub>. We have obtained the X-ray transmission images of the sample at 20 GPa during heating. Obtained images were sufficiently clear, despite of the Re gasket and boron-doped diamond heater surrounding the sample. We have reconstructed cross-section images of the sample before and after heating. These cross-section images showed that the shape of the sample was largely altered by heating due to melting. The technique developed in this study will provide new method to determine the melting temperature of the sample at high pressure. Our current results demonstrate that the X-ray laminography can be a powerful tool for understanding dynamic process in the deep Earth' s interior, such as melting of the terrestrial materials.

キーワード:ダイヤモンドアンビルセル、X線ラミノグラフィ、その場三次元構造解析 Keywords: Diamond Anvil Cell, X-ray Laminography, In situ 3D textural observations

# Evaluation of the pressures measured in the double stage diamond anvil cell technique Evaluation of the pressures measured in the double stage diamond anvil cell technique

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The double stage diamond anvil cell (dsDAC) is claimed as an advance technique to generate a TPa static pressure (Dubrovinskaia et al. 2016). Although the nanocrystalline diamond semi-balls were used for the TPa generation, it is need to prepare an desired anvil shape; i.e., the culet and bevel size and so on, in order to control the pressure distribution at the tip of the 2<sup>nd</sup> anvils. We have been trying to develop the dsDAC as a well-controlled experiment device using the focused ion beam (FIB) system (Sakai et al. 2015).

Here we report the results of the dsDAC experiments using the newly synthesized nanopolycrystalline diamond (NPD) with a single-nano grain size as a micro-anvils material. The  $2^{nd}$  stage micro-anvils are shaped with 3 um culet and 10 um bevel using FIB system (Scios, FEI). The tiny rhenium disc (3 um diameter and 1 um thickness) was used as a sample. The other experimental procedure was generally same as in Sakai et al. (2015). The X-ray diffraction (XRD) experiments were performed at SPring-8 BL10XU in order to determine the generated pressure from the lattice parameter of rhenium. The diffraction patterns from the rhenium sample showed very broad peaks due to the large pressure gradient at the tip of the micro-anvils as contrasted with the sharp peaks observed in previous works (Dubrovinsky et al. 2012, 2015; Dubrovinskaia et al. 2016). The deconvolution of the peak results that the rhenium was compressed to be V/V<sub>0</sub> = 0.633. According to the equation of state of rhenium (Re-EoS) reported by Anzellini et al. (2014), it corresponds to about 430 GPa. On the other hand, it is 630 GPa if we adapt the Re-EoS by Dubrovinsky et al. (2012). In the term of V/V<sub>0</sub> value, we reproduced the result of Dubrovinsky et al. (2012) although we observed the X-ray diffraction peaks with large FWHM as an unavoidable result from the large pressure gradient at the tip of the 2<sup>nd</sup> stage micro-anvils.

The compression behavior of NPD micro anvils shows a monotonous volume decrease along the equation of state of the diamond (Dewaele et al. 2008); however it becomes incompressible when the compression by the 2<sup>nd</sup> stage micro-anvils started. It is a well-known phenomenon induced by the uniaxial stress, i.e., the overestimation of the volume. This large effect of uniaxial stress was released when the 2<sup>nd</sup> stage micro-anvils failed, which means the sudden volume decrease occurred although the pressure was dropped. This "incompressible" feature is the opposite of the "compressible" behavior which reported in Dubrovinsky et al. (2012).

The dsDAC certainly has a potential ability to generate an ultra-high pressure. Since the X-ray beam is comparable in size to the culet of the 2<sup>nd</sup> stage micro-anvils, it needs further evaluation of the

relationships between the X-ray beam intensity profile and the pressure distribution and the sample distribution to interpret the XRD patterns measured in the dsDAC experiments correctly.

キーワード:2段式ダイヤモンドアンビルセル、ナノ多結晶ダイヤモンド、テラパスカル、集束イオンビーム 加工装置、状態方程式

Keywords: Double stage diamond anvil cell (dsDAC), Nanopolycrystalline diamond (NPD), Tera Pascal (TPa), Focused ion beam (FIB) system, Equation of state (EoS)

# Generation of ~90 GPa in Kawai-type multianvil apparatus using nano-polycrystalline diamond anvils.

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Nano-polycrystalline diamond (NPD) has higher hardness, toughness, elastic stiffness, and X-ray and light transmittance than conventional sintered diamond (SD). These properties make it suitable for use as an anvil material in high-pressure experiments. Kawai-type multi-anvil apparatus (KMA) has been widely used in high-pressure experiments, where accurately controlled pressure and temperature in larger sample volumes relative to diamond anvil cell are available using tungsten carbide (WC) or SD as the second-stage anvil materials. However, the generated pressures in KMA with these conventional anvils at high temperatures have been limited to about 40 GPa and 100 GPa, respectively, by using these materials as the anvils. We have been attempting to generate further higher pressures using NPD cubes with the

"6-6-8" anvil configurations. *In situ* X-ray diffraction measurements and radiographic imaging observations were performed at the large-volume press beamline, BL04B1, SPring-8. Baked pyrophyllite gasket and semi-sintered  $Al_2O_3$  pressure medium were used, and a folded gold foil was placed in the center of the pressure medium as a pressure marker. The maximum pressure so far achieved at room temperature is about 88 GPa at a press load of 3.4 MN, which is far higher than that achieved using SD anvils (~56 GPa) with the identical cell assembly and the press load. Moreover, it was found that both in situ X-ray diffraction measurements and imaging observations are possible even through the NPD anvils, which is great advantage over the experiments using SD anvils where the invisibility of the sample becomes a serious issue due to the plastic deformation of anvils under such high pressure. Thus, we conclude NPD is highly promising anvil material for the next generation KMA technology.

### Pressure generation of 120 GPa and stability of bridgemanite

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Physical and chemical properties and structure of materials are strongly depend on the pressure and temperature.  $MgSiO_3$  bridgemanite, which is the most abundant mineral in the lower mantle, undergoes the phase transition to post-perovskite structure (CaIrO<sub>3</sub>, Cmcm) at pressure and temperature corresponding to the D" layer conditions, discovered by diamond anvil cell high pressure experiments (Murakami et al., 2004). This phase transition is considered to a key to understand the mantle dynamics and therefore precise determination of the phase boundary is important, for example, effect of the other elements (e.g., Fe, Al and Fe<sup>2+</sup>/Fe<sup>3+</sup>). In this study, we developed the high pressure generation technique in a Kawai-type multianvil apparatus, which enables us to obtain large volume sample (~0.1 mm<sup>3</sup>) with stable heating and homogeneous high temperature distribution in the sample, and tried to determine the phase boundary between bridgemanite and post-perovskite.

We conducted pressure generation test by using a Kawai-type large volume press (SPEED mk.II) at SPring-8 synchrotron facility. For the cell assembly, we used Cr-doped MgO as pressure medium,  $BN+TiB_2$  as heater because of high transparency for X-ray and soft fired pyrophyllite as gasket. Temperature was monitored by  $W_{97\%}Re_{3\%}$ - $W_{75\%}Re_{25\%}$  thermocouple whose junction was located in the heater. Before experiment, we prepared the sintered starting material of the mixture of  $Mg_{0.9}Fe_{0.1}SiO_3+5wt$  %  $Al_2O_3$  bridgemanite and gold which was used as the standard to estimate the pressure (Tsuchiya, 2003) in the ration of 1/6 in weight. During compression in the experiments, we frequently pre-heated the sample to 800-1100 K at every 5-10 GPa for the relaxation of stress stored in the cell assembly to reduce the probability of "blow out".

We finally succeeded to generate pressure to 120 GPa with press load of 13 MN at an ambient temperature after pre-heating at 800K. Then we again heated up sample to 1673 K to observe the phase transition from bridgemanite to post-perovskite at 105 GPa because a large pressure drop occurred down to 105 GPa at higher temperature than 800 K during heating up. The obtained diffraction pattern was completely indexed as bridgemanite, indicating the stability field of bridgemanite with the composition of  $Mg_{0.9}Fe_{0.1}SiO_3+5wt \% Al_2O_3$ . The present result is consistent with previous study in MgSiO<sub>3</sub> (Tateno et. al., 2009). They reported the phase boundary to be 110 GPa at ~1673 K. As a conclusion, the effect of 10 mol % of iron component and 5 wt % of  $Al_2O_3$  is less than 5 GPa on phase boundary shift in pressure.

# 地球ニュートリノ到来方向測定にむけた発光位置の三次元再構成 3D reconstruction of light emission points for geo-neutrino directional measurement

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地球ニュートリノ観測は、地球内部を直接観測することのできる新たな方法である。地球ニュートリノと は、地球内部に存在するウランやトリウム、カリウムなどの放射性元素がβ崩壊を起こす際に放出する反電子 ニュートリノのことであり、その観測により地球内部の化学組成や熱源分布に関する情報を得られる。東北大学 が主導するKamLAND実験は世界で初めて地球反ニュートリノを観測することに成功し、地球モデルに制限を与 えた。

しかし、KamLANDのような液体シンチレーター型の検出器は、地球ニュートリノのような低エネルギー領 域のニュートリノに感度を持つ一方で、その到来方向を知ることはできない。そこで、液体シンチレーターを 用いて、ニュートリノの方向測定を行うための研究を進めている。Li入りの液体シンチレーターと発光位置を 高精度で撮像するイメージング検出器を用いて、ニュートリノの方向測定を行うことを計画してい る。ニュートリノの到来方向の測定によって、地球ニュートリノにおける地殻とマントルの寄与の分離や バックグランドとなる原子炉ニュートリノの分離が可能になると期待されてい。

ニュートリノの到来方向情報を得るためには、反応の際の先発信号となるガンマ線と後発信号となる中性子 捕獲による発光のそれぞれの反応点を測定することが必要となる。これまでの研究で、一台のイメージング検 出器を用いて放射性線源からのγ線による反応点を測定できることが実証された。本研究では、二台のイ メージングを用いて同時測定を行うことにより、発光位置を三次元的に再構成することを目指している。到来 方向観測実現に向けて実験室で行っている新技術の確立の現状について発表する。

キーワード:地球ニュートリノ、ニュートリノ方向検出 Keywords: geo-neutrino, neutrino directional measurement

# ベイズ推定を用いたニュートリノフラックスシミュレーション用岩相分布 モデル

## Lithology Distribution Model for Neutrino Flux Simulations Obtained by Using Bayesian Inference

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It is well-known that geo-neutrino observations provide critical constraints on the mantle chemistry. Because chemistry (i.e., distribution of U and Th concentration) in the local crust also affects to the neutrino flux at the detector, it is widely recognized that developing local chemistry model is one of the most important steps in the geo-neutrino simulations. In previous studies, they used various geological insights to obtain the chemistry models, however, in most cases, the modeling is not well tractable, and the uncertainties of the obtained models are not very clear. Because our final goal is to obtain the probability density function of the neutrino flux at the detector, we need more quantitative and reproducible approach.

In this study, we propose Bayesian approach to obtain the statistical chemistry model. To do this, we adopted two-step approach; we fist obtain statistical lithology distribution model and then combine it with the statistical concentration model for each lithology type that is presented by Ueki (2017, this meeting). In this presentation, we focus on the method and results of the first step.

The lithology model in this study consists of probability of the lithology type at each point in the local crust. It is definitely different from the previous models that definitely state the lithology type. To obtain this probability, we use the Bayesian theorem. We first define some a priori probability and then modify it using observational and experimental information. To take the regional specialty of Japanese crust into account, we assume the bulk composition of the Hidaka metamorphic belt as the a priori probability. To modify it, we use the information of the P wave tomography model by Matsubara et al. (2008), laboratory measurements of P-velocity of each lithology by Christensen and Mooney (1995), and the temperature structure model by Furukawa (1995). The detailed method and results will be shown in the presentation.

キーワード : ニュートリノ、岩相、トモグラフィー Keywords: neutrino, lithology, tomography

# ジオニュートリノモデリングに向けた日本列島地殻岩石U-Th含有量 データベースの構築

U, Th concentrations of Japanese rocks for geo-neutrino modeling

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KamLANDで得られる世界最高精度の地球ニュートリノデータを用いて、核-マントル中に含まれる放射 性元素の量を世界最高精度で決定することを目標として、我々は地震波速度構造や地質学的情報を用いた島弧 地殻の岩相モデリングを行っている。地震波速度構造から得られた岩相分布の結果を用いて日本島弧地殻のウ ラン・トリウム濃度を推定するために、一万点以上のデータ数、約100の論文や報告書のデータからな る、日本列島を構成する岩石の化学組成(一部主要元素及びウラン・トリウム濃度)のデータベースを構築し た。さらに、特にデータ数が少ない日本列島下部地殻起源の岩石に関して、捕獲岩のサンプリングや分析を 行った。データベースを用いてモデル化された日本列島を構成する各種の岩石のウラン・トリウム濃度を用い ることで、日本島弧地殻ウラン・トリウム濃度の推定、ひいては地殻由来のニュートリノフラックスのより現 実的な推定が可能となる。

日本列島を構成する岩石のU-Th含有量のバリエーションは、溶融や結晶分化などのメルトプロセス、海洋底 での変質によるウラン付加、地表でのウラン喪失で説明できる。また、特に下部地殻に相当する岩石は大陸地 殻での推定よりもやや枯渇したものとなった。

コンパイルされた組成データを用いて、化学組成分布、そしてニュートリノフラックスを計算するため に、確率分布への当てはめを行った。地球化学での先行研究では、対数正規分布や正規分布が広く使用されて きたが、本研究では新たにガンマ分布を用いた。数学的にも有利な点が多いほか、標本の平均を正確に再現す ることが出来る、マイナスの値を持たない、対称及び非対称両方の分布に対応可能であるという利点があ る。また、ガンマ分布は化学組成のモデル化に適用されている実績がある。確率密度関数化された岩種毎の組 成分布を使用することで、より現実的な日本列島島弧地殻の組成分布やニュートリノフラックスの計算が可能 となった。

キーワード:島弧地殻、地球ニュートリノ、放射性元素 Keywords: Arc crust, Geo neutrino, radiogenic elements

# 到来方向検知型地球ニュートリノ検出器開発の現状 Current Status of Development for Geo-Neutrino Directional Measurement

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ニュートリノは素粒子の一種であり、近年その性質がよく知られてきている。液体シンチレータ検出器は低 エネルギー反ニュートリノに感度がある反面、水チェンレンコフ検出器のように、反ニュートリノの到来方向 に感度はない。液体シンチレータ検出器が反ニュートリノの到来方向に感度を持った場合、地球内部の放射性 物質の分布測定の更なる高精度化や原子炉の運転状況に依存しない高精度データを得ることが出来るようにな る。また、小型検出器を作成した場合は、原子炉モニターに応用することも出来る。本研究では小型検出器に よる反ニュートリノの到来方向測定を第一目標として研究を進めている。

反ニュートリノは逆ベータ崩壊反応により放出される陽電子と中性子が陽子により捕獲された際に放出され る2.2 MeVのガンマ線を測定することによって検出される。これは遅延同時計測法と呼ばれ、この測定手法に よりバックグラウンドを大幅に抑制することが出来ている。この時放出される中性子は反ニュートリノの到来 方向情報を保持しているが、現状の液体シンチレータ検出器では陽子の中性子捕獲断面積が小さいため、液体 シンチレータ内で中性子が長距離飛行してしまうのに加え、陽子が中性子を捕獲した際、液体シンチレータ内 を長距離飛行するガンマ線を放出するため、中性子の捕獲点を精度よく特定することが出来ない。これによ り、反ニュートリノの到来方向の情報は失われてしまう。このような問題点を改善するため、従来の液体シン チレータに、中性子捕獲断面積が940 barnと、陽子の0.3 barnよりもはるかに大きい<sup>6</sup>Liを導入した。<sup>6</sup>Liは中 性子を捕獲した際、即座に発光するアルファ線と<sup>3</sup>Hを放出するため捕獲点を精度良く決めることが出来る。上 記のような理由で、反ニュートリノの到来方向情報が失われる前に中性子を捕獲することが出来、陽電子の発 光点と中性子の捕獲点をベクトルで結ぶことで反ニュートリノの到来方向を測定することが可能となる。

また、これらの発光点を分離するために高位置分解能の検出器を開発する必要がある。高位置分解能の検出 器として反射型光学系と多チャンネルの光検出器を使用する予定であり、現在のその開発・テストを行ってい る最中である。

本発表では、反ニュートリの到来方向測定に向けたイメージング検出器の開発状況について報告を行う。

キーワード:ニュートリノ、液体シンチレータ Keywords: neutrino, Liquid scintillator

# Geoneutrino Flux Estimation based on Probabilistic Lithology and Compositional Models

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Geoneutrino observation with the KamLAND detector at Kamioka, Gifu, is expected to bring unique knowledge on the interior of the earth. However, due to a large contribution of the nearby crust to the total geoneutrino flux at Kamioka, detailed understanding of the Uranium and Thorium distributions in Japanese crust is crucial. For this purpose, we have been developing a lithology model by seismic tomography, rock composition models based on evaluated vast samples, and a method to properly propagate all the probabilistic information to an estimation of the geoneutrino flux at Kamioka.

Geoneutrino observations are statistical, therefore results from the observations, such as the total heat budget in the mantle, are described with probability distributions. In order to properly do this, the nearby crustal model must be described in the language of probabilities, where estimation of uncertainties, not just the central value, has essential importance. In spite of this, no geoneutrino flux model with objective uncertainty estimation has never been constructed, presumably due to lack of input information and methodological difficulty of doing it.

At this presentation our effort on developing the method of estimating the geoneutrino flux based on probabilistic input models will be discussed. Currently our major difficulty is description and evaluation of correlations among values in the input models, such as quantitative description of regional lithological similarities and modeling of compositional variations / similarities among rocks classified as same rock type. In parallel to the effort of constructing the best optimal models, we evaluated a conservative uncertainty by assuming the maximum correlations among everything.

Although the estimated conservative uncertainty, 60<sup>~</sup>70%, is too large to be meaningful in geophysics, this is the first objective estimation of the uncertainty on the regional geoneutrino flux. We will also discuss the future prospects to further improve the estimation. In addition, some other interesting side-products, such as a heat-source distribution map of the 3-D Japan crust, will be presented.

Keywords: geoneutrino, BSE, thermal evolution, crustal composition

A review of thermal state of the shallow part of the Earth's lithosphere: What we know and do not yet know A review of thermal state of the shallow part of the Earth's lithosphere: What we know and do not yet know

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To improve our understanding of the thermal evolution and structure of the deep Earth, it is necessary to know the shallow part of them. Surface heat flow provides important constraint on in. However, the number of heat flow data is limited and spatially very inhomogeneous and even in regions with measurements the data quality varies. To provide an attempt at a higher resolution map of heat flow, thermal conductivities are measured using sampled cores and used from existing and newly collected data. Also, to estimate the heat flow using geothermal gradient data, the closest thermal conductivity data is used for each gradient data. This approach does not take into account geological and hydrodynamical models to use the thermal conductivity, but this assumption works well enough to provide rough estimates of heat flow from geothermal gradient.

Meanwhile, there exist many indicators that are proxies for quantifying the thermal structure. One of the promising indicators is the cut-off depth of shallow seismicity. Several studies have been conducted to assess the inverse correlation between the cut-off depth and heat flow, since it has attributed primarily to the temperature. Another indicator is the depth of magnetic sources based on spectrum analysis of magnetic anomaly data. This analysis is still controversial, however, good correlation between estimated depths of crustal magnetic sources and heat flow suggests that this depth may reflect the broad average temperature. We address the advantages and limitations of each data and method.

 $t = - \nabla - \kappa$ : heat flow, thermal conductivity, seismogenic layer thickness Keywords: heat flow, thermal conductivity, seismogenic layer thickness

## High precision analysis of W isotopes for OIB and MORB samples

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<sup>182</sup>W is a decay product of <sup>182</sup>Hf ( $t_{1/2}$ =890 million year) which is extinct at now. The amount of <sup>182</sup>W can give information on evolution of very early solar system at the timescale from several million years from the solar system initial. Hf and W is a highly refractory element and the <sup>182</sup>W isotope evolution process in the bulk Earth could be the same as in chondrites. However, W is a highly siderophile element and Hf is a lithophile element. These elements could be partitioned into metal (core) and silicate (mantle) phases, which leads to higher Hf/W ratio of mantle.

To elucidate the core-mantle evolution of the early Earth, we have developed the high precision W isotope analysis using MC-ICP-MS (Thermo co. Ltd. NEPTUNE Plus) and have applied it to some OIB and MORB samples, such as Hawaiian basalts, South Africa Kimberite, Ontong Java Plateau lavas and Indian MORB.

We will present the W isotopic composition obtained for these samples and will discuss the early core-mantle co-evolution and core-mantle interaction, based on the W isotope, Os isotopes.

キーワード:核マントル共進化、タングステン同位体比、Hf-W系 Keywords: Core-Mantle co-evolution, Tungsten isotope ratio, Hf-W system

# Micro-volume stable isotope measurement using IRMS and its application in high pressure research

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Sulfur, oxygen, hydrogen and carbon are potential light elements candidates that might be present in the core in significant quantities to counter the density deficit of the metallic core. Based on geophysical consideration and high-pressure experiments, the core composition and its evolution have been focus of several previous studies. However, recent studies have predicted that there is a possibility of isotope fractionation at high temperature and high pressure conditions, especially in the magma ocean environment and core segregation (e.g. Satish-Kumar et al., 2011; Labidi et al., 2016). In order to understand the light element isotope fractionation processes in the deep earth it is necessary to measure isotope composition accurately in micro to nano scales from high pressure experimental run products. At Niigata University, MAT-253 mass spectrometer (Thermo Fisher Science) was installed by the MEXT Grant-in-Aid for Scientific Research on Innovative Areas. The carbon and oxygen is measured using CO<sub>2</sub> and sulfur stable isotope measurement is carried out using SF<sub>6</sub> gas. We have completed the construction of vacuum inlet line for standard and sample gas, and evaluated the precision of carbon and oxygen isotope using CO<sub>2</sub> and for sulfur using SF<sub>6</sub> using the normal bellows sample reservoir. A new micro-volume inlet system was also installed and fundamental parameters such as pressure effect and capillary effect relating to micro-volume inlet system were tested. In the measurement using CO<sub>2</sub>, standard gas in normal bellow showed a drift in both of carbon and oxygen isotopes were observed for six hours of continuous measurements (  $\delta^{13}$ C = -0.172 ‰,  $\delta^{18}$ O = -0.366 ‰) Therefore, we increased the volume of standard gas and obtained a better precession for the same sample duration. Internal carbon isotope standard sample of graphite (SP1 graphite powder), gave a precession of 0.045 ‰(n = 10). In the poster, we also present the details of the newly-constructed SF<sub>6</sub> gas preparation using curie point pyrolizer and gas purification system using gas chromatography. A new method for micro sampling using a femto-second laser ablation is also being tested for the analysis of small volume samples obtained using high-pressure experiments. **References:** 

Satish-Kumar et al., 2011, EPSL, 310, 340-34 Labidi et al., 2016, GCA, 175, 181-194

キーワード:硫黄同位体、炭素酸素同位体、質量分析計 Keywords: Sulfur isotope, Carbon and oxygen isotopes, Mass spectrometer

# Metasomatic mobilization of PGE in the suboceanic mantle: an implication from sub- $\mu$ m-sized sulfides from Tahitian peridotite xenolith

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Platinum-group elements (PGEs: Os, Ir, Ru, Rh, Pt and Pd) are strongly partitioned into metallic phases. Hence PGEs are thought to have been mostly sequestered in Earth' s core during core-mantle differentiation. In spite of such preferential distribution of PGEs into the core, investigations of natural mantle peridotites have revealed that PGE concentrations of the mantle are enriched, i.e. supra-chondritic PGE patterns that are not simply predicted from modeled pristine mantle left after the core separation (Mann et al., 2012 Geochim. Cosmochim. Acta.). With devoting efforts to compile bulk-rock PGE data of worldwide mantle peridotites in the past decades, metasomatic PGE inputs have been postulated (e.g., Lorand and Luguet, 2016 Rev. Mineral. Geochem. and references therein). Recent approaches of in-situ analyses for base metal (Fe-Ni-Cu) sulfides (one of the representative PGE-host minerals) along with bulk-rock analyses supported such PGE mobility during metasomatic events (e.g., Alard et al. 2011 J. Petrol., Delpech et al., 2012 Lithos). However, direct petrographic evidence for the metasomatic mobilization of PGE has not yet been documented because the samples are imposed on 'multiple' metasomatic events (e.g., Lorand et al., 2004 Chem. Geol.). Here we introduce sub- µm-scale investigations of 'armored' sulfide inclusion array of metasomatic origin within silicate mineral in a Iherzolite xenolith. With employing analyses by a field-emission transmission electron microscope with energy dispersive X-ray spectroscopy (FE-TEM-EDS), we introduce direct evidence of PGE mobilization in response to a metasomatic event and delineate the mechanism of PGE migration in the mantle. The Iherzolite xenolith we use here was collected at Tahiti island. Since the Iherzolite contains (1) vein-like clinopyroxenes in equilibrium with carbonaceous melt, (2) secondary CO<sub>2</sub> fluid inclusions, and (3) secondary carbonaceous silicate glass inclusions, we suppose that the lherzolite was subject to carbonatite metasomatism. Our intense investigations into sub- $\mu$ m-sized sulfide inclusion array in a clinopyroxene crystal revealed that they partly coexist with carbonaceous aluminosilicate glass, implying that immiscible sulfide melt and carbonaceous aluminosilicate melt filled microcracks before hearing of the host clinopyroxene. From the fact that the sulfides contain appreciable amounts of Ir-Pt-Rh (~20 atomic%), we conclude that Ir, Pt and Rh were mobilized through carbonatite metasomatism. We speculate that the PGEs were transported via miscible carbonatite-silicate-sulfide melts, which reached a new immiscibility field owing to a decrease in pressure and temperature. Although immiscible sulfide melts were minor in volume, most of the PGE were partitioned into the sulfide melts.

キーワード: PGE、交代作用、マントル捕獲岩、硫化鉱物、カーボナタイト、TEM Keywords: PGE, Metasomatism , Mantle xenolith, Sulfide, Carbonatite, TEM

## レーザー局所分析による金属 - ケイ酸塩メルト間の希ガス分配係数の実験 的決定

## Determination of the noble gas partition coefficients between metal-silicate melts using laser microprobe analysis

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Analyses of ocean island basalts (OIBs) reveal a geochemical reservoir characterized by unradiogenic, "primordial" noble gas signatures (e.g., high <sup>3</sup>He/<sup>4</sup>He and low <sup>40</sup>Ar/<sup>36</sup>Ar ratios), likely residing in the deep mantle. There has been much debate about the area holding the "primordial" noble gases deep in the Earth (Porcelli & Ballentine, 2002), including that the "primordial" noble gasses have been retained in the deepest region of the mantle since 4.4 Ga (Mukhopadhyay, 2012) or in the core since the core-mantle separation (Trieloff & Kunz, 2005). However, the validity of latter strongly depends on the quantity of noble gases the core incorporates during accretion and can hold in the present day.

In this study, in order to investigate noble gas partitioning behavior between the core and mantle, noble gases were dissolved into metal-silicate melts under high temperature and pressure conditions, and then the samples were quenched. Two series of sample synthesis were performed at different pressure-temperature ranges and experimental approaches. At the Geophysical Laboratory, Carnegie Institute of Washington, Ar partitioning experiments were conducted using a piston cylinder apparatus. Temperatures were 1700 °C, and pressures were 1 GPa. Experimental samples were contained by a double capsule: Pt outer capsule and graphite inner capsule. A Fe metal-silicate mixture was packed into the graphite capsule. Argon was added to the Pt outer capsule as a liquid, and the Pt capsule was welded shut while held in a bath of liquid N<sub>2</sub>. At the Geodynamics Research Center, Ehime University, noble-gas doped hydrous silicate glass and iron were melted and equilibrated under high pressure and temperature (~ 30 GPa, 1700 °C) using a laser-heated diamond anvil cell. After that, the noble gas concentrations contained in the each phase were analyzed using an ultraviolet laser ablation apparatus and a noble gas mass spectrometer at the University of Tokyo.

Preliminary results for argon showed that the partition coefficient D, where D = (noble gas in metal phase)/(noble gas in silicate phase), is in the order of  $10^{-4}$ , which is three orders of magnitude lower than the previous work (Matsuda *et al.*, 1993). However, the apparent noble gas concentrations in the metal phase seem significantly controlled by contaminant phases, such as metal inclusions and micro- or nano-noble gas bubbles. Further experiments are necessary to distinguish noble gases dissolved in metal and retained in the contaminants to better constrain noble gas behaviors between silicate and metal.

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キーワード:核、マントル、希ガス、分配係数、高圧高温実験 Keywords: core, mantle, noble gas, partition coefficient, high P-T experiment

# Viscosity and atomic-local-structures of basaltic melt under high pressure

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High pressure properties of basaltic melt are of importance in deep Earth science related to such as early magma ocean and subsequent differentiation processes (Agee 1998; Ohtani and Maeda 2001; Suzuki, *et al.* 2005)

Recently, experimental studies reported that the viscosity of basaltic melt decreases with increasing pressure (Allwardt, *et al.* 2007; Sakamaki, *et al.* 2013). They suggested based on the results of classical molecular dynamics simulation (Nevins and Spera 1998) and <sup>27</sup>Al magic-angle spinning nuclear magnetic resonance (Allwardt, *et al.* 2007) that this anomalous behavior is related to the coordination change of Al. However, other silicate melts which contain none of Al also show a common behavior of viscosity (McMillan *et al.*, 2009). It means that the microscopic origin of the anomalous pressure response of viscosity of the basaltic melt is still unclear. For this reason, in this study, we perform *ab initio* molecular dynamics simulations and analyze atomic–local-structures in basaltic aluminosilicate melt under pressure. At the last meeting, we reported the structural changes around Al atom. This time, we discuss relationship between the viscosity and structural changes not only around Al but other elements.

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キーワード:第一原理分子動力学シミュレーション、玄武岩質メルト、粘性、微視的構造 Keywords: Ab initio molecular dynamics simulation, Basaltic melt, Viscosity , Microscopic structures

## Viscosity of CO<sub>2</sub>-bearing sodium aluminosilicate melt at high pressure

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Viscosity is one of the important transport properties controlling the migration of magma in the Earth's interior. Experimental and geochemical studies showed that magma in the deep interior was generated in the presence of  $CO_2$ . However, our knowledge on the effect of  $CO_2$  on the viscosity of magma (silicate melt) is still insufficient. Here we report the viscosity of sodium aluminosilicate melt with jadeite composition containing 0.5 wt% of  $CO_2$  under high pressure. Viscosity was measured by the falling sphere method by using X-ray radiography image. Experiments were carried out using the MAX-III apparatus installed at the station NE7A of PF-AR synchrotron radiation facility in KEK (High Energy Accelerator Research Organization), Tsukuba, Japan. Viscosity was calculated using the Stokes equation with the correction of wall effect. Viscosity measurements were carried out up to 2.4 GPa. We observed that viscosity of the  $CO_2$ -bearing melt was one order of magnitude lower than those of  $CO_2$ -free jadeite melt.

キーワード:マグマ、揮発性元素、二酸化炭素、マントル、高圧、放射光

Keywords: magma, volatile elements, carbon dioxide, maltle, high pressure, synchrotron radiation

# Stability and thermos-elastic properties of iron oxide hydroxide: water transportation in the Earth's interior

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Hydrogen in the Earth's interior plays an important role in the Earth's interior, e.g., reduction of melting temperature and enhancing the deformation. Hydrogen is also a candidate of the light element in the core on the basis of melting experiments. Therefore, the stability and physical properties of hydrous minerals are fundamentally important. We found a high pressure polymorph of diaspore over 19 GPa and named  $\delta$ -AlOOH (Suzuki et al., 2000). Crystal structure of  $\delta$ -AlOOH was determined to be InOOH type with an orthorhombic unit cell. On the basis of the structural similarity between  $\delta$ -AlOOH and a high pressure phase of SiO<sub>2</sub> with CaCl<sub>2</sub> structure, we estimated that  $\delta$ -AlOOH is an important candidate of the water reservoir in the lower mantle.

A high pressure phase of iron oxide hydroxide,  $\varepsilon$  -FeOOH, has also an InOOH-related structure. Recently, high-pressure X-ray diffraction study of  $\varepsilon$  -FeOOH was carried out, and the pressure-volume-temperature (P-V-T) equation of state was determined (Suzuki, 2016). The P-V-T data up to 11 GPa and 700K fitted to a third-order Birch-Murnaghan equation of state yield: isothermal bulk modulus  $K_{\tau n}$  of 135(3) GPa; its pressure derivative K' of 6.1(9);  $(\partial K_T / \partial T)_P$  of -0.05(2) GPa K<sup>-1</sup>; a<sub>0</sub> of 2.6(7)×10<sup>-5</sup> K<sup>-1</sup> and a<sub>1</sub> of 1.0(3)×10<sup>-7</sup>  $K^{-2}$ , where the volumetric thermal expansion coefficient is described as  $\alpha_{0,T} = a_0 + a_1 \times (T-300)$ . Here we report the results of X-ray diffraction study on goethite. Experiments were performed by using a Kawai-type multi-anvil apparatus driven by a 700 ton uniaxial press on the station NE7A at PF-AR, a synchrotron radiation facility in KEK, Tsukuba, Japan. Powder X-ray diffraction data were collected by the energy-dispersive method using a Ge-SSD detector at a fixed diffracted angle 2 theta of 6.0 degree. Goethite ( $\alpha$ -FeOOH) is stable at ambient condition. We observed transformation to  $\varepsilon$ -FeOOH at 7.8+-0.5 GPa and 873K. The reduction of volume by the transformation was about 3.5%. The P-V-T data of goethite were collected up to 7.55 GPa and 600 K. Fitting the volume data to the third-order Birch–Murnaghan EoS yielded an isothermal bulk modulus,  $K_0$  of 85.9(15) GPa, and a pressure derivative of the bulk modulus, K', of 12.6(8). The temperature derivative of the bulk modulus,  $(dK/dT)_{p}$ , was -0.022(9) GPa K<sup>-1</sup>. The thermal expansion coefficient  $a_0$  was determined to be 4.0(5) ×10<sup>-5</sup> K<sup>-1</sup>. Dobson and Brodholt (2005) proposed that the banded iron formation subducted to the core-mantle boundary and stagnated there. The banded iron formation contains iron oxide-hydroxide. Goethite ( $\alpha$ -FeOOH) transforms to  $\varepsilon$ -FeOOH at high pressure. At the core-mantle boundary,  $\varepsilon$ -FeOOH may react with the core, and oxygen and hydrogen are partitioned. We estimate that iron oxide hydroxide can transport hydrogen to the deep interior and supply hydrogen to the outer core. Also wüstite may be formed at the core-mantle boundary.

キーワード:マントル、含水相、水、核、核-マントル境界、高圧 Keywords: mantle, hydrous phase, water, core, core-mantle boundary, high pressure

# AIに富む含水ブリッジマナイトの状態方程式 P-V-T equation of state of AI-bearing hydrous bridgmanite

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Water is the most abundant volatile component on the Earth. It has significant influences on the chemical and physical properties of mantle minerals (e.g., melting temperature, elastic properties, 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 Earth's 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). However, the physical properties of Al-bearing hydrous bridgmanite under high pressure are unknown. Therefore, we clarified P-V-T equation of state of Al-bearing hydrous bridgmanite will be reported.

In situ P-V-T experiments of Al-bearing hydrous bridgmanite were conducted using multi-anvil high pressure apparatus (SPEED-Mk.II) with sintered diamond 2nd stage anvil at SPring-8 BL04B1. As we observed the dehydration of Al-bearing hydrous bridgmanite between 900 and 1500 K in our in situ open system experiment, we developed in situ closed system experimental method using Ag capsule. The experimental conditions were 35-45 GPa and 300-1500 K. In addition, the room temperature compression data of Al-bearing hydrous bridgmanite was obtained using diamond anvil cell (DAC) with He pressure medium at PF BL18C up to ~55 GPa in quasi-hydrostatic condition (Takemura, 2001). The unit cell volume of Al-bearing hydrous bridgmanite decreased smoothly up to 52 GPa. This result indicated that the hydrogen bond symmetrization is not occurred at least up to 52 GPa at room temperature. The bulk modulus of Al-bearing hydrous bridgmanite is much smaller than that of Al-bearing anhydrous bridgmanite. In this presentation, we will report the thermo-elastic properties of Al-bearing bridgmanite in detail. Moreover, the water affect to physical properties will be discussed.

キーワード:ブリッジマナイト、水、下部マントル、状態方程式 Keywords: bridgmanite, water, lower mantle, equation of state

# 高圧下でのAIに富んだ含水及び無水ブリッジマナイトの弾性波速度 Sound velocity of AI-bearing hydrous and anhydrous bridgmanites under high pressure

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Bridgmanite is a major constituent mineral in the lower mantle, and it is important to clarify the sound velocity to elucidate the mineral assembly (composition) of the lower mantle. Recently we reported that Al-bearing bridgmanite (Mg-silicate perovskite) can contain significant amount of water up to ~0.8 wt%, and confirmed the possible H position in the bridgmanite by means of the powder neutron diffraction analysis in J-PARC, together with the single crystal X-ray structural analysis in PF. Because of the H in the bridgmanite, the physical properties of the bridgmanite should be changed. So the determination of the effect of water for the sound velocity of bridgmanite is very important to discuss the possible water storage in the lower mantle.

For the comparison, the sound velocity measurement of anhydrous bridgmanite is also important. However, even in the anhydrous bridgmanite, the substitution forms are complicated. We recognize that both "Tschermak substitution" and "oxygen-vacancy substitution" forms exist in anhydrous bridgmanite. So the special attention was made to synthesize the two different anhydrous bridgmanites by preparing the appropriate compositional starting materials and conducting experiments in extremely anhydrous condition.

We succeeded to synthesize the polycrystalline hydrous and anhydrous bridgmanites using the Kawai-type high pressure apparatus (Orange 3000) in Ehime University suitable for the sound velocity measurements. In situ ultrasonic experiments combined with X-ray were conducted in BL04B1 beamline, SPring-8. In this talk, we will explain the experimental results in details.

#### キーワード:含水ブリッジマナイト、無水ブリッジマナイト、下部マントル、放射光X線その場観察実験、弾 性波速度

Keywords: hydrous bridgmanite, anhydrous bridgmanite, lower mantle, Synchrotron X-ray in situ experiment, sound velocity

# Ar/D<sub>2</sub>及びD<sub>2</sub>Oを拡散源とした水素拡散炉による結晶中の水素拡散機構の 評価

Development for hydrogen diffusion experiments under  $\mathrm{Ar/D}_2$  and  $\mathrm{D}_2$  O condition

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There are many uncertainties about the origin of hydrogen in the earth. Especially, hydrogen isotopic compositions of the early earth are unclear. The characteristics of water of mantle in the early earth would be able to expect to estimate from those of hydrous minerals, for example, apatite crystals in the hadean and archean. However, without an understanding of hydrogen diffusivity in these hydrous minerals, it is difficult to esimate whether original hydrogen isotopic compositions from crystallization are preserved or the subsequently modified by reactions with water or  $H_2$  gas after crystallization. Therefore, this study reports development of the diffusion experiment for hydrous minerals with diffusion source of water and  $Ar/D_2$  gas.

The diffusion annealing system in this study could chose between  $D_2O$  line and  $Ar/D_2$  line for the diffusion source. In addition, this system chose flow type and close type with vacuum system for the control of partial pressure in the crystal surface. Therefore, we need to estimate the residue of H2O and  $D_2O$  absorbed in the line and quarts tube when the  $Ar/D_2$  gas line are selected.

The quantitative analyses for residue of absorbed water were estimated by annealing of apatite crystals in the different condition with the depth profile by Kyoto 4f-e7 secondary ion mass spectrometry (SIMS). This talk will discuss the results of different diffusion source in the apatite crystals and methods of control the partial pressure of  $Ar/D_2$  diffusion experiments.

キーワード: Hydrogen、diffusion、SIMS Keywords: Hydrogen, diffusion, SIMS

## Lattice thermal conductivity of (Mg,Fe)O magnesiowustite

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The Earth has been cooling since it was born about 4.6 billion years ago. To decipher the thermal history of the Earth, thermophysical properties of the lower mantle materials that constitute more than half the volume of the Earth is of great importance. A number of research has suggested the possibility that (Mg,Fe)O ferropericlase, one of the main constituent minerals of the lower mantle, exists with very iron-rich chemical composition at the Earth' s core-mantle boundary (CMB). Such iron-rich (Mg,Fe)O magnesiowustite at the CMB may cause regional variation of thermal conductivity of the lowermost mantle due to its distinct iron concentration, which potentially influences the mantle convection style, inner core age, inner core structure, geomagnetic field reversal frequency and so on [e.g. Olson, 2016]. However, there is no systematic study to examine the effect of iron on the thermal conductivity of (Mg,Fe)O solid solution under high pressure. In this study, we measured lattice thermal conductivity of (Mg,Fe)O magnesiowustite with various iron contents at high pressures, and evaluated its compositional dependence. Our results show much lower lattice conductivity of iron- rich magnesiowustite than that of MgO and FeO due to strong iron impurity phonon scattering, which would help to estimate the thermal conductivity of the expected iron- rich region in the lowermost mantle.

Reference: Olson, P. Mantle control of the geodynamo: Consequences of top-down regulation, *Geochem. Geophys. Geosys.* 17, 1935–1956, (2016).

キーワード:熱伝導率、下部マントル、フェロペリクレース、マグネシオウスタイト Keywords: thermal conductivity, lower mantle, ferropericlase, magnesiowustite

# *Ab initio* lattice thermal conductivity of MgO using a full solution to the linearized Boltzmann transport equation

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Lattice thermal conductivity,  $\kappa_{lat}$ , of MgO at high pressures and temperatures, up to 150 GPa and 4000 K, are determined using lattice dynamics calculations and the linearized phonon Boltzmann transport equation (BTE) beyond the relaxation time approximation (RTA) from first principles. It is found that the complete solution of the linearized BTE substantially corrects values of  $\kappa_{lat}$  calculated with the RTA by <sup>°</sup>30%, from <sup>°</sup>39 W m<sup>-1</sup> K<sup>-1</sup> to <sup>°</sup>50 W m<sup>-1</sup> K<sup>-1</sup> under ambient conditions. The calculated values of  $\kappa_{lat}$  are in good agreement with those from the existing experiments. At conditions representative of the Earth' s core-mantle boundary (P = 136 GPa and T = 3800 K),  $\kappa_{lat}$  is predicted to be <sup>°</sup>31 W m<sup>-1</sup> K<sup>-1</sup> and <sup>°</sup>39 W m<sup>-1</sup> K<sup>-1</sup> by RTA and the full solution of BTE, respectively. We report a detailed comparison of our study with earlier theoretical studies.

キーワード:下部マントル鉱物、格子熱伝導率、コンヒ<sup>°</sup>ュータシミュレーション、フォノン-フォノン相互作 用、密度汎関数理論

Keywords: Lower mantle minerals, Lattice thermal conductivity, Computer simulation, Phonon-phonon interaction, Density-functional theory
# Melting relations in the MgO-MgSiO $_3$ system under the lower mantle conditions

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Melting mechanism has important implication for chemical evolution of the Earth. Knowledge of the melting phase relation in the lower mantle is a key to understand the chemical differentiation in the early Earth and the nature of the ultralow-velocity zones (ULVZs) at the base of the mantle. While melting relations of mantle materials at relatively low pressure (below 30 GPa) have been extensively studied using a multi-anvil apparatus, the melting experiments at higher pressures are still limited. Only in a few model rock compositions, such as peridotite and mid-oceanic ridge basalt (MORB), the experiments were conducted under the CMB conditions using a laser-heated diamond anvil cell (LHDAC). Since chemical heterogeneity of both major elements and minor ones should have a large effect on the melting behavior, the melting phase diagrams as a function of composition are fundamental to understand the detail of the early melting history of the Earth and the nature of the ULVZs. In this study, we determined the melting relations in the MgO-MgSiO<sub>3</sub> system, which is a major component in the lower mantle. The experiments were performed up to 115 GPa using a CO<sub>2</sub> laser heated diamond anvil cell. The quenched samples were polished and analyzed by a dualbeam focused ion beam (FIB) and a field emission scanning electron microscope (FE-SEM), respectively. The eutectic compositions and liquidus phase were determined on the basis of chemical and textual analyses of sample cross sections. Our experimental results show that the eutectic composition is Si/Mg molar ratio of ~0.76 at around 35 GPa and it decreases with increasing pressure below 45 GPa. Above 45 GPa, it becomes relatively constant at about 0.64-0.65 Si/Mg molar ratio. Additionally, the eutectic composition was described by thermodynamic calculation under the whole lower mantle conditions. We obtained the Si/Mg molar ratio of ~0.64 at the base of the mantle. The liquidus phase changes from MgO-periclase to MgSiO<sub>2</sub>

-bridgmanite at around 35 GPa in the Fe-free simplified pyrolite composition ( $^{\circ}0.7$  Si/Mg molar ratio). In the other model rock composition such as chondrite ( $^{\circ}0.84$  Si/Mg molar ratio), MgSiO<sub>3</sub>-bridgmanite becomes the liquidus phase in the entire lower mantle. Thus MgSiO<sub>3</sub>-bridgmanite should be the dominant phase to crystallize from a deep global magma ocean in the lower mantle.

## 微細組織観察によって決定された<sup>~</sup>50 GPaまでのMgOの融点 Melting temperatures of MgO up to <sup>~</sup>50 GPa determined by micro-texture analysis

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ペリクレース (MgO) は地球下部マントルでブリッジマナイトに次いで二番目に豊富な鉱物であり、その高圧 融点は下部マントルのレオロジーと融解挙動を制約する上で重要である。MgOの融点に関して、レーザー加熱 式ダイヤモンドアンビルセル(LHDAC)と、動的圧縮実験及び理論予測との間には重大な食い違いが存在してい る。我々はLHDACを用いて高圧下におけるMgOの融点計測を行った。融解は回収試料の微細組織観察に よって検出された。

過去のLHDAC実験の融点まで加熱された回収試料の微細組織はランダムに集積された等粒状の組織を形成していた。これは融解によるものではなく、試料の塑性変形によってもたらされたものである。つまり、過去のLHDACの融点は低く見積もられていたことを示唆している。一方で、その過去の融点より1500-1700 K程度高い温度まで加熱された回収試料は、金属鋳造で見られる典型的な固化組織とよく似た特徴的な内部組織を示していた。我々はこの組織の観察を基にして<sup>~</sup>50 GPaまで融点を決定した。

我々の融点をサイモンの式にフィッティングして得られる*dT<sub>m</sub>/dP*は、0圧力で103 K/GPaであった。この値 は理論予想(90~120 K/GPa)と整合的である。我々の融解曲線をCMB (135 GPa)まで外挿して得られるMgOの 融点は~7900 Kであった。この高いMgOの融点は、冷たい沈み込みスラブが過去に考えられていた以上の高い 粘性率を持つことを示唆しており、これは、MgOの組織的な相互連結が下部マントル内におけるスラブ沈降の 停滞に寄与していないことを示している。本研究の結果は、下部マントル内の、コア-マントル境界に存在して いるとされる、最深部マグマがペリドタイト的な組成であることも示唆している。

キーワード:融解、鉱物物理、高圧実験

Keywords: Melting, Mineral physics, High pressure experiments

## Phase relations of $MgSiO_3$ -FeSiO<sub>3</sub> system up to about 60 GPa and 2300K using multianvil apparatus with sintered diamond anvils

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MgSiO<sub>3</sub> bridgmanite is the most abundant mineral in the Earth' s lower mantle, which can accommodate certain amount of FeSiO<sub>3</sub> under the P-T conditions of the lower mantle. Because of geophysical importance of FeSiO<sub>3</sub>-bearing bridgmanite, phase relations of MgO-FeO-SiO<sub>2</sub> system have been investigated using both laser-heated diamond anvil cell (LHDAC) and Kawai-type multi-anvil apparatus (KMA), but there are some inconsistencies among their studies. Dorfman et al. (2013) made experiments up to 155 GPa and 3000 K using LHDAC, which reported a sharp increase of the solubility of the FeSiO<sub>3</sub> component in bridgmanite at 50-70 GPa. In contrast, Tateno et al. (2007) reported more continuous solubility of FeSiO<sub>3</sub> with pressure using similar techniques of LHDAC. On the other hand, Tange et al. (2009) precisely determined the phase relations in the system MgO-FeO-SiO<sub>2</sub> on the bases of KMA experiments using sintered diamond (SD) anvils, but the maximum pressure and temperature in this study were limited to 47 GPa at 1773 K.

Based on the newly developed high pressure and temperature techniques, we studied detailed phase relations in the system MgO-FeO-SiO<sub>2</sub> using KMA with SD anvils at pressures up to 61 GPa at a temperature of 2000 K. Synthetic pyroxene samples with chemical compositions of  $(Mg_{0.4}Fe_{0.6})SiO_3$  and FeSiO<sub>3</sub> were used as the starting materials. Both quench experiments and in situ X-ray observations were adopted to constrain the phases present. Single-phase bridgmanite and an assemblage of wüstite + stishovite were formed in the MgSiO<sub>3</sub>-rich and FeSiO<sub>3</sub>-rich regions, respectively, under the present pressure and temperature conditions of up to ~60 GPa, which is generally consistent with the phase relations in the earlier studies. We found the solubility of FeSiO<sub>3</sub> in bridgmanite increases almost linearly with increasing pressure from Fe\* (Fe/Fe+Mg) = 0.19 for 27 GPa to 0.38 mole for 60 GPa.

キーワード:ブリッジマナイト、高温発生、焼結ダイヤモンドアンビル Keywords: bridgmanite, high temperature generation, sintered diamond anvil

### Thai Seismic Array (TSAR) Project: Progress in FY2016

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The Thai Seismic Array (TSAR) project has started under the project "Seismic and geo-electromagnetic observation for core and mantle", which is one of the KAKENHI grants for an innovative area

"Core-mantle co-evolution". In the JpGU2016 meeting, we reported the scope of the project, results of the site survey and status of the 2 pilot stations (Tanaka et al., 2016). In this presentation, we will show the progress in FY2016 and current status.

Since November 2016, we have started the deployment. As of February 13th, 2017, 30 stations are under operation, which are distributed in the central, northern, eastern, and northeastern Thailand. However, due to heavy rain and severe flooding in the southern Thailand in December 2016 and January 2017, we abandon the deployment of the stations in the Malay peninsula. Instead, we will construct a dense array in the central part of Thailand. The deployment of the additional 10 stations will be completed until the end of February.

### Local strong slow S-wave anomalies at western edge of Pacific LLSVP

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Seismic tomography studies have revealed two broad slow shear-wave speed anomalies regions beneath the Pacific and Africa called as LLSVPs (Large Low Seismic Velocity Provinces). There are geographic correlations between the LLSVPs and hotspots, and the LLSVPs could probably play an important role for convection throughout the mantle and thermal structure and evolution of the earth. The LLSVPs have been considered to be heterogeneous in composition since the boundaries between the normal mantle are sharp. To investigate the details of the sharp LLSVP edge we measure ScS–S and SKS–S differential traveltimes in the hypocentral distance of about 60 –90° using Japanese and Chinese seismic networks. We found anomalously large (more than 5 sec) ScS –S travel times accompanying normal SKS –S travel times, suggesting local strong slow region in the vicinity of the ScS bounce points (red circles in Figure 1). Such ScS bounce points locate to the northeast of New Guinea Island extending over 20 degrees in NE-SW direction. However below New Guinea Island, both ScS –S and SKS –S travel times are normal (green circles in Figure 1), indicating abrupt end of the local strong slow anomalies.

キーワード:核マントル境界、LLSVP、ScS波、SKS波 Keywords: core mantle boundary, LLSVP, ScS wave, SKS wave



# Waveform tomography for 3-D shear velocity structure in the lowermost mantle beneath the Northern Pacific

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We conduct waveform inversion (Kawai et al. 2014, GJI) to infer the 3-D SH-velocity structure in the lowermost mantle beneath the Northern Pacific, using ~20,000 transverse components of broadband body-wave seismograms for the first step. We use S, ScS and other phases that arrive between them. The 3-D SH-velocity models obtained by our inversion show three prominent features: (i) horizontal high-velocity anomalies up to about 3 per cent faster than the Preliminary Reference Earth Model (PREM) with a thickness of a few hundred km and a lower boundary which is at most about 150 km above the core-mantle boundary (CMB), (ii) low-velocity anomalies about 2.5 per cent slower than PREM beneath the high-velocity anomalies at the base of the lower mantle, (iii) a thin (about 200 km) low-velocity structure continuous from the base of the low-velocity zone to at least 400 km above the CMB. We interpret these features respectively as: (i) remnants of slab material where the Mg-perovskite to Mg-post-perovskite phase transition could have occurred within the slab, (ii,iii) large amounts of hot and less dense materials beneath the cold paleoslab remnants just above the CMB which ascend and form a passive plume upwelling at the edge of the slab remnants (Suzuki et al. 2016, EPS).

As a second step, we conduct waveform inversion using both the transverse and radial components to infer the more detailed isotropic shear velocity structure in the lowermost mantle beneath the Northern Pacific. We also infer the transversely isotropic (TI) shear-velocity structure for this region using two horizontal components. We conduct synthetic resolution check to examine the ability of our methods and dataset to resolve the TI shear-velocity structure.

キーワード:最下部マントル、波形インバージョン、S波速度構造 Keywords: Lowermost mantle, Waveform inversion, Shear velocity structure

# 3-D S-velocity velocity structure in D"obtained by waveform inversion after redetermination of the earthquake source parameters

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Our group previously investigated the 3-D S-velocity structure within the D" layer beneath central America using waveform inversion (Kawai et al. 2014, GJI; Borgeaud et al. 2016, JPGU). In these studies, the source parameters were fixed to the Global Centroid-Moment-Tensor (GCMT) Project solutions. The GCMT solutions are determined using not only body-waves, but also surface-waves, and mantle-waves, and the data are filtered in a different frequency range from that used in our waveform inversion studies. In this study we redetermine the CMT solutions using body-wave data only, filtered in the same frequency range (12.5-200 s) as that used in our waveform inversion studies. Then, we re-infer the 3-D S-velocity structure of the D" layer beneath central America using the new CMT solutions. We compare the respective 3-D models to see whether (1) waveform inversion is robust to small changes in the source parameters, and (2) whether the models obtained by waveform inversion are improved by using the redetermined Source parameters. We find that the variance reduction for the model inferred using our redetermined CMT solutions is better than that for the model inferred using the GCMT solutions. Also, although this is somewhat subjective, the new 3-D model appears to provide sharper images with a better visualization of paleoslab-like high-velocity structures.

キーワード:波形インバージョン、震源パラメータ、最下部マントル Keywords: Waveform inversion, Earthquake source parameters, Seismic velocity structure of D<sup>"</sup>

### D111-type guide block for high-pressure deformation experiments

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For accurate understanding of material and heat transports in the Earth's interiors, knowledge of rheological property under high-pressure and high-temperature is indispensable. To study rheological property of materials at high-pressure quantitatively, deformation experiments has been carried out using various deformation devises including rotational Drickamer apparatus and deformation-DIA apparatus. Recently a new type apparatus, deformation T-Cup (DT-Cup), which is based on Kawai-type multi-anvil apparatus was developed by Hunt et al. (2014). In the DT-Cup, by driving two second-stage anvils using differential actuators, well-controlled deformation experiments can be conducted up to confining pressure of 18 GPa. However, more improvement is needed to achieve deformation at the condition of the Earth's lower mantle (>23 GPa).

To study the rheological property at the lower mantle condition experimentally, we are planning to install a "D111-type guide block" on a synchrotron beamline NE7A at PF-AR, KEK, Tsukuba. By combining D111-type guide block with the MAX-III press, it acts as a deformation apparatus (D111-type deformation device) that is improved version of DT-Cup. The our D111-type device can be used under higher press load (max. 700 tonf) which enables us to conduct quantitative deformation experiments at the lower mantle pressures. Stress and strain during deformation can be measured in situ using the monochromatized synchrotron X-ray. The installation of the D111-type guide block is planned on March 2017. We expect fruitful results on the deep Earth rheology based on experiments using the D111-type device in near future.

キーワード:変形実験、地球深部のレオロジー、下部マントル Keywords: deformation experiments, deep Earth rheology , lower mantle

## Toward the in-situ deformation experiments under the lower mantle conditions using D-DIA apparatus

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Rheological properties of lower-mantle forming minerals such as bridgmanite are important to understand the cause of seismic anisotropy and the viscosity structure in the lower mantle. To explore the creep behavior and crystallographic preferred orientation of high-pressure minerals, two types of deformation apparatus, namely, the D-DIA type (Wang et al., 2003) and the rotational Drickamer apparatus (RDA: Yamazaki and Karato, 2001) have been adopted to deformation experiments at high pressures. Even though the upper limit of confining pressure is 4 GPa in the Griggs rig (e.g., Rybacki et al., 1998), the upper limit is more than 18 GPa in the case of D-DIA and RDA (Miyagi et al., 2013; Kawazoe et al., 2016). Recently, Girard et al. (2015) and Tsujino et al. (2016) succeeded to deform bridgmanite at lower mantle pressures and temperatures using a RDA and a Kawai-type apparatus for triaxial deformation (KATD: Nishihara, 2008), respectively. Even though the pressure and temperature conditions available in a RDA and a KATD have been extended to the lower mantle conditions, in-situ D-DIA experiments are still limited to the conditions of lower part of the mantle transition zone (Kawazoe et al., 2016). The main cause disturbing further pressure generation using an in-situ D-DIA apparatus is relatively low toughness of the x-ray transparent anvils made from sintered diamond or cubic BN. In the geometry of cubic-type multianvil apparatus, the available press load needs to be low (< 0.6 MN) to avoid the breakage of the x-ray transparent anvils. Also, conventional WC anvils are not suitable for the generation of lower mantle pressures in the geometry of cubic-type multianvil apparatus. The advantages of D-DIA apparatus are as follows: i) sample deformation can be precisely controlled by two deformation rams (i.e., deformation with a constant strain rate) and ii) temperature can be monitored by using a thermocouple. To explore the quantitative deformation experiments at lower mantle conditions, we adopted the 'jacketed' 6-6 type anvils (Yamada et al., 2016) and optimized the cell assembly using preformed gaskets (e.g., Kawazoe et al., 2010). Combining these techniques, we succeeded to generate 24 GPa at room temperatures using a D-DIA apparatus. Pressures higher than 20 GPa are also available with our in-situ experimental setup, suggesting a possibility of quantitative deformation experiments at lower mantle conditions in near future.

キーワード: D-DIA型変形装置、下部マントル、6-6型アンビル Keywords: D-DIA apparatus, lower mantle, 6-6 type anvil

## 玄武岩質マグマとFe-FeS融体間の硫黄分配 Sulfur distribution between basaltic magma and Fe-FeS melt

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Earth is consist of crust, mantle, and core. The crust and mantle are made of silicates and oxides. The core is mainly composed of iron with light elements such as H, C, O, S, and Si. This is because the density of the core is smaller than that of pure iron under the core conditions. The Earth' s structure was considered to have formed during the differentiation of magma ocean in the early stages of formation of Earth. During the magma ocean, the metallic liquid reacted with the magma at the bottom of the magma ocean.

Since sulfur is depleted in the mantle compared to CI chondrites (e.g., Murthy and Hall, 1970) and sulfides are found in meteorites, sulfur is one of the most plausible candidate elements in the Earth's core. Therefore, the study on Fe-S system provides us some significant information about magma ocean and core formation. In magma ocean, metallic melts sank to the bottom of the magma ocean because of gravitational separation. At the same time, a partitioning between liquid silicate and liquid metal occurred under very high temperature and pressure conditions. Sulfur distribution and isotope fractionation are affected by these parameter (T, P,  $f_{02}$  etc.). Therefore, research on sulfur distribution leads to understanding the process of the differentiation between core and mantle in early Earth. In this study, partitioning experiments between silicate (basaltic composition) and metal (Fe-14 wt%S alloy) were performed using Kawai-type 3000 ton multi-anvil press at Tohoku University. The experiments were carried out at pressures ranging from 1 to 7 GPa and heated to temperatures of 1400 °C to 1800 °C. Chemical composition of the sample were analyzed using SEM-EDS.

Experimental results show that correlations between distribution coefficients of sulfur and temperature changed by pressure. Distribution coefficients of sulfur at 3 GPa decreased with increasing temperature while those at 5 GPa increased with increasing temperature. Also, correlations between distribution coefficient of sulfur and pressure were changed by temperature. Distribution coefficients of sulfur at 1650 °C increased with increasing pressure, on the other hand, those at 1800 °C decreased with increasing pressure. As a whole, it was observed that they had a negative relation between distribution coefficient and pressure.

The average distribution coefficients in this study was 76±36. McDonough (2003) reported that the total abundance of sulfur in Earth was 6530 ppm. Using the average and the abundance, we estimated that the amount of sulfur in Earth's mantle was 82±7 ppm. This abundance is less than expected previously (e.g., Palme and O' Neill, 2001; McDonough, 2003). However, it is actually expected to be higher content of sulfur in Earth's mantle because magma ocean experienced higher temperature condition than this study, with higher lithophile nature. Oxygen fugacity is also an important parameter that influence element partitioning. Under reducing condition, sulfur tends to be distribute to silicate phase than in oxidizing condition. The present  $\Delta$ IW (oxygen fugacity to Iron-Wüstite buffer) of the experiments were in the range of -1.16 and -1.44. Assuming more reductive condition than the present  $\Delta$ IW in magma ocean, the content of sulfur in Earth's mantle might increase and match the geological estimate.

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## Outer core composition estimated from thermoelastic properties of liquid Fe alloys

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The Earth's core is thought to include substantially large amounts of light elements (LEs), which account for observed density deficits of ~10% for the liquid outer core and ~5% for the solid inner core (e.g. Birch, 1964; Brown and McQueen, 1986; Jephcoat and Olson, 1987; Uchida et al., 2001; Anderson et al., 2003; Dewaele et al., 2006; Ichikawa et al., 2014). The density jump across the inner-outer core boundary (ICB) evaluated by seismic wave observations is ~4.5-6.7 % (Shearer and Masters, 1990, Masters and Gubbins, 2003), which cannot be accounted for by the melting phase transition of pure iron alone and requires a LEs partitioning more into the outer core (Alfè et al., 2002a). Although oxygen, silicon, carbon, nitrogen, sulfur, and hydrogen have been proposed as candidates for the LEs (Stevenson, 1981), little is known about the amount and the species so far. However, experimental determination of these properties for the liquid states are still not practical at the outer core pressure and temperature (from ~136 GPa to ~329 GPa and from ~4,000 K to ~6,000 K) due to technical limitations. The ab initio density functional computation method is instead quite powerful to investigate liquid properties under such extreme condition. Here, we show integrative analyses of the compositional model of the Earth' s outer core based on the ab initio thermoelasticity of iron-nickel-LE alloy liquids. Results indicate that combination of LEs in the outer core cannot be fully constrained only by the comparison between elastic properties and seismic observation. Comprehensive considerations covering density jump at the ICB, phase relations, geochemical constraints, and the  $\Delta V_{\rm P}$  of low-velocab initioity anomalies in the outermost core are used to refine the compositions of the outer core.

キーワード: Composition of the Earth's outer core、Light elements、ab initio molecular dynamics simulation

Keywords: Composition of the Earth's outer core, Light elements, ab initio molecular dynamics simulation

## 高圧下におけるFe-FeS二成分系融体の密度 Density of Fe-FeS binary melts at high pressures

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水星とガニメデの磁場の起源となるダイナモは、流体核の上部で析出した固体鉄の沈降によって起こる組成 対流に駆動されていると考えられている。内部の圧力が低い小さい天体の流体核は、断熱温度勾配が融点勾配 より大きいため冷却に伴い上部から固化する。従って、高圧高温下のFe合金メルトの密度と熱膨張率の研究が 小さい天体の磁場の起源と進化の解明の鍵となる。Fe-Ni-S系メルトは水星や月などの比較的小さい天体の金属 核を構成していると考えられている。本研究では高圧下の密度測定からFe-FeS二成分系メルトの密度(モル体 積)を3.5GPa、1500K~2000Kにおいて調べた。高圧下のFe-FeS二成分系メルトの密度測定にはSPring-8の BL22XUに設置されている高温高圧プレス装置を用いた。挿入光源からの強力な単色X線を利用してX線吸収 法で密度を決定した。Fe-FeS二成分系メルトの密度はイオウ含有量の増加とともに小さくなる。Fe-FeS2成分 系メルトは数GPaでは負の過剰体積を持つと報告されている(Nishida, 2008; Buono & Walker, 2011)が、今 回の結果からFeメルトFeSメルトの混合は理想混合から大きく外れてはいないことが示された。X線吸収法は 従来の浮沈方や熱力学解析より精度が高いので、Fe-Sメルトの圧縮特性や熱化学的性質の研究に有効であると 考えられる。

キーワード:惑星核、Fe-Sメルト、密度、熱膨張率 Keywords: planetary core, Fe-S liquids, density, thermal expansivity

## 地球核条件下にレーザー衝撃圧縮された鉄合金融体の音速と密度の関係 Sound velocity and density of liquid iron alloys under Earth's core pressures by laser-shock compression

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Sound velocity at Earth' s core conditions are one of the most important physical properties in Earth science because it can be directly compared with the seismological Earth model (PREM: Preliminary Reference Earth Model) [1]. The composition of solid inner core is estimated from the comparison of the model [1] and the extrapolation of sound velocities as a function of density of iron and iron alloys obtained by the static compression experiment [2, 3]. Birch' s law, a linear sound velocity–density relation [4], is used to extrapolate sound velocities to densities in the core condition. On the other hand, the composition of liquid outer core is estimated from the partitioning and solubility data in the inner core boundary condition for the composition of solid core. There has been some works for the sound velocity of iron and iron alloys on the Earth' s core condition by dynamic techniques using explosive [5], gas gun [5-9], and laser [10-12]. Huang et al. estimated that the outer core composition is Fe with 0.5 wt.% O and 9.5 wt.% S by the comparison of PREM and sound velocities of Fe-S-O system [9]. In this study, we measure the sound velocity and density of liquid iron alloys by shock-compression method using high-power laser.

We conducted shock-compression experiments using a High Intensity Plasma Experimental Research (HIPER) system at the GEKKO-XII laser irradiation facility [13] at the Institute of Laser Engineering, Osaka University. The samples were Fe-Ni alloys, Fe-Si alloys, and pyrrhotite. The sound velocities and densities of shock-compressed iron alloys using the high-power laser were measured by x-ray radiography [10-12] at pressures up to 1000 GPa.

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キーワード:音速、衝撃圧縮、鉄合金、地球核、バーチ則 Keywords: Sound velocity, Shock compression, Iron alloy, Earth's core, Birch's law

# Anomalous behavior of core phase PKP*bc-df* differential travel times from observations of South Sandwich Islands earthquakes by Alaskan and US seismic arrays

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We report anomalous behavior of core phase PKPbc-df differential travel times recorded by stations of the Alaska regional network and current USArray for several South Sandwich Islands (SSI) earthquakes. The data sample the inner- and outer-core for the polar paths, as well as the lowermost mantle beneath eastern Alaska. Our major observations are: (1) the fractional travel time residuals of PKPbc-df (residual divided by PKPdf travel time in the inner-core) increase rapidly from 147° to 149° (up to 0.01, corresponding to travel time of ~1s), and keep almost constant after 149°. (2) From southwest to northeast, there is a decrease in fractional residual at distance larger than 150°. Either a rapid velocity change in the uppermost inner core or existence of a large lateral velocity variation at lowermost mantle, which is seen in a recently tomography model (Young et al., 2013), may explain the observation. The preliminary analysis indicates that modeling for discontinuities with different velocity jump in the inner-core does not seem to reproduce the observed fractional residuals, and that it may suggest a probable complexity at lowermost mantle. One possible interpretation is that PKPbc and PKPdf sample different portions of the heterogeneity at larger distance, which results in the sudden increase of the fractional residuals. The large residuals observed from the polar path data for SSI events are usually explained by strong anisotropy in the uppermost inner-core, which might have been misinterpreted if its affected by some structure at the lowest mantle. Further work including waveform modeling is need to resolve what causes the anomalous behavior of our observation.

### Sound velocity of hcp-Fe at multi-megabar pressures

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Earth' s inner core consists of mainly hexagonal close-packed iron (hcp-Fe). Therefore, the physical properties of hcp-Fe can provide significant knowledge about the core. Despite seismological observations providing density-sound velocity data of Earth' s core, there are few experimental reports about the sound velocity of hcp-Fe at ultrahigh pressure. Direct comparison of the sound velocity of hcp-Fe with that of observed inner core can provide a clear difference between them, which is an important information to determine the core composition. Here, we report the compressional sound velocity ( $V_p$ ) of hcp-Fe up to 250 GPa using an inelastic X-ray scattering technique at BL43LXU of SPring-8. Based on the data, we can provide a standard of hcp-Fe (a linear relation of  $V_p$  with density: Birch' s law), which enables us to indicate a better constraint on the composition of the Earth's core.

キーワード:核、音速、高圧 Keywords: core, sound velocity, high pressure

# Sound velocity of iron-nickel alloys determined by femtosecond acoustic measurement in diamond anvil cell

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Iron-nickel (Fe-Ni) alloy is believed to be a major component of the Earth's core based on the cosmochemical models and the studies of iron meteorites, although accurate chemical composition of the Earth' s core is still unknown. Comparison between seismic wave velocity profile in the Earth and laboratory data of sound velocity of Fe alloys enables us to decipher chemical composition and comprising minerals there. Acoustic velocity of  $Fe_{0.92}Ni_{0.08}$  has been obtained from nuclear resonant inelastic x-ray scattering (Lin et al., 2003), while experimental study on sound velocity of Fe-Ni alloy has not been performed in a wide range of nickel content. Here we measured longitudinal wave velocities of Fe,  $Fe_{0.95}Ni_{0.05}$  and  $Fe_{0.85}Ni_{0.15}$  up to 61 GPa and 300 K by means of a femtosecond acoustic technique in a diamond anvil cell (Decremps et al., 2014). The obtained sound velocity of Fe is in good agreement with previous studies. We also found that the acoustic velocities of iron-nickel alloys are slightly lower than that of pure iron.

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キーワード:コア、音速、鉄ニッケル合金、高圧 Keywords: core, sound velocity, iron-nickel alloy, high pressure

### Atomic diffusion in solid iron at Earth' s inner core conditions

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Crystalline iron is the main constituent of the Earth's inner core<sup>1</sup>. The thermomechanical properties of solid iron at high pressure and temperature therefore mainly control the dynamics and evolution of the inner core. One of those properties is atomic diffusion which plays a key role in many processes, such as plastic deformation (viscosity) and crystal growth. Ongoing debate about the seismologically observed elastic anisotropy of the Earth's inner core<sup>2,3</sup> has led to several suggestions whether to find its origin in non-uniform core growth<sup>4</sup>, dendritic crystal growth<sup>4,5</sup> (core solidification) or in solid-state flow<sup>4,6,7</sup> (formation of LPO), all which depend on atomic diffusion processes. In addition, the diffusion anisotropy of iron at inner core conditions provides a link between seismic anisotropy and plastic deformation of the inner core. Therefore, a thorough understanding of atomic diffusion mechanisms in iron polymorphs is essential to gain better insight into the evolution of the Earth's inner core.

Since experiments are extremely difficult to perform at inner core pressure and temperature conditions, computational mineral physics provides an alternative to study atomic diffusion in iron under those conditions. In this work, the effect of pressure on vacancy diffusion is investigated by means of defect energetics as it largely determines the rate of vacancy diffusion. First principles simulations have been performed to calculate activation enthalpies for self-diffusion in FCC- and BCC- and HCP-Fe at a pressure range up to the conditions of the Earth' s inner core. Our results show that pressure significantly increases defect energetics and in particular is responsible for suppressing defect concentration substantially in iron at inner core conditions. Consequently the rate of vacancy diffusion will be strongly inhibited. Intrinsic vacancy concentration plays an important role in metals in contrast to ionocovalent minerals where extrinsic vacancy concentration may determine effective vacancy diffusion. The question then arises whether other mechanisms allow to enhance vacancy concentration in iron under inner core conditions. If not, the latter will have direct consequences for the interpretation of the seismologically observed inner core anisotropy in terms of intracrystalline plasticity.

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Keywords: Earth's inner core, atomic diffusion, plastic deformation

### Pressure-volume-temperature relations for hydrogen volume and content in iron hydride at high pressure and high temperature

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The Earth's core has supposed to be constituted by iron, nickel and some light elements. In order to elucidate the property of the Earth's core, many studies to quantify the content of light elements in the Earth's core has been progressed through sound velocity and magnetic measurements, or theoretical research. Hydrogen is one of the most probable candidate among the light elements constituting the Earth's core due to the relations between iron and hydrous melt in the magma ocean in the early Earth, and the discovery of the post-perovskite phase and that melting temperature. Although several studies on iron hydride (FeH,) have been conducted, precise measurement of hydrogen content in metallic iron under high pressure and high temperature conditions has not been conducted due to the difficulty of the experiment. Hydrogen cannot be directly observed by traditional methods such as x-ray diffraction method. On the other hand, in neutron diffraction experiments, most of the direct observations of hydride has been carried out through substitution from hydrogen to deuterium because hydrogen has strong incoherent scattering. Therefore in many previous studies, the volume and the content of the hydrogen in metallic iron are assumed through the studies of several metallic hydride. However, such assumptions without precise measurement cause uncertainty, for example, when deriving the hydrogen content from the volume of FeH<sub>x</sub>. In this study, to determine the hydrogen content and volume at high pressure and high temperature, high pressure neutron diffraction experiment for FeH, was conducted under nearly isobar condition at 5-6 GPa and 8-9 GPa up to 1100 K in BL11 beamline, J-PARC. The phase transition and hydrogenation of iron were observed by dhcp-FeH, and fcc-FeH, phases, which are high pressure and high temperature phase of FeH<sub>2</sub>. The structure of FeH<sub>2</sub> and the content of hydrogen were determined by Rietveld refinement. The content of hydrogen x was obtained to 1.0-0.5, which is decreased by increasing temperature. We report the relations between the volume and the content in FeH, at high pressure and high temperature.

キーワード:鉄水素化物、中性子回折、高圧 Keywords: Iron hydride, Neutron diffraction, High pressure

# The band structure and impurity resistivity of hcp and fcc Fe based alloys: Implications for planetary cores

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It is widely known that the Earth' s Fe dominant core contains a certain amount of light elements such as H, C, N, O, Si and S (e.g. Hirose et al., 2013). The electronic band structure of Fe provides fundamental thermodynamic quantities (e.g. Boness et al. 1986). Gomi et al. (2016) calculated the band structure of substitutionally disordered hcp Fe-Si and Fe-Ni alloys, which suggest the broadening of the band structure due to Si is related to the impurity resistivity. However, only a few studies have investetaged the effect of alloying. In this study, we report the results of first-principles calculations on the band structure and the impurity resistivity disordered hcp and fcc Fe based alloys.

The first-principles calculation was conducted by using the AkaiKKR (machikaneyama) package, which employed the Korringa-Kohn-Rostoker (KKR) method with the atomic sphere approximation (ASA). The local density approximation (LDA) was adopted for the exchange-correlation potential (Moruzzi et al., 1978). The coherent potential approximation (CPA) was used to treat substitutional disorder effect (e.g. Akai, 1989). We mainly focused on Si, Ni, C, N, O and S impurity elements. The impurity resistivity is calculated from the Kubo-Greenwood formula with the vertex correction (Butler, 1985; Oshita et al., 2009; Gomi et al., 2016).

In dilute alloys with 1 at.% impurity concentration, calculated impurity resistivities of C, N, O, S are comparable to that of Si. On the other hand, in concentrated alloys up to 30 at%, Si impurity resistivity is the highest followed by C impurity resistivity. Ni impurity resistivity is the smallest. N, O and S impurity resistivities lie between Si and Ni. Impurity resistivities of hcp-based alloys show systematically higher values than fcc alloys. We also calculated the electronic specific heat from the density of states (DOS). For hcp and fcc Fe, the results show the deviation from the Sommerfeld value at high temperature, which is consistent with previous calculation (Boness et al., 1989). However, the degree of deviation becomes smaller with increasing impurity concentration.

The violation of the Sommerfeld expansion is possible source of the violation of the Wiedemann-Franz law (Gomi and Hirose, 2015; Secco et al., 2017), but the present results predict that the effect may not significant. Therefore, we conclude that the combination of the Wiedemann-Franz law and the resistivity saturation (Gomi et al., 2013; Ohta et al., 2016) can reasonably predict the thermal conductivity of the Earth' s and planetary cores.

キーワード:核、電気抵抗率、バンド構造、KKR-CPA Keywords: core, electrical resistivity, band structure, KKR-CPA

## 10 GPaにおけるFe-FeSi系の相関係:水星核への応用 Phase relations in the Fe-FeSi system at 10 GPa: Implications for Mercury's core

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Mercury' s magnetic field, which shows dipole, has been observed by Mariner 10. Core dynamo is the most reliable model for generating the dipolar magnetic field. A high electrical conductive fluid, i.e., a liquid core, plays an important role for generating the core dynamo. Assuming the pure iron core, the present core would be completely solidified based on the Mercury' s thermal history. Therefore, other factors are needed to maintain the molten Mercury' s core. One of the most plausible factor is a depression of the melting point of pure Fe core due to dissolving light elements. Recent studies have suggested that Mercury' s core may contain several wt% silicon based on high-pressure experiments. Therefore, the melting relations of the Fe-FeSi system at high pressures can provide knowledge of the Mercury' s core structure. However, high-pressure phase relations of this system are not yet known precisely. In order to get the better understanding of the core structure, it is needed to perform melting experiments under the core conditions.

In this study, we determined the phase diagram for the Fe-FeSi system at a pressure of 10 GPa and temperatures between 920 °C and 1800 °C based on in-situ X-ray and quenched experiments using a Kawai-type multi-anvil apparatus. Our results showed that the system had two eutectic points at approximately 10 wt% Si and 20 wt% Si and sub-solidus phases are fcc-Fe (<10 wt% Si) and Fe<sub>3</sub>Si (10-20 wt% Si) and FeSi (>20 wt% Si). Based on our results, we suggest three models of Mercury's core evolution depending on the initial core composition.

キーワード:水星核、Fe-Si合金、相図、高圧 Keywords: Mercury's core, Iron-silicon alloys, Phase diagram, High pressure Experimental investigation into the cause of a high attenuation zone of the lunar seismic waves: A possible partialy molten layer at the lowest lunar mantle

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Existence of a partially molten layer at the lunar core mantle boundary is suggested by recent seismic studies. It is important to study experimentally the chemical and physical condition at the boundary. However, the chemical compositions of the lunar mantle are still poorly understood. There is a long-standing hypothesis that dense Ti-rich cumulate minerals were crystallized from the lunar magma ocean at shallow depth (~100 km) at the final stage of the lunar formation history. Furthermore, those minerals subsequently sank deep into the moon because of gravitational instability. Convective mixing of the late and early cumulates could result in a hybrid lunar mantle.

In this study, high temperature (1200 - 1500°C) and high pressure (4 - 5 GPa) experiments are conducted to investigate the solidus of the lunar lowermost mantle which could be composed of the mixture of the late and early cumulates. The composition of the late cumulate suggested by Elkins-Tanton et al. (2011) was selected in this study. The solidus temperatures were determined to  $1225 \pm 10^{\circ}$ C at 4 GPa and to  $1275 \pm 25^{\circ}$ C at 5 GPa, defining a slope for the solidus of 5 °C/ kbar. Based on the solidus temperatures determined in this study, melting temperature at lunar core- mantle boundary (approximately 4 - 5 GPa) can be extrapolated as  $1225-1275^{\circ}$ C, which is also lower than previous studies (e.g. Van Orman and Grove, 2000; Thacker et al., 2009).

Because the lower limit temperature at lunar core-mantle boundary (e.g. Flourish and Nakamura, 2009), which was estimated by terrestrial heat flow and seismic studies, has been reported to be higher than the solidus of the later cumulates determined in this study. Therefore, later cumulate could be a strong candidate for component of partial molten layer at lunar core- mantle boundary.

キーワード:核-マントル境界、低速度層、部分熔融 Keywords: core-mantle boundary, low-velocity zone, partial melt

### Melting experiments of plagioclase under the shock-vein conditions

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High-pressure phase transitions of minerals have been frequently observed in heavily shocked meteorites, mainly within or around the shock veins (e.g., Chen et al. 1996). The plagioclase entrained in or adjacent to the shock veins transformed into maskelynite (e.g., Chen and El Goresy 2000), lingunite (e.g., Gillet et al. 2000) or jadeite plus amorphous materials (Miyahara et al. 2013). These transformations likely occurred in solid state, and the processes could be highly affected by the crystallization kinetics, as demonstrated by the kinetics studies of Kubo et al. (2010, 2016) at 18-25 GPa below 1673 K. On the other hand, the shock-metamorphic products of plagioclase exhibit some melting features (e.g., Chen and El Goresy 2000), and it is also likely that the shock metamorphism of plagioclase proceeded under the shock-vein conditions, typically 20-24 GPa and 2273-2673 K (Chen et al. 1996). Thus, high-temperature studies are necessary for further understanding the shock metamorphism of plagioclase in heavily shocked meteorites.

In this study, subsolidus and melting phase relations of  $Ab_{85}An_{10}Or_5$  (oligoclase, the typical composition for the plagioclase found in heavily shocked meteorites) have been investigated by multi-anvil experiments at 16-23 GPa and 2273-2700 K. At 19-22 GPa, the subsolidus phase assemblage of  $Ab_{85}An_{10}$  $Or_5$  is jadeite (Jd) + stishovite (St) + hollandite (Holl) + CAS phase, and the melting sequence is Jd (the solidus phase), Holl, CAS phase and St (the liquidus phase). The liquidus temperature of  $Ab_{85}An_{10}Or_5$  is at least 100 K higher than that of KLB-1 peridotite at 19-22 GPa. If the liquidus temperature of KLB-1 peridotite is used to infer the shock-vein temperatures, and if oligoclase completely melted at 19-22 GPa during impact, the oligoclase needed to be hotter than the shock veins, and therefore a localized heating in oligoclase is essential. It is found that Na-rich Holl and Na-rich CAS phase are stable in the composition of  $Ab_{85}An_{10}Or_5$  at 22 GPa and ~ 2500 K; the silicate liquid formed by melting crystallized into Holl, CAS phase and St during quenching. These phenomena likely relate with the natural occurrence of lingunite (e.g., Gillet et al. 2000) and CAS phase (Beck et al. 2004) in heavily shocked meteorites, but the kinetics problem must be further discussed. In addition, the intergrowth of CAS phase and St observed in some Martian meteorites (Beck et al. 2004) has been reproduced by quenching a labradorite melt at 23.5 GPa.

### キーワード:斜長石、高温高圧、相関係、衝撃変成

Keywords: Plagioclase, High Pressure and High Temperature, Phase Relation, Shock Metamorphism