

## 下部マントル条件下での熔融実験のための新超硬合金アンビル

New tungsten carbide anvils potentially important for melting experiments under lower mantle conditions

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Kawai-type multianvil apparatus (KMA) is important for accurate determinations of melting relations and element partitioning to understand the processes relevant to the interaction and co-evolution of the Earth's mantle and core. Recent developments in KMA technology with sintered diamond (SD) anvils has enabled to expand the pressure range available in this apparatus toward Mbar regime. However, the use of SD anvils has been limited only to very few laboratories due to both technological and financial reasons, as SD anvils are much expensive compared to tungsten carbide (WC) anvils and also specially designed large-volume apparatus is required to successfully pressurize the cell assemblage using SD anvils. Recently, a new class of "binderless" WC (Fujillo TJS01) has been developed by Fuji Di. Co. Ltd., which is claimed to be harder than any other commercially available WC. We have tested this novel WC as second-stage anvils for KMA based on in situ X-ray observations at SPring-8, and found that the anvils made of this WC indeed yield pressures significantly higher than those available with other WC anvils frequently used in the KMA community. Pressures up to about 50 GPa were confirmed at room temperature with an anvil truncation (TEL) of 1.5 mm, which is about 20% higher than that achievable using the hardest known WC (Fujillo TF05) anvils. Thus, this novel WC is potentially important for melting experiments of silicate-metal systems under simultaneous high pressure and high temperature conditions of the deep interior the early Earth (e.g. 30-50 GPa, ~3500K), which are currently difficult to be reached in KMA with either conventional WC or SD anvils

キーワード：高圧発生、タングステンカーバイトアンビル、熔融実験

Keywords: high-pressure generation, tungsten carbide anvil, melting experiment

## Problems with 1D seismic model fitting

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Tests of lower mantle composition models often compare mineral physics data bearing on the elasticity and density of lower mantle phases to the average seismic velocity profile determined by seismology, such a PREM or ak135. Here we demonstrate why such comparisons between mineralogy and seismology are an inadequate method for definitive discrimination between different scenarios. One issue is that the seismic velocity is more sensitive to temperature than composition for most lower mantle minerals. In practice, this allows one the freedom to choose the geotherm that brings the predicted seismic and density data into agreement with observations. It is commonly assumed that the temperature profile should be adiabatic, however, such a profile presupposes a particular state of the mantle and is only applicable in the absence of layering, buoyancy fluctuations, compositional segregation, and rheological complexities. The mantle temperature should depend on the composition since the latter influences the viscosity of rocks. However, the precise relation between composition, viscosity, and heat transfer would need to be specified, but unfortunately remains highly uncertain. If the mantle contains a mixture of domains with multiple bulk compositions, then the 1D seismic profile comparison is inherently non-unique. For example, while Wang et al. \cite{Wang2015} show a good match to PREM for a pyrolite model composition, they could also fit PREM just as easily by averaging domains of olivine-rich and bridgmanite rich rocks (i.e., harzburgitic and solar/chondritic, respectively). Rocks with different bulk composition likely have different isotopic abundances, and can exhibit differing degrees of internal heating and therefore distinct temperatures. Different composition domains can also exhibit variable densities, and tend to congregate at different depths in ways that also affect their thermal evolution and temperature. Therefore, we urge the deep Earth community to progress beyond fitting a 1D seismic model for evaluating lower mantle composition.

Keywords: mantle composition, mantle mineralogy, mantle seismology

## 高圧下における玄武岩質メルトの粘性:第一原理分子動力学シミュレーション

Viscosity of Basaltic Melt under High Pressure: *ab initio* molecular dynamics simulations\*大村 訓史<sup>1</sup>、新井 達之<sup>2</sup>、土屋 卓久<sup>3</sup>\*Satoshi Ohmura<sup>1</sup>, Tatsuyuki Arai<sup>2</sup>, Taku Tsuchiya<sup>3</sup>

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High-pressure behavior of basaltic aluminosilicate melt has been intensively studied due to its 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). 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, so far there exist no *ab initio* simulations of basaltic melt in the pressure range, where the anomaly in viscosity is observed experimentally. In this study we therefore perform *ab initio* molecular dynamics simulations gradually changing volume and successfully reproduce a viscosity minimum in the pressure range corresponding to the experiments. We analyze relationships between the anomalous pressure response of viscosity and variations in the atomic-scale local structure.

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キーワード：玄武岩質メルト、粘性、第一原理分子動力学法

Keywords: basaltic melt, viscosity, *ab initio* molecular dynamics

## 高温高压下におけるオリビンと窒素の反応

## Reaction between olivine and nitrogen at high pressure and high temperature

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Volatiles represented by hydrogen greatly affect deep-earth dynamics. Behavior of volatiles will contribute to understandings of budget of light elements, evolution of the earth, geodynamics and so on. Among volatile components, behavior of nitrogen in the deep earth is still unclear. Nitrogen is a main constituent of atmosphere and also exists in the crust by substituting potassium ions in silicate minerals. Chondrite-normalized nitrogen concentration of the bulk earth is one order of magnitude lower than those other volatiles such as He, Ne, Ar, H<sub>2</sub>O and so on. There could be a hidden nitrogen reservoir in the deep earth. We are going to test a possibility of a hidden nitrogen reservoir from high pressure and high temperature experiments.

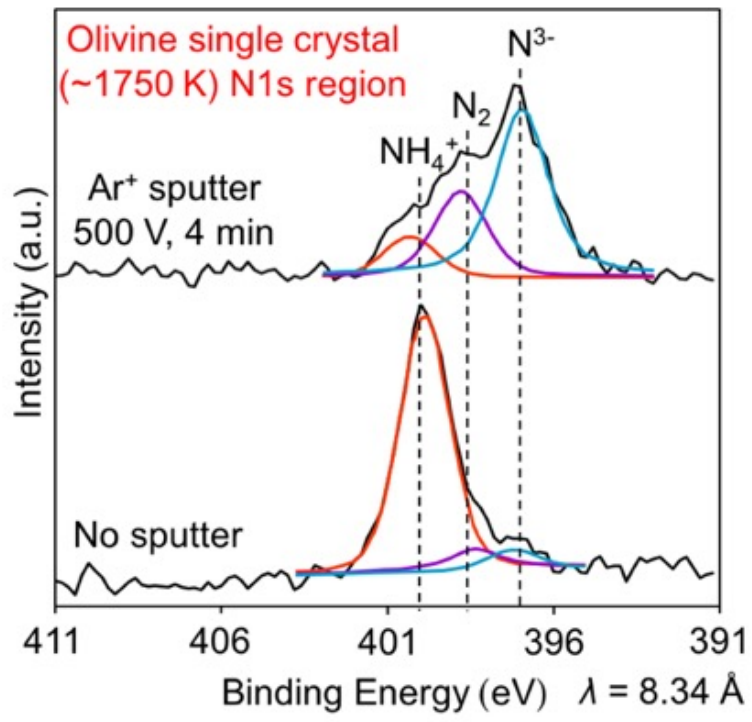
San Carlos olivine or synthetic forsterite were loaded as a starting material in a diamond anvil cell with nitrogen in liquid state or compressed gas (180 MPa). After applying pressure at 5 GPa, a sample was heated using CO<sub>2</sub> laser or fiber laser. X-ray diffraction patterns, SEM-EDS images, XPS spectra were obtained on the recovered samples.

XRD measurements on the recovered samples revealed the formation of enstatite (MgSiO<sub>3</sub>) suggesting the decomposition of Mg<sub>2</sub>SiO<sub>4</sub> into MgSiO<sub>3</sub> and MgO. This reaction is contrastive to the reaction occurring in H<sub>2</sub> fluid (Shinozaki et al., 2013), Mg<sub>2</sub>SiO<sub>4</sub> decomposed into SiO<sub>2</sub> and MgO. Moreover, EDS mapping observations revealed that there are some Mg-rich (Si-depleted) spots.

XPS spectra shown in Fig. 1 revealed that nitrogen was detected from an olivine sample recovered from 5 GPa and 1700 K. Before Ar-sputtering, species assignable to NH<sub>4</sub><sup>+</sup> is dominant. Presumably, the sample surface is covered with adsorbed molecules. After Ar-sputtering, a broad band attributable to intrinsic nitrogen reacted with the mineral was observed. The present results suggest the formation of nitride species (N<sup>3-</sup>) in a mantle-derived silicate mineral. This study proposes nitride as a hidden nitrogen reservoir in the deep mantle.

キーワード：窒素、マントル、オリビン

Keywords: nitrogen, mantle, olivine



## 下部マントルにおける内部減衰・散乱減衰の相対的重要性

## Relative Importance of Intrinsic and Scattering Attenuation in the Lower Mantle

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It is well known that the lower mantle has significant attenuation, but cause for the attenuation (i.e., relative importance of intrinsic and scattering attenuations) has not been well resolved. To address this problem, we conducted detailed analysis of seismogram envelopes.

Seismogram envelopes contain rich information to resolve intrinsic and scattering attenuations. Indeed, Lee et al. (2003, GRL) analyzed S and ScS envelopes of regional earthquakes in the Hindu Kush region and concluded the predominance of scattering attenuation in the lower mantle. They measured decay of coda envelopes for lapse time as long as 2000s and analyzed the data under the assumption of isotropic scattering. In this study, we analyze envelopes observed by a dense broadband array, F-net, and confirm that similar decay is observed in the envelopes of these modern data. We also try to better resolve the attenuation structure by analyzing envelopes for longer lapse time (7000s) without using the assumption of isotropic scattering. We apply our inversion method that systematically conducts waveform inversion of seismogram envelopes for various initial models. At the time of the presentation, we plan to show our models together with trade-offs among various unknown parameters.

## 地球ニュートリノ観測で拓く地球科学

## Towards "Neutrino Geoscience" with Geo-neutrino Measurement

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素粒子ニュートリノの性質が徐々に明らかにされ、その高い透過性を利用した不可視の天体内部の観測が現実的なものになっている。日本主導のもとに行なわれているKamLAND実験によって、地球内部放射性物質起源のニュートリノ（地球ニュートリノ）の世界初観測に2005年に成功してから10年余り経過し、その観測精度を向上させてきた。地表での観測データは地球内放射性元素崩壊頻度、つまり地球深部の放射性元素由来の発熱量に焼き直すことができ、全く独立の手法で地球科学的知見を与える事が出来る。

本講演では、地球ニュートリノ観測の現状とその将来展望、地球科学への応用について講演する。

キーワード：地球ニュートリノ、放射化熱

Keywords: geo-neutrino, Earth's radiogenic heat

## 下部マントル相中の親鉄元素の粒界拡散

## Grain boundary diffusion of siderophile elements in lower mantle phases

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Abundance of siderophile elements, especially platinum group elements, in the Earth's mantle, is fairly higher than that expected from the distribution coefficients between Fe alloy and silicate minerals determined at low pressure. There are several explanations to solve this problem. The most popular hypothesis is late veneer. The amounts of siderophile elements would have been supplied after the core was formed by later meteorite bombardment. The other possible explanation is that before the core separation re-equilibration of Fe alloy and silicate minerals was established at the bottom of magma ocean. So far we have not paid attention to the siderophile element process after core formation. Hayden and Watson (2007) studied grain-boundary diffusion of siderophile elements through polycrystalline MgO at 2.5 GPa, and 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. It means that grain-boundary diffusion as a potential fast pathway for chemical communication between the core and mantle. However, the dominant mantle mineral is not periclase but bridgmanite at the core-mantle boundary. In this study, grain boundary diffusion of W and Re in bridgmanite aggregates is determined. The starting material for experiments to determine the grain boundary diffusion was mixture of San Carlos olivine or orthopyroxene with Mg#90 and 3 wt.% Al<sub>2</sub>O<sub>3</sub> and Pt powder. Synthesis experiments of aggregates of postspinel or bridgmanite with tiny amount of Pt particle were conducted in a Kawai-type multianvil press at 25 GPa and 1873K. The synthesized aggregates were sliced into several disks with a few hundreds of micrometers. The disk was sandwiched by diffusion source (meta foil). This mixture was placed in an MgO cylinder. Hot-press and diffusion experiments were also performed using a Kawai-type multianvil press at 25 GPa and 1873 or 2073K. Experimental durations were more than 20 hours. The concentration of W and Re in the Pt sink was quantified using electron microprobe analyzer. The diffused siderophile element was recorded by the Pt particles behaving here as sink, which are implanted in the aggregate. A semi-infinite model for diffusion was used to calculate D from the concentration profile. The effective diffusivities of W and Re, which includes grain boundary effect were around 10<sup>-16</sup> or 10<sup>-14</sup> m<sup>2</sup> s<sup>-1</sup> at 1873K for bridgmanite and postspinel. These effective diffusivities are several orders of magnitude slower than the published diffusion data for MgO aggregates. On geological scales and for coarse-grain rocks, siderophile element diffusivity in grain boundaries is not fast enough to induce chemical interaction at the core-mantle boundary. The relative large grain size of mantle rocks will ensure a very limited siderophile element transport by effective diffusion, and a good conservation of siderophile element in the Earth's core. However, to estimate more reliable grain boundary diffusivities at the core-mantle boundary, more knowledge on effect of temperature and pressure on the siderophile element diffusivities is needed.

キーワード：親鉄元素、下部マントル、粒界拡散

Keywords: siderophile element, lower mantle, grain boundary diffusion



## WおよびOsの高精度同位体比測定によるコア-マントル共進化解明の展望

## High precision analysis of Os and W for early evolution of core-mantle

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Tungsten is one of the highly siderophile and refractory elements. There are 5 stable isotopes of W as 180,182,183,184, and 186.  $^{182}\text{W}$  is a decay product of  $^{182}\text{Hf}$  ( $t_{1/2}=890$  million year) which is extinct at present. Therefore, the amount of  $^{182}\text{W}$  can give information on evolution of very early solar system at the timescale from tens of thousands of years to hundreds of thousands of years. Because Hf and W are highly refractory elements,  $^{182}\text{W}$  isotope evolution process in the Earth could be same as in chondrites. W and Hf have been considered to be partitioned into metal (core) and silicate (mantle) phases, respectively, which leads to higher Hf/W ratio of mantle. Due to the decay of  $^{182}\text{Hf}$ , the amount of  $^{182}\text{W}$  should have increased in a planetary mantle 1 billion years after the beginning of the solar system.

In the early stage of applications of the  $^{182}\text{Hf}$ - $^{182}\text{W}$  isotope system has been used as a chronometer of the Earth's core formation (Lee et al., 1995) to use that iron meteorites possess lower  $^{182}\text{W}/^{184}\text{W}$  isotope ratios than those of chondrites and Earth's rocks. Variation of this isotope ratio is presented as  $\epsilon$  value using W isotope standard solution (NIST SRM-3163).

High precision isotope analysis of W ( $< 0.3 \epsilon$ ) was difficult until 2010 even if extremely sensitive and precise mass spectrometers of N-TIMS and MC-ICP-MS were used. Recently, the mass spectrometry in MC-ICP-MS or N-TIMS and chemical separation methods were significantly improved (Touboul et al., 2011), and high precision tungsten isotope analysis of  $\pm 5 \mu (=0.05\epsilon)$  is possible at present. These high precision analyses lead to findings of W isotope anomaly in the early Earth's rocks such as komatiite (older than 2.8 billion years). Kostomuksha komatiite has positive anomaly ( $+20\mu$ ) (Touboul et al., 2012). Variation of these W isotope ratios was discussed together with PGE abundance and Os or Nd isotopes of mantle rocks. The PGE and Os isotopes could give constraints on the timing and processes of early mantle evolution such as Late Veneer, the core-mantle or mantle-silicate differentiation.

In our study, we are trying to develop the methodology of extremely high precision measurements of W, Nd and Os isotopes using N-TIMS and MC-ICP-MS and will try to reveal the core mantle coevolution on the early Earth.

キーワード：コア-マントル相互作用、タングステン同位体、オスミウム同位体、地球初期進化

Keywords: core-mantle interaction, W isotope, Os isotope, early earth chemical evolution

マグマオーシャン中の金属-ケイ酸塩間の塩素分配：地球の塩素枯渇の起源への示唆

Metal-silicate partitioning of chlorine in a magma ocean: Implications for the origin of chlorine depletion on Earth.

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The chlorine of the Earth is highly depleted relative to other lithophile and volatile elements [1]. There are two hypotheses for terrestrial missing chlorine; Chlorine incorporation into the core and an erosion of primordial ocean. Here we experimentally investigate the former case. More specifically, the metal-silicate partitioning of chlorine in a magma ocean is experimentally investigated.

In this study, we investigated the effect of pressure and temperature on the metal-silicate partition coefficient of chlorine in order to estimate the core-mantle partitioning of chlorine. Starting materials were a mixture of high-purity oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{FeO}$ ), metallic iron, and iron sulfide. Chemical compositions in the silicate portion match those of CI- or EH-chondrites. Chlorine was added to the mixture as  $\text{FeCl}_2$ . The starting materials were encapsulated into either a graphite capsule or a single-crystal  $\text{MgO}$  capsule. The experiments were performed at 4 - 23 GPa and 1923 - 2673 K using multi-anvil presses at the University of Tokyo and Ehime University. The elemental compositions of recovered samples were analyzed with wavelength-dispersive electron microprobe (WDS-EPMA) and secondary ion mass spectrometry (SIMS). Our experimental results show that (1) chlorine is highly lithophile, (2) becomes more siderophile with increasing temperature, and lithophile with increasing pressure. Based on the experimental results and thermodynamic consideration, we estimated the metal-silicate partitioning coefficient of chlorine at the base of a magma ocean. The  $P$ - $T$  conditions at the base of a magma ocean were estimated from the peridotite melting curve. Calculation results show that the metal-silicate partition coefficients of chlorine at the base of a magma ocean are much lower than the required value for explaining terrestrial missing chlorine. This result strongly suggests that Earth's core is unlikely to account for terrestrial missing chlorine. Given that the fluid-melt partition coefficient of chlorine is above the unity [e.g., 2], chlorine may have been partitioned into primordial ocean. If this is the case, terrestrial missing chlorine may require an extensive loss of primordial ocean during the planetary accretion phase.

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キーワード：地球、塩素、マグマオーシャン

Keywords: Earth, Chlorine, Magma ocean

## 下部マントル鉱物の格子熱伝導率

## Lattice thermal conductivity of lower mantle minerals

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Heat in the Earth's interior is transported dominantly by convection in the mantle and core, and by conduction at thermal boundary layers. The thermal conductivity of the bottom thermal boundary layer of the mantle determines the magnitude of heat flux from the core, and is intimately related to the formation of mantle plumes, the long-term thermal evolution of both mantle and core, and the driving force for generation of the geomagnetic field (Lay et al. 2008). Recent technical progress both in the experiment and the theoretical calculation enables us to reveal high-pressure and high-temperature behavior of lattice thermal conductivity of lower mantle minerals,  $\text{MgSiO}_3$  perovskite (bridgmanite) and  $\text{MgO}$  periclase. However, the effect of iron incorporation into these minerals on the lattice thermal conductivity is still controversial.

We measured the lattice component of thermal conductivities both of  $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$  bridgmanite and  $(\text{Mg,Fe})\text{O}$  ferropericlase at the Earth's lower mantle pressures and 300 K using a pulsed light heating thermoreflectance technique in a diamond anvil cell. We found that iron incorporation into bridgmanite shows minor effect on the thermal conductivity. On the other hand, the obtained conductivity of ferropericlase was considerably lower than that of  $\text{MgO}$  periclase. The estimated lattice thermal conductivity of bridgmanite-dominant lowermost mantle is comparable to conventionally assumed value of 10 W/m/K (Stacey, 1992). However, our results imply that local existence of  $(\text{Mg,Fe})\text{O}$  ferropericlase in the lower mantle induce strong heterogeneity of thermal conductivity.

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キーワード：下部マントル、熱伝導率、ブリッジマナイト、フェロペリクレーズ

Keywords: lower mantle, thermal conductivity, bridgmanite, ferropericlase

## 波形インバージョンによる北部太平洋及びアラスカ下のD"の3次元S波速度構造推定

Waveform inversion for 3-D shear wave velocity structure within D" beneath the Northern Pacific and Alaska

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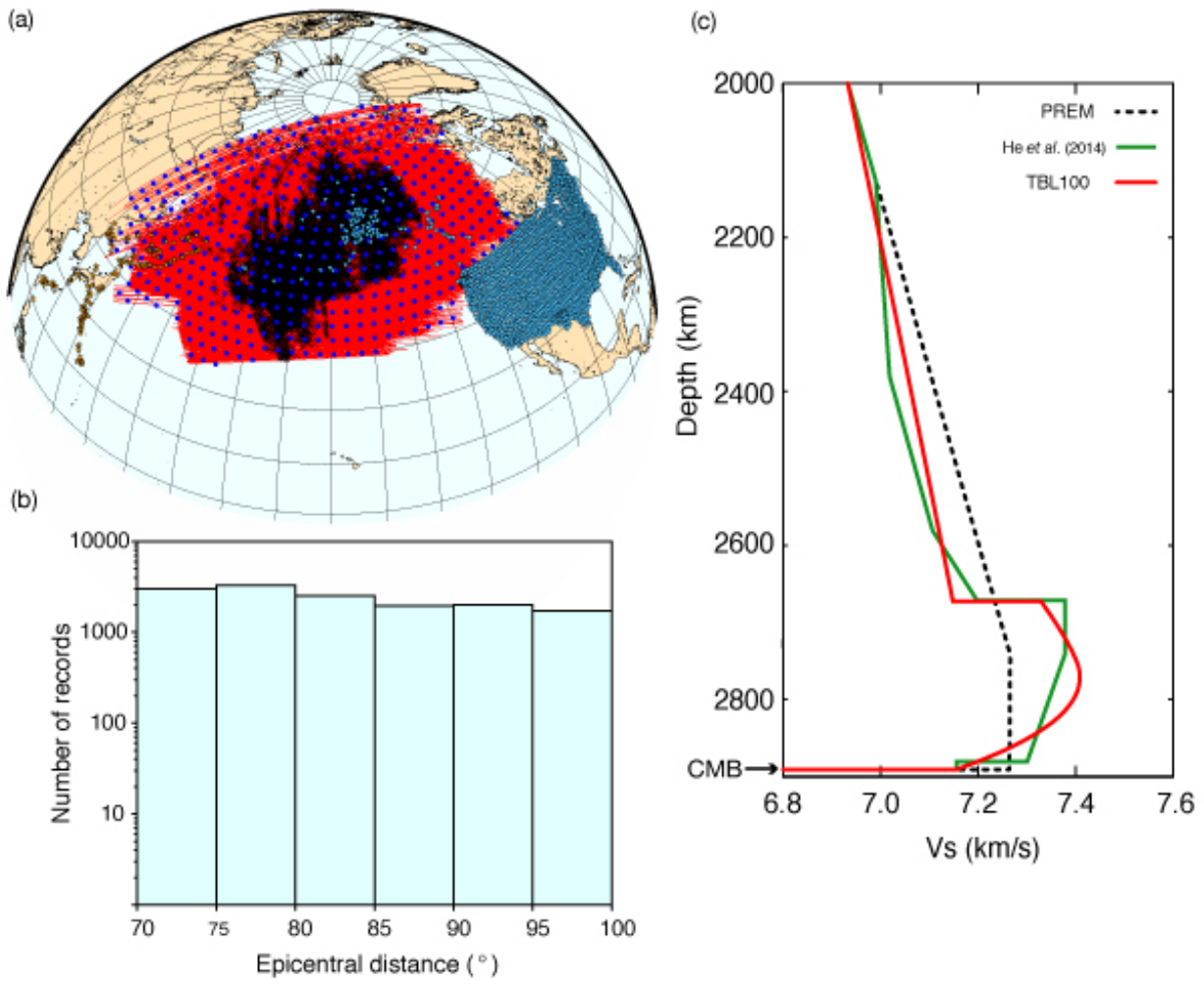
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We conduct waveform inversion to infer the 3-D shear wave velocity structure within D" beneath the Northern Pacific and Alaska (Fig. 1a). This region is suitable as the target for waveform inversion, since we are able to use data that densely sample the target region (the lowermost 400 km of the mantle beneath the Northern Pacific and Alaska). Our dataset consists of ~20,000 transverse components of broadband body-wave seismograms observed at North American stations (from dense receiver networks such as the USArray). We use 114 intermediate and deep events that are widely distributed throughout the western Pacific (Japan and Izu Bonin) region. We use S, ScS and other phases that arrive between them. Our dataset is homogeneous in terms of epicentral distance (Fig.1b). Resolution tests indicate that our method and data can resolve the lateral and vertical velocity profile within D" in the target region. We use two different one dimensional shear wave velocity models (Fig. 1c) as the starting model for the inversion: PREM, and a model based on mineral physics, which includes a thermal boundary layer of 100 km effective thickness. The 3-D models obtained by our inversion show that there is a high velocity area that can be interpreted as subducted paleoslabs down to about 200 km above the core-mantle boundary (CMB), a plume like low-velocity structure, and also lateral and vertical complexity that may come from interaction between the subducted paleoslabs and development of plumes within D".

キーワード：S波速度構造、D"領域、波形インバージョン

Keywords: S-wave velocity structure, D", waveform inversion



Ultrahigh-pressure polymorphism in GeO<sub>2</sub> glass: implications for structure of magma at the core-mantle boundary

Ultrahigh-pressure polymorphism in GeO<sub>2</sub> glass: implications for structure of magma at the core-mantle boundary

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Silicate magma at the core-mantle boundary is one of the most important components in understanding nature and evolution of the Earth's deep interior. However, structure and properties of silicate magmas at the pressure condition of the core-mantle boundary remain poorly understood, because of experimental challenges. Pioneering works by Murakami and Bass (2010; 2011) showed a kink in the pressure dependence of shear-wave velocity in SiO<sub>2</sub> and MgSiO<sub>3</sub> glasses around 130-140 GPa, which was interpreted as evidence of ultrahigh pressure structural transition. However, no structural information is available under such high pressures. Here we show new experimental evidence of ultrahigh pressure structural transition in GeO<sub>2</sub> glass with Ge-O coordination number (CN) significantly greater than 6, investigated using a newly developed double-stage large volume cell combined with multi-angle energy dispersive X-ray diffraction technique for in situ amorphous structure measurement. The Ge-O coordination number (CN) is found to remain constant at ~6 between 22.6 and 37.9 GPa. At higher pressures, CN begins to increase rapidly to 6.4 at 49.4 GPa and reaches 7.4 at 91.7 GPa. The structural change to CN higher than 6 is closely associated with the change in oxygen packing fraction (OPF). This transformation begins when the OPF in GeO<sub>2</sub> glass is close to the maximal dense packing state (the Kepler conjecture= $\sim 0.74$ ), which provides new insights into structural changes in network-forming glasses and liquids with CN higher than 6 at ultrahigh pressure conditions. For example, extrapolation of OPF-pressure trend in SiO<sub>2</sub> glass shows that OPF of SiO<sub>2</sub> glass reaches to 0.74 around 108 GPa, where structural change to CN higher than 6 is expected. The data imply that silicate magma at the core-mantle boundary may possess ultrahigh-pressure structure with CN higher than 6.

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キーワード : high pressure、magma、core-mantle boundary

Keywords: high pressure, magma, core-mantle boundary

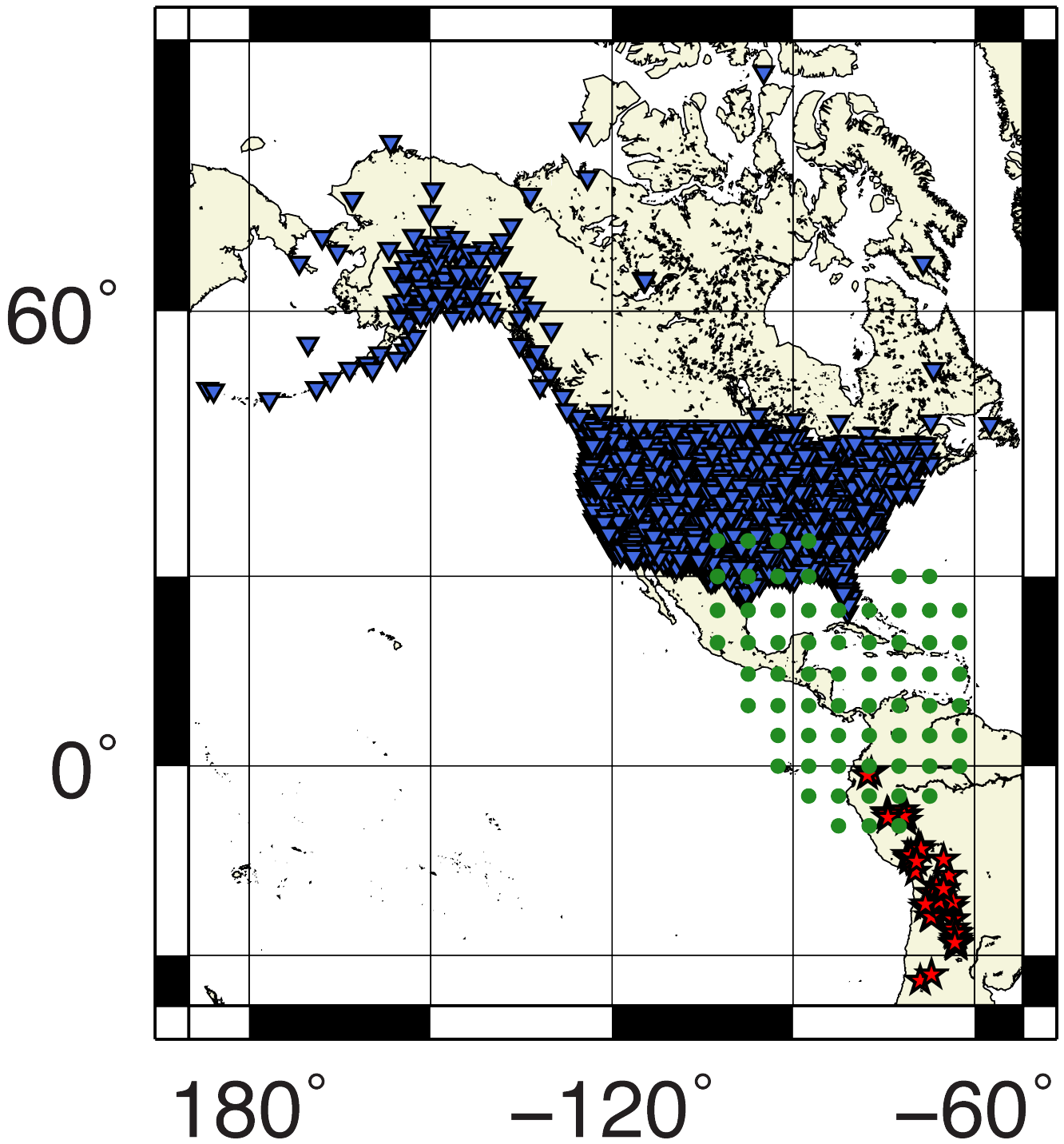
## Full-waveform inversion for localized 3-D S-velocity structure in D" beneath the Caribbean using USArray data

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We take advantage of the dense coverage made available by USArray stations (enhanced by records from the IRIS/USGS, SCSN, PNSN, BDSN, and CNSN networks) to invert for the localized 3-D S-velocity in the lowermost 400 km of the mantle beneath the Caribbean (see in the Fig. below the distribution of stations (blue), events (red), and the location of the voxels that define the target region (green)). We use a much larger dataset than Kawai *et al.* (2014), with an improved eastward geographical coverage. We use around 13,000 S and ScS transverse component waveforms (including possible ScS precursors important to image strong velocity contrasts) down to 12.5 s for 68 intermediate and deep focus events in the period 1993–2015 beneath South America. The resulting 3-D model shows a more complex S-velocity structure than that resolved by global tomography, with vertical high velocity anomalies extending from the top of our target region down to the CMB with the strongest high-velocity perturbations 300 km and 100 km above the CMB. Our model is consistent with that of Kawai *et al.* (2014), where they overlap, and reveals another high velocity anomaly located beneath the north of South America, which is in agreement with previous works using ray tomography. Our 3-D model is consistent with the presence of cold slab material surrounded by hotter material.

Keywords: Full-waveform Inversion, 3-D S-velocity, Central America





## Thai Seismic Array (TSAR) Project

## Thai Seismic Array (TSAR) Project

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Thailand is located in an important area for teleseismic observations to study the core-mantle boundary and the inner core. However, the number of broadband stations is limited. On the occasion of the KAKENHI project for an innovative area "Core-mantle co-evolution", we plan to construct a mobile broadband seismic array in Thailand as a part of the project "Seismic and geo-electromagnetic observation for core and mantle". This array will be also useful for the understanding of a local structure and seismicity in Thailand.

To date, we have conducted the site survey for 3 times (Nov.16-27, 2015; Dec.13-22, 2015; Jan. 9-16, 2015) to determine 40 possible sites. Along the western edge of Thailand to the center of Malay Peninsula, the part of TSAR will form a linear array whose approximately 15 stations run in north-south direction with a length of more than 1,000 km. In the central part of Thailand, TSAR will cover an area of about 400 km (from east to west) x 600 km (from north to south) length with station spacing of approximately 100 km. After the 3rd site survey, we have constructed two pilot stations in Suphanburi and Kanchanaburi, where we test the durability of the stations for high temperature, heavy rain, lightening and check the data quality. Since November, 2016, we plan to deploy additional 38 broadband seismic stations for a period of 2 years.

キーワード：タイ、広帯域機動地震観測網、予備調査

Keywords: Thailand, Mobile broadband seismic array, Site Survey

## 高圧下における含水鉱物の解離に伴う水素の鉄への溶解

Dissolution of hydrogen into iron by the dissociation of hydrous minerals under pressure

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Although hydrogen is the most abundant element in the solar system and one of the candidates of the light element in the core, the process how the hydrogen can get into iron remains not so clear. High-pressure and high-temperature in situ neutron diffraction study on the iron-hydrous mineral system using "PLANET" at J-PARC clearly showed that when the dissociation of hydrous mineral occurred at about 4 GPa, the released water reacted with iron and formed both iron oxide and iron hydride. Iron oxide reacted with silicates and formed iron containing olivine and pyroxene. Iron hydride remained stable after further increase in temperature. This formation of iron hydride occurred below 1000K, at the temperatures no materials melted. This suggest the possibility that in the very early stage of Earth evolution, hydrogen has dissolved into iron before any other light elements have dissolved.

キーワード：水素、鉄、中性子

Keywords: hydrogen, iron, neutron

## 液体鉄合金の熱弾性特性から推定される外核の化学組成

## Outer core compositions by thermoelastic properties of liquid Fe alloys

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In the outer core, many light elements, such as carbon, nitrogen, oxygen, hydrogen, sulfur, and silicon, have been proposed as possible constituents. The concentrations of these elements have long been intensely debated. Here we calculate equations of state (EoS) of pure Fe and Fe-light elements alloy liquids by means of ab initio molecular dynamics at the outer core P-T conditions and evaluate P-wave velocity based on the derived EoS, which is consistent with thermodynamic properties such as Grüneisen parameter in the similar way as Ichikawa et al. 2014. Then, we search for plausible compositions which reproduce both P-wave velocities and densities of the seismological data (PREM) (Dziewonski and Anderson, 1981) under the whole outer core conditions. Finally, we analyze the plausible compositions of the outer core, which reproduce seismological values reasonably. We found several compositions with different light elements that reproduce the seismological data to the same degree. The results also show that the influence of addition of Ni with reasonable fraction is negligibly small.

キーワード：外核の組成、軽元素、第一原理分子動力学計算

Keywords: Composition of the outer core, light elements, Ab initio molecular dynamics calculation

Electrical resistivity of substitutionally disordered hcp Fe-Si and Fe-Ni alloys:  
Chemically-induced resistivity saturation in the Earth's core  
Electrical resistivity of substitutionally disordered hcp Fe-Si and Fe-Ni alloys:  
Chemically-induced resistivity saturation in the Earth's core

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The thermal conductivity of the Earth's core can be estimated from its electrical resistivity via the Wiedemann-Franz law. However, previously reported resistivity values are rather scattered, mainly due to the lack of knowledge with regard to resistivity saturation (violations of the Bloch-Grüneisen law and the Matthiessen's rule). Here we conducted high-pressure experiments and first-principles calculations in order to clarify the relationship between the resistivity saturation and the impurity resistivity of substitutional silicon in hexagonal-close-packed (hcp) iron. We measured the electrical resistivity of Fe-Si alloys (iron with 1, 2, 4, 6.5, and 9 wt.% silicon) using four-terminal method in a diamond-anvil cell up to 90 GPa at 300 K. We also computed the electronic band structure of substitutionally disordered hcp Fe-Si and Fe-Ni alloy systems by means of Korringa-Kohn-Rostoker method with coherent potential approximation (KKR-CPA). The electrical resistivity was then calculated from the Kubo-Greenwood formula. These experimental and theoretical results show excellent agreement with each other, and the first principles results show the saturation behavior at high silicon concentration. We further calculated the resistivity of Fe-Ni-Si ternary alloys and found the violation of the Matthiessen's rule as a consequence of the resistivity saturation. Such resistivity saturation has important implications for core dynamics. The saturation constrains an upper limit of the resistivity, and the saturation resistivity value has almost no temperature dependence. As a consequence, the core thermal conductivity has a lower bound and exhibits a linear temperature dependence. We predict the electrical resistivity of the Earth's core to be about  $1.0 \times 10^{-6} \Omega\text{m}$ , which corresponds to the thermal conductivity of 100 and 135 W/m/K at 4000 K and 5500 K, respectively. Such high thermal conductivity suggests high isentropic heat flow, leading to young inner core age ( $< 1$  Gyr old) and high initial core temperature. It also strongly suppresses thermal convection in the core, which results in no convective motion in the inner core and possibly thermally stratified layer in the outer core.

キーワード：核、電気抵抗率、抵抗率飽和、ダイヤモンドアンビルセル、KKR-CPA、熱伝導度

Keywords: core, electrical resistivity, resistivity saturation, diamond-anvil cell, KKR-CPA,  
thermal conductivity

ニュートリノ振動を用いた地球深部の化学組成測定  
Spectrometry of the Earth using neutrino oscillations

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Neutrinos have favorable properties for measuring the elemental composition deep inside the earth's interior. First, they propagate a long distance almost undisturbed through the earth due to their weak interactions with matter. Secondly, neutrino oscillations in matter are sensitive to the electron density of the medium traversed by them. Therefore, neutrinos can be used for a probe to determine the average atomic mass ratio  $Z/A$  of the earth's core by comparing with the earth's nucleus density distribution that is inferred from seismic observations. There is little uncertainty in densities of the earth's core, but our knowledge of its main light element is very limited. With the advent of the new-generation megaton neutrino detectors, neutrino oscillation spectrometry will allow us to constrain directly the light elements in the earth's outer core. We report the detail of this novel technic and the sensitivity study.

キーワード：化学組成、ニュートリノ、地球外核  
Keywords: chemical composition, neutrino, Earth's outer core

高温高压下での非弾性X線散乱法によるFe<sub>3</sub>Sの音速測定

Sound velocity Fe<sub>3</sub>S at high pressure and high temperature based on inelastic X-ray scattering

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Mars, the 4th planet from the sun, has been investigated since 1960s. In spite of the investigations, the interior of Mars have not been understood well. Although the surface of Mars has been investigated by Opportunity and Curiosity in the project of NASA, the structure and seismic properties of the Martian core have not been understood well. The core of Mars have been thought to include sulfur as a light element. Sohl and Spohn (1997) proposed the seismic wave velocity and density profiles of the interior of Mars. However, there were almost no data of seismic wave velocity of the Martian core materials such as FeS and Fe<sub>3</sub>S. Therefore, we have measured sound velocities of Fe<sub>3</sub>S under high pressures and temperatures in order to discuss the Martian core. In addition, the InSight project of NASA will observe seismic wave velocity and probably be able to give some information of the Martian core.

There have been only a limited number of works for  $V_p$  of Fe and Fe alloys with light elements, especially Fe alloys with sulfur. Recently, sound velocities of Fe, Fe-Ni, FeS, FeS<sub>2</sub>, FeO, Fe<sub>3</sub>C, Fe-Ni-Si alloys have reported based on an inelastic X-ray scattering (IXS) (Fiquet et al., 2001; Antonangeli et al., 2004; Fiquet et al., 2004; Badro et al., 2007; Fiquet et al., 2009; Antonangeli et al., 2010). In the Fe-S system,  $V_p$  of FeS, the end member of the Fe-FeS system, and FeS<sub>2</sub>, more sulfur-rich compound, have been studied but these compounds are not appropriate for the core materials of Mars because Fe-S system has a lot of intermediates such as Fe<sub>3</sub>S<sub>2</sub>, Fe<sub>2</sub>S, Fe<sub>3</sub>S under high pressures (Fei et al., 1997, 2000). In addition, Fe<sub>3</sub>S coexists with  $\epsilon$ -Fe as a subsolidus phase from 20 GPa to at least 200 GPa (Kamada et al., 2010, 2012). Therefore, it is essential to study the  $V_p$  of Fe<sub>3</sub>S to understand seismic properties of the Martian core. We have measured sound velocities of Fe<sub>3</sub>S under high temperature and pressure at BL35XU of SPring-8.

In this study, a synthesized Fe<sub>3</sub>S was used as a starting material. A symmetric diamond anvil cell was used to generate high pressures. IXS and XRD experiments were performed at the beamline 35XU of SPring-8, Japan (Baron et al., 2000).  $V_p$  of Fe<sub>3</sub>S were measured up to 45 GPa and 1900 K. We will discuss temperature effect on  $V_p$  of Fe<sub>3</sub>S and the Birch's law and seismic wave velocity profile of the Martian core.

キーワード：高压高温、非弾性X線散乱法、惑星核

Keywords: High pressure and temperture, Inelastic X-ray Scattering, Planetary core

## Pressure dependence on carbon isotope fractionation between diamond and iron carbide melt

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Stable isotope fractionation has been thought to be less affected by pressure until recently. In this study we present data on the pressure dependence of carbon isotope fractionation between diamond and iron carbide melt. Carbon, the fourth most abundant element in the solar system, is believed to be an important light element constituent in the Earth's core. The high carbon content of CI chondrites (3.2 wt.%) compared to bulk earth estimates, the presence of graphite/diamond and metal carbides in iron meteorites, the high solubility of carbon into iron melts in the Fe-C system suggests the plausible presence of carbon in the Earth's core. However, the distribution of carbon isotopes in the core is still not well understood. We carried out experimental studies in the Fe-C system and present the results on the equilibrium carbon isotope fractionation between graphite/diamond and iron carbide melt at varying pressures between 5GPa and 15 GPa and at temperature range of 1200 to 2100 °C. Our previous results have shown that the iron carbide melt will preferentially gather <sup>12</sup>C than <sup>13</sup>C, which is temperature dependent (Satish-Kumar et al., 2011), consistent with the recent theoretical calculations of Horita and Polyakov (2014). The pressure dependence of this fractionation trend between iron carbide melt and graphite/diamond is examined in this study. Based on the preliminary results, we infer that pressure dependence is also important factor to consider when carbon cycle is considered in the core-mantle interface. It is anticipated that the combined pressure-temperature dependent fractionation of carbon isotopes between iron carbide melt and graphite/diamond is an effective mechanism that created a "12C enriched core" with large scale differences in the distribution of the carbon isotopes in the metallic core and bulk silicate Earth during the accretion and differentiation of early Earth. Our findings also have implications on the deep carbon cycle of the Earth, where the light carbon from the core might have transported to the mantle and crust through deep mantle plumes.

References: Horita, J. and Polyakov, V.B., 2014 PNAS doi/10.1073/pnas.1401782112; Satish-Kumar et al. 2011 Earth and Planetary Science Letters, 310, 340-348

Keywords: Carbon isotope fractionation, Diamond, Iron carbide melt

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

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Silicate earth is in strong depletion of K compared with chondrites [Wasserburg, 1964, Science]. The ratios of K isotope barely vary suggesting evaporation cannot be responsible for the missing of K [Humayun and Clayton, 1995, GCA]. The finding that the change in electronic structure of K from alkaline- to transition metal-like at high pressure highlighted the possibility of its incorporation into the core [Parker, 1996, Science]. If K is present, even in ~ppm, the radiogenic heat produced by <sup>40</sup>K could be an important energy source for mantle dynamics [Labrosse, 2001, EPSL]. However, previous researches didn't enclose the controversy over the K partitioning behavior between silicate and metallic system, with its partitioning coefficient range from  $10^{-6}$  to 2.5 [Bouhifd et al., 2007, PEPI; Watanabe, 2014, PEPI], leaving the K content in the core uncertain. In this study, ab-initio molecular dynamics simulations are performed to investigate whether and how much K can enter the metallic system. K partition coefficients are determined by Gibbs free energy changes of its exchange reactions between silicate and metallic systems. Helmholtz free energy is obtained based on "thermodynamic integration" by computing the difference between two systems with different potential energy functions.

Our preliminary results show that the K content entered into the core is limited, though it would be affected by the temperature, pressure, composition of the metallic (the type and content of light elements) and silicate system (NBO/T).

Keywords: Ab-initio simulation, Potassium, Core Mantle Boundary



## 鉄と鉄-炭素合金の高温高圧弾性特性

High- $P, T$  elasticity of iron and iron-carbon alloy

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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 carbon (e.g., Chen et al., 2014).

In this study, we perform ab initio molecular dynamics simulations of iron and iron-carbon alloy. Also computations are conducted in a wide  $P, T$  range including, but not limited to, the inner core conditions to clarify the  $P, T$  effects on their elasticity more comprehensively, and to provide an internally-consistent thermoelastic model. In addition to checking the validity of the Birch's law, the obtained Poisson ratio and aggregate anisotropy, with and without the pre-melting effect, are compared against seismological constraints to reinvestigate the viability of iron and iron-carbon alloy in the inner core.

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キーワード：内核、第一原理計算、弾性特性

Keywords: Inner core, Ab initio computation, Elasticity

## ε鉄の自己拡散に関する予備的結果

## Preliminary result on iron self-diffusion in ε-iron

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Viscosity of the inner core is a key to understand the dynamics and structure of the core. The inner core super-rotation respect to the mantle is significantly related to the viscosity (e.g., Buffett, 1997). The seismic anisotropy observed in the inner core may be caused by the lattice preferred orientation of constituting materials (Morelli et al., 1986) formed during deformation of the inner core and hence viscosity is essential to understand the deformation rate. Recent seismic observations revealed that the seismic attenuation is heterogeneous in the inner core. The attenuation is larger in the western side of the inner core than that in the eastern side (Monnereau et al., 2010). Because the seismic attenuation can be regarded to be a function of viscosity, it is important for interpretation of the observed attenuation to estimate viscosity from the mineral physics. Diffusion is the most fundamental transportation properties and it is main controlling factor for deformation rate in any deformation mechanism. However, because of the difficulty for diffusion experiment on ε-iron, which is main constituting material of the inner core (Tateno et al., 2012), due to the limited stability of ε-iron higher than 40 GPa at >1300 K, direct measurement is not available yet.

In this study, by using sintered diamond anvils, we conducted diffusion experiments at pressure ~50 GPa in a Kawai-type multianvil apparatus, "6-axis press", installed at Okayama University. In the experiments, the natural isotopic iron and <sup>54</sup>Fe enriched iron was used as diffusion couple. On the recovered sample after diffusion annealing, diffusion profiles were obtained by the isotope imaging technique using SIMS1270 at Hokkaido University.

Diffusion coefficient at 1400 K was determined to be  $\sim 10^{-17}$  m<sup>2</sup>/s in the present study although our result at present is preliminary one because diffusion length is small compared with the length of convolution effect and data is limited. The obtained value is 2-3 order smaller than self-diffusion coefficient in γ-iron at same temperature but ambient pressure. When homologous temperature scaling is applied, diffusion coefficient in the inner core condition is estimated to be  $\sim 10^{13}$  m<sup>2</sup>/s by using  $T/T_m = 0.9$  (where  $T_m$  is melting temperature) and melting curve of iron (Anzellini et al., 2013). The estimated diffusion coefficient suggests that Harper-Dorn creep may be the dominant deformation mechanism among dislocation creep, diffusion creep and Harper-Dorn creep. Assuming the dominant of Harper-Dorn creep, viscosity of the inner core is calculated to be  $10^{12}$  Pas consistent with previous estimations based on mineral physics (Van Orman, 2004) and geophysics (Buffett, 1997). In the future work, effect of light element on diffusion will be investigated to understand the origin of the heterogeneity observed in seismology.

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Electron-phonon contribution to electrical resistivity of hcp Fe  
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Determination of electron transport property of the Earth's core is a key to understanding its thermal property. Electrical resistivity ( $\rho$ ) of a solid metal comprises electron-phonon and electron-electron scattering mechanisms. Two recent first-principles studies however show a significant difference in the electron-phonon contribution ( $\rho_{\text{el-ph}}$ ) of hcp Fe (M. Pozzo, C. Davies, D. Gubbins, and D. Alfe, *Nature*, 485, 355, 2012; P. Zhang, R. E. Cohen, and K. Haule, *Nature*, 517, 605, 2015). While Pozzo *et al.* reported  $\rho_{\text{el-ph}}$  smaller than the conventional estimates (e.g. F. D. Stacey and O. L. Anderson, *Phys. Earth Planet Int.*, 124, 153, 2001), Zhang *et al.* showed approximately two times larger  $\rho_{\text{el-ph}}$  than Pozzo *et al.*'s and closer to the conventional values. To aim for verifying these previous studies, we develop a technique to compute electron-phonon interaction and  $\rho_{\text{el-ph}}$  of metals based on the density-functional perturbation theory. In this talk, in addition to our technical advantage, preliminary results on the electrical resistivity of hcp Fe under high- $P, T$  condition are presented.

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