

## Determination of pressure effect on the thermocouple electromotive force using multi-anvil apparatus

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Our understanding of Earth's interior highly depends on physical and chemical properties of Earth materials which were determined based on high-pressure and high-temperature experiments. Temperature in high-pressure and high-temperature experiments is mostly determined using a thermocouple without any pressure correction. This may lead to erroneous results in estimated temperature and thus physical and chemical properties of Earth materials due to significant pressure effects of the thermocouple electromotive force (EMF). Getting and Kennedy (1970) determined the pressure effect on the EMF of two types of thermocouples up to 3.5 GPa and 1000°C. However, no new knowledge has been obtained on the absolute pressure effect on thermocouple EMF for more than 40 years.

In this study, we developed a method to determine the absolute pressure effect on thermocouple electromotive force, based on a single wire method using Kawai-type multi-anvil apparatus. By applying this method, single wire EMFs were measured up to a pressure of 7 GPa and temperature of 600°C for chromel and alumel, which passes through the entire length of the pressure medium. The chromel and alumel wires were contained in semi-sintered MgO and dense Al<sub>2</sub>O<sub>3</sub> insulating tubes, and the portions of the wires in MgO and Al<sub>2</sub>O<sub>3</sub> were subjected to higher and lower pressures, respectively. The temperature along the single wires was calibrated by separate experiments employing multiple thermocouples. Pressure conditions along the wires were evaluated based on in situ X-ray diffraction using synchrotron X-ray radiation and a thermal equation of state of Ni. The pressure effect of the Seebeck coefficients of chromel and alumel, determined by the analyses of single wire EMFs and pressure-temperature profiles along the wires, was virtually consistent with that of previous lower-pressure or lower-temperature studies. The difference between the nominal temperature by chromel-alumel thermocouple (type K) and the real temperature was calculated to be from 0 to -3°C in conditions up to 7 GPa and 600°C. Since the multi-anvil apparatus is capable of achieving much higher pressure and temperature, the method presented in this study promises to reveal absolute temperature correction for thermocouples over a wide range of pressure and temperature conditions.

Keywords: thermocouple, high-pressure and high-temperature experiments

## Development of P wave and S wave GHz buffer rod-transducer for DAC experiments

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P wave and S wave GHz buffer rods are now under developing. Both the transducers will be used for ultrasonic velocity measurement under high pressure in the combination of diamond anvil cell. The way of electrode for transducer is found to be critical for stable operation of buffer rod; I examined Au sputtering on the ZnO transducer, and got reasonable results. Simultaneously, I examined Sapphire, YAG, TiO<sub>2</sub>, Si, and SiO<sub>2</sub> crystals for feasibility of GHz buffer rod, and found substantial attenuation of GHz wave in Si and SiO<sub>2</sub> crystals. I confirmed the performance of Sapphire, YAG, and TiO<sub>2</sub> buffer rods with observing the reflection pulse from diamond plate (~2 mm thickness). I also detected a P-S conversion signal in YAG crystal; it is almost ready to assemble S wave GHz buffer rod made of YAG crystal. Furthermore I have a plan to make diamond buffer rod as well in near future.

Keywords: GHz, buffer rod, elasticity

## Lattice thermal conductivity of bridgmanite at the lower mantle pressures

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The amount of heat flow from the Earth's core to mantle critically determines the thermo-chemical evolution both of the core and the mantle. Bridgmanite, iron and aluminum bearing  $\text{MgSiO}_3$  perovskite, is the most abundant mineral in the Earth's lower mantle, and thus its thermal transport property controls heat transport in the lower mantle. Here we measured lattice thermal diffusivity of bridgmanite with chemical composition of  $\text{Mg}_{0.832}\text{Fe}_{0.209}\text{Al}_{0.060}\text{Si}_{0.916}\text{O}_3$  up to 39 GPa at 300 K using the pulsed light heating thermoreflectance technique in a diamond anvil cell. The results indicate that the lattice thermal conductivity of the bridgmanite sample is slightly lower than that of iron and aluminum free bridgmanite determined by using the same experimental technique (Ohta et al., 2012). Our result exhibit insignificant effect of iron and aluminum incorporation into bridgmanite on its thermal conductivity, which imply temperature variation in the lower mantle is only factor to induce heterogeneity of thermal conductivity and core heat flux there that could drive large scale dynamics both in the core and mantle.

Reference: Ohta, K. et al. Lattice thermal conductivity of  $\text{MgSiO}_3$  perovskite and post-perovskite at the core-mantle boundary. *Earth Planet Sc Lett* 349-350, 109-115 (2012).

Keywords: thermal conductivity, lower mantle, bridgmanite

## The effects of ferromagnetism and interstitial hydrogen on the equation of states of hcp $\text{FeH}_x$

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Hydrogen is one of the important candidates of the light elements of the Earth's core, because only a small amount of interstitial hydrogens may drastically change the physical properties of compressed iron (e.g. melting temperature, density and elastic properties). Since the solubility of hydrogen has strong pressure dependence, hydrogen content must be determined by in-situ observations. Combined with X-ray diffraction measurements, the following relation is widely used for this purpose:  $x = (V_{\text{FeH}_x} - V_{\text{Fe}}) / V_{\text{H}}$ , where  $x$  is the hydrogen content,  $V_{\text{H}}$  is the volume expansion caused by unit concentration of hydrogen,  $V_{\text{FeH}_x}$  and  $V_{\text{Fe}}$  are volumes of  $\text{FeH}_x$  and pure iron, respectively (Fukai, 1992). Ambient pressure experiments on many face-centered cubic (fcc) metals suggest that  $V_{\text{H}}$  is insensitive to the hydrogen content  $x$ . However, it has not been confirmed for compressed iron. We computed the equation of states of hexagonal-closed pack (hcp) iron with interstitial hydrogen with  $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$  and  $1.0$  by using the AkaiKKR firstprinciples package. Coherent potential approximation (CPA) was adopted to treat non-saturated hydrogen atoms, which randomly occupied the octahedral sites. The results of pure ( $x = 0.0$ ) and hydrogen saturated ( $x = 1.0$ ) iron are consistent with previous experiments (Hirao et al., 2004; Narygina et al., 2011). However, we found a discontinuous volume change as functions of hydrogen content for non-saturated  $\text{FeH}_x$  because of the ferromagnetic transition. We also found almost no  $x$  dependence on the volume in the ferromagnetic phase. Previous Mossbauer spectroscopy measurements suggest the ferromagnetic state is stable up to about 25 GPa for iron hydride (Mitsui et al., 2010; Narygina et al., 2011). This means that previous experiments possibly overestimate the hydrogen content of ferromagnetic  $\text{FeH}_x$ .

Keywords:  $\text{FeH}_x$ , ferromagnetism, equation of states, KKR-CPA, firstprinciples calculation

## Sound velocity and density of liquid iron sulfide up to 600 GPa 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 sulfide 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 [10] at the Institute of Laser Engineering, Osaka University. The sample is pyrrhotite ( $\text{Fe}_{0.9}\text{S}$ ). The sound velocities and densities of shock-compressed pyrrhotite using the high-power laser were measured by x-ray radiography [10-12] at pressures up to 600 GPa.

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Keywords: Sound velocity, Laser, Shock compression, Pyrrhotite, Earth's core

### 3D shear wave structure in the North American upper mantle from interstation phase and amplitude data of surface waves

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The North American continent encompasses a variety of complex structural features, including regions with east-west extension, active volcanoes in the west, and stable cratons in the central and eastern areas. The high-quality broadband seismic data derived from the high-density Transportable Array (USArray) have facilitated many new tomographic studies in this region. We have recently developed a new technique to measure interstation phase speeds and amplitude ratios for fundamental-mode surface waves based on non-linear waveform fitting between two stations (Hamada and Yoshizawa, 2015, GJI). The amplitude anomalies of surface waves are affected by not only anelastic attenuation, but also elastic focusing/defocusing, which reflect the second derivatives of phase velocity across the ray path. Thus, the amplitude data are sensitive to shorter-wavelength structure than the conventional phase data.

The method has been applied to observed waveforms of USArray from 2007 to 2014, and we could achieve fairly uniform ray-path coverage across the U.S. We collect a large-number of phase speed and amplitude data for short interstation distances less than 1000 km, which can be helpful in enhancing the horizontal resolution of velocity models in North America. The measured interstation phase speed and amplitude ratios are inverted simultaneously for phase speed maps as well as local amplification factor at receiver locations. Our phase speed maps derived from both phase and amplitude data tend to exhibit better recovery of the strength of velocity perturbations than those from phase data only, with enhanced local-scale tectonic features characterized by strong velocity gradients. The results indicate that interstation amplitude data can be of help in reconstructing shorter-wavelength structures of the upper mantle.

Isotropic 3-D shear wave models in the depth range from 50 to 200 km are constructed from the phase speed maps of fundamental-mode Rayleigh waves. The isotropic S wave speed models show significant slow anomalies in Rio Grande Rift and Yellowstone in the western United States at shallower depth above 100 km. Smaller-scale tectonic features are also mapped clearly in the eastern areas; e.g., slow anomalies in New Madrid Seismic Zone as well as Great Meteor Hotspot Track, which can be found down to the depth of about 100 km.

Keywords: Surface waves, Seismic tomography, North America

## Multi-scale heterogeneities in continental lithosphere and their implications for lithospheric discontinuities

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Lines of evidence from recent seismological observations have revealed the nature of large-scale and fine-scale heterogeneities in the continental lithosphere. Large-scale 3-D images of the continental lithosphere have been constrained primarily from surface waves, which indicate the fast waves speed anomalies of the cratonic lithosphere with the typical lithospheric thickness of about 200 km. Surface wave observations in Australia also provide the evidence of strong radial anisotropy with faster SH wavespeed than SV, particularly at the shallower depth above 90 km as well as in the asthenosphere, while the strength of radial anisotropy tends to be weak in the middle to lower lithosphere (Yoshizawa, 2014, PEPI).

Discontinuities in the lithosphere have been well constrained by the body-wave receiver functions that indicate the wave conversions and reflections underneath seismic stations. One of the striking features in the S-wave receiver function analysis in Australian cratons is the clear signals of discontinuities in the mid-lithosphere at around 70-90 km (Ford et al., 2010, EPSL), which might indicate the rapid velocity drop or change in the character of radial anisotropy at the middle depth of the continental lithosphere where the wave speed is highest in general. This estimated depth of the enigmatic mid-lithosphere discontinuity (MLD) from receiver functions coincides well with the rapid change in the strength of radial anisotropy derived from surface waves (Yoshizawa & Kennett, 2015, GRL).

The latest observations from high-frequency P-wave reflectivity profiles derived from the auto-correlograms of ambient noises in the vertical component (Kennett, 2015, EPSL) provide us with an additional constraint on the nature of the lithospheric heterogeneity. The P reflectivity profiles have suggested vertical changes in the characters of fine-scale structures in the Australian continent, indicating stronger reflectivity in the crust and upper lithosphere underneath the cratons. Such observations support the existence of fine-scale laminated heterogeneity in the lithosphere, as suggested by the numerical simulations for high-frequency scattering of seismic waves for the paths in the cratonic areas (Kennett & Furumura, 2008, GJI; 2016, G-cubed). The existence of such horizontally laminated fine-scale heterogeneity in the upper lithosphere causes equivalent effects as the shape preferred orientation, which may eventually generate apparent change in the radial anisotropy as well as apparent discontinuities in the mid-lithosphere. Linking all these independent observation from a variety of seismic signals with different frequency band will be of help in the further understanding of the nature of lithospheric heterogeneity and anisotropy.

Keywords: Lithosphere, Anisotropy, Heterogeneity, Discontinuity, Surface Waves

## Lowermost mantle dynamics driven by the plate subduction

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Subducted oceanic plates should be one of the significant factor deciding structures and the evolution of the Earth's lower mantle. The typical large and strong heterogeneity is large low shear velocity provinces on the lowermost mantle indicated by seismic tomography models. Seismic analyses indicate that these structures have prominent features, such as steep edges, a correlation between margins and hot spot locations, and the stability over a long term. We investigate that influence of the lower mantle properties on the mechanical interactions between the subducted plate and the compositionally dense layer, using mantle convection model in which plate-like motion is realized without any forces imposed on the surface plate.

Our 2-D Cartesian numerical model has chemically distinct materials with the density contrast of  $+77.3 \text{ kg m}^{-3}$  on the core mantle boundary (CMB) and the post-perovskite phase change with the Clapeyron slope of  $+8 \text{ MPa K}^{-1}$  and the density contrast  $+1.4\%$ . In this study, we focus on the following parameters that affect the slab subducting history and the evolution of the dense layer; depth dependence of the thermal expansivity, the depth profile of the background mantle viscosity and the yield strength of the slab. We also incorporate phase diagrams of hydrous minerals and hydration effects on the density and the viscosity.

In our result with the thermal expansivity decreasing with the depth, the dense material piles can remain on the CMB during the calculation. Moreover, the thermal expansivity depending on the depth makes the slab velocity slow down, even when the viscosity is small. This effect leads to the convection layered at the boundary between the regular mantle and dense segments, such that the slow convection is generated in the regular mantle layer and the active convection is in the dense layer. Steep difference in the temperature overlaps at the chemical boundary between dense materials and the surrounding mantle. Upwelling plumes are generated on the top of the dense layer. These plumes entrain only small amount of the dense material. On the other hand, the constant thermal expansivity destabilizes the dense layer. The dense segments deform strongly and rise off the CMB by the subducted slab plunging into the dense material piles. The subducted slab deformation near the 660 km depth discontinuity occurs except when the thermal expansivity is constant and the yield strength is 300 MPa. The amplitude and the wavelength of the slab buckling become larger with lower mantle viscosity. This deformation influences contact area between the dense structure and the slab, and spatial distribution of water in the lower mantle. We did not find significant effects of the slab buckling on the evolution of the lowermost mantle structures in the long term.

Keywords: subducted slab, LLSVPs, thermal expansivity



## Effects on onset and stability of plate-like behavior in the global mantle water cycle

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In our previous study, the rheological properties of hydrous mantle minerals would have the negative thermal feedback (high heat flow across the oceanic lithosphere and colder mantle temperature when the rheological strength of hydrous mantle minerals is strong enough) [Nakagawa et al., 2015]. However, the yield strength in that study was not consistent with that found from deformation experiments [Kohlstedt et al., 1995]. Moreover, the hydrous oceanic crust might occur to the lubrication that could enhance the activity of plate-like behavior caused by mantle volatiles [Cramer et al., 2012; Bercovici, 1998]. Here we examine to find the stable plate tectonics-like behavior from weak to strong oceanic lithosphere that seems to be consistent with the laboratory experiments in numerical mantle convection simulations with water migration [Nakagawa and Speigleman, to be submitted]. Two water cycle regime with the stable plate-like behavior would be found as a function of ductile yield strength and friction coefficient of brittle deformation, which would be 'regassing dominated cycle' for weaker oceanic lithosphere and 'balanced water cycle' for stronger oceanic lithosphere because the faster plate velocity could be expected for the weaker oceanic lithosphere than for the stronger oceanic lithosphere. With the constraint of mantle water content [Hirschmann, 2006; Hirschmann and Kohlstedt, 2012], the balanced water cycle regime would be preferable for reconciling the mantle water cycle. The onset timing of plate-like behavior would be much earlier than the dry mantle convection case with pseudo-plastic yielding rheology.

Keywords: water, mantle convection, plate tectonics, yield strength

## Numerical tests on hypothetical primitive origins in a growing planet with core formation

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The presence of large-scale heterogeneity in the deep mantle has been proposed on the basis of the interpretation of strong seismic anomalies in the present Earth's mantle. We hypothesize that the origin is in the protoplanetary material that survived the late accretion stage of planetary formation. In order to examine this hypothesis, we performed the 3-D Stokes flow simulation under a self-gravitating field with a free-surface treatment. The numerical calculation starts with a Mars-sized protoplanet (PP) which may serve as the sources of primitive reservoir by assuming that it has the undifferentiated material or primitive mantle differentiated in an early oxidized state. From this Mars-sized initial embryo, the planet grows under continuous impacts which create local magma ponds which eliminate the chemical signature of PP. We found that generations of such melt ponds may not completely remove the PP material from the growing planet. We suggest that such remaining PP material may be the origin of the primitive reservoir in the deep mantle inferred from geochemical analyses. Our analysis may contribute to the understanding of the thermochemical structure of the early Earth.

Keywords: core formation, primitive reservoir, Stokes flow