

## Phase study of Fe-Si alloys at 3.5 GPa Phase study of Fe-Si alloys at 3.5 GPa

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### Introduction

Silicon has been proposed as a probable candidate to solve the density deficit between seismic observations of the Earth Core and high pressure, temperature iron [1]. Besides, Fe-Si alloy is also a quite good soft-magnetic material and its phases and properties are quite complex as Si content, pressure and temperature varying. Our study focused on the Fe-Si system at 3.5GPa, trying to realize its phase changes and order variation as Si content and temperature changing.

### Experimental

Synthetic Fe-Si alloy with different stoichiometric compounds at different temperatures (2041, 1423 and 1173K) annealing by piston-cylinder at 3.5GPa were observed by Scanning Electron Microscopy and Electron Microprobe to determine the structures and compositions. Phase determinations were conducted by both X-Ray Powder Diffraction Spectrometry and Transmission Electron Microscopy. Lattice parameters were calculated using GSAS software from the angular position of main XRD peaks.

Local atomic orders of Fe<sub>2</sub>Si alloys were studied by <sup>57</sup>Fe Mossbauer Spectrometry. The spectra exhibiting magnetic sextets were described by means of a discrete number of magnetic components, values of the isomer shift, quadrupolar shift and hyperfine field independently refined by Normos software.

Fe<sub>3</sub>Si containing 25wt% <sup>57</sup>Fe prepared for Diamond Anvil Cell experiments synthesized at 2041K, 3.5GPa by piston-cylinder was polished to the foil (~20 microns thickness, ~150 microns diameter). We chose 400 microns diameter diamond cell and Re gasket as sample holder. Two rubies were added to measure pressure and noble gas Neon was inflated into cell as pressure medium. In-situ magnetization order measurements in DAC were carried out by Mossbauer spectrometry at 300K with increasing 3-4GPa every time by step from room pressure.

### Results and Discussion

Fe-Si alloys containing >26at% Si will decompose into DO<sub>3</sub> Fe<sub>3</sub>Si and some other phases at room pressure [2]. But in our sample of low temperature, the decomposition did not happen until the sample Fe<sub>2</sub>Si. We found the sample Fe<sub>5</sub>Si<sub>2</sub> at 1173K was still one phase while Fe<sub>2</sub>Si at 1173K decomposed into three phases. I think decomposition nearly begins at the composition of Fe<sub>2</sub>Si because of very little fraction of epsilon-FeSi and eta-Fe<sub>5</sub>Si<sub>3</sub>. The microprobe data supported this opinion because of Si contents of alpha-phase in the decomposed samples were all in the range of 29-32at%, which is also different from the room pressure. The phenomenon may represent higher stability of alpha-phase as pressure increasing and that is why Fe<sub>2</sub>Si found at room pressure cannot be found at 3.5GPa instead by DO<sub>3</sub> Fe<sub>2</sub>Si and B2 phase FeSi appears in very high pressure.

Mossbauer evolutions clearly demonstrated mean hyperfine field of the Fe-Si alloy at 3.5GPa decreased as the Si content increasing like room pressure. It is interesting that the spectrum of Fe<sub>3</sub>Si (exact composition is 24.73at% Si content) is quite different from room pressure. The DO<sub>3</sub> Fe<sub>3</sub>Si in room pressure can be emphasized by only two Fe sites: A4 and D6 [2]. But our sample showed there were at least four sites Fe. Except the normal D6 (36%), A4 (31%), there are a site (17%) between A4 and D6 and a site (16%) of which hyperfine field is smaller than D6. More than two Fe sites mean not completely order because of replacement of Si atoms and quench at high pressure.

Because of weakening signal in DAC, we just use two Fe sites, D6 and A4 to fit the Mossbauer spectra. The mean hyperfine fields of Fe-Si alloys decrease as pressure increasing. Because of broken of diamond at 17GPa, we have not got the nonmagnetic pressure of Fe<sub>3</sub>Si but hyperfine field still showed a good decrease trend. At >10GPa pure Fe will become nonmagnetic but our sample Fe<sub>3</sub>Si at 17GPa still have clear magnetic feature.

### References

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## 高圧下でのフォルステライトとマグネシウムペロブスカイトのリキダスの熱力学計算

### Thermodynamics and Melting of Forsterite and Mg-Perovskite at high pressure

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Melting of rock forming minerals at high pressure and high temperature is critical to understand differentiation in the magma ocean and melting at the present-day deep Earth. Liquidus curves of minerals can constrain the maximum temperature and the depth range of the magma ocean. Moreover, liquidus curves can constrain location of the eutectic point of a multicomponent-multiple phase system. However, the melting curve of Mg-perovskite, Ca-perovskite and ferropericlase, which are the major minerals at the lower mantle, have not yet determined because of the experimental difficulty and lack of the thermodynamic data. Therefore, in this study, we calculated thermodynamically the liquidus curve of Mg-perovskite, which is a primary mineral end-component in the lower mantle. Thermodynamics can provide consistent relation between the phase relation and the properties of the phases. We determined the melting temperature at which the Gibbs free energy of liquid equals that of solid. First to test the applicability of equation of state for liquid at high pressure, the liquidus curve of forsterite is calculated up to 20 GPa. It has been revealed that the third-ordered Birch-Murnaghan equation of state (EOS) is appropriate to predict volumes of liquid and solid end-components at high pressure and high temperature. The liquidus curve of perovskite with the optimized thermodynamic parameters with Birch-Murnaghan EOS of liquid and solid reproduces the experimentally determined liquidus very well, including the properties of liquid at high pressure. The liquidus temperature of perovskite at CMB pressure is predicted to be 8500 K. Therefore, the composition of the eutectic point in Mg-perovskite and periclase system, which represents a composition of partial melt of the lower mantle, is supposed to be located on the MgSiO<sub>3</sub> side, suggesting the liquid is likely to be less dense than the surrounding mantle.

キーワード: 熱力学, 高圧, マントル, 溶融, メルト

Keywords: Thermodynamics, high pressure, mantle, melting, melt

## ペロフスカイトとペリクレーズからのリングウッドイトの反応縁の成長速度とマン トルプリュームのダイナミクスへの応用

### Growth rate of ringwoodite reaction rim between perovskite and periclase with implica- tions for dynamics of mantle plumes

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Seismological studies have shown that some upwelling mantle plumes are originated from the lower mantle (e.g., Montelli et al. 2004). The 660-km seismic discontinuity is thought to be responsible for the phase boundary from ringwoodite to perovskite and periclase (post-spinel transformation) (e.g., Ito and Takahashi, 1989). Hence, when the plumes pass across the 660-km seismic discontinuity, ringwoodite will be formed via a reaction of perovskite and periclase. The reaction rate on the ringwoodite formation from perovskite and periclase has an effect on dynamics of the plumes. If the reaction rate is slow, perovskite and periclase should be survived as a metastable phase after the plumes pass across the 660-km discontinuity. Therefore, negative buoyancy operating inside the plumes increases, which leads to generate a resisting force for the mantle convection. Thus, dynamics of the plumes could be controlled by the reaction rate of ringwoodite formation from perovskite and periclase. In this study, we examine the reaction rates of ringwoodite formation from perovskite and periclase by utilizing reaction rim method. Based on the results, we discuss the dynamics of the plumes taking the growth kinetics into account, and the rate-limiting step in the ringwoodite formation from perovskite and periclase.

High-pressure and high-temperature experiments were carried out using a Kawai-type multi-anvil high-pressure apparatus. The starting materials were single crystals of  $\text{MgSiO}_3$  perovskite and periclase. They were polished, and contacted with each other. The experiments were conducted at 22.5 GPa, and 2073K for 1-12 hours. After the experiments, the ringwoodite reaction rims produced between perovskite and periclase was observed by using Field-emission scanning electron microscope. From the back-scattered electron (BSE) images, the thickness ( $L$ ) of the ringwoodite rims in each sample was measured.

The ringwoodite was produced at the interface between perovskite and periclase.  $L$  increases with proportion to square root of time ( $t$ ), indicating that the reaction proceeds by a diffusion-controlled mechanism (e.g., Schmalzried, 1978). The reaction constant,  $k$  ( $k = L^2/t$ ), is determined to be  $4.2 * 10^{-15} \text{ m}^2/\text{s}$ . The microstructural observation showed that the ringwoodite formation was restricted to the perovskite-ringwoodite interface, which suggested that the reaction rate was controlled by diffusion of MgO in ringwoodite. In addition, previous diffusion studies have shown that Mg diffusion rates are much faster than O diffusion in ringwoodite (Farber et al. 2000; Shimojuku et al. 2009). Thus, the O diffusion is likely to be rate-controlling step of ringwoodite formation. By using the determined reaction constant, the difference of depth ( $h$ ) at which transformations from perovskite plus periclase to ringwoodite occur in mantle plumes and surrounding mantle was calculated. The calculation shows  $h$  takes at most 0.1 m under the feasible conditions of the mantle plumes. This value is much smaller than depth variation expected from Clapeyron slope for the post-spinel transformation (e.g., Litasov et al. 2005). Thus, growth kinetics of the ringwoodite reaction from perovskite and periclase could have a minimal effect on the topography of the 660-km seismic discontinuity and negative buoyancy in the mantle plumes.

キーワード: ペロフスカイト, ペリクレーズ, リングウッドイト, マントルプリューム, 成長速度, 反応縁

Keywords: perovskite, periclase, ringwoodite, mantle plumes, growth rate, reaction rim

## 遷移層までの圧力におけるマントル鉱物の熱的性質の測定

## Thermal property measurements of mantle minerals under pressures to the transition zone

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Determination of thermal diffusivity or thermal conductivity under high pressure and at high temperature is a vital issue for the study of the mantle dynamics, and knowledge of heat capacity under pressure has a significance for assessment of the equations of state of the Earth's interior. So far thermal diffusivity and thermal conductivity of upper mantle minerals were measured using the pulse-heating method of one-dimensional heat flow. This simultaneous measurement also yields heat capacity data. It was found that the thermal conductivity or thermal diffusivity of olivine and garnet, increased 3-4 % per 1 GPa, and that olivine likely maintained anisotropy in thermal diffusivity or thermal conductivity under the conditions in the upper mantle. Thermal properties of jadeite, an analogue material of pyroxene, were also measured, however, the thermal properties of pyroxene under pressure have not yet been well elucidated. Antigorite, a high-temperature form of serpentine, has low thermal diffusivity and low thermal conductivity which are much lower than those of olivine. All the experiments were conducted at pressures up to 10 GPa and temperatures to 1100 K, therefore, another cell assembly is needed to expand the pressure range of measurement.

A new pressure-cell assembly similar to our previous one is designed for a sample of 3 mm in diameter and 0.7 mm in thickness. This smaller cell is immediately necessary for measurement of pyroxene of which sample size is limited owing to use natural single crystals of this mineral. In addition, this cell enables us to make measurements of thermal properties at pressures exceeding 15 GPa, which will cover the condition in the mantle transition zone. The measurements will be conducted using the Kawai-type apparatus at the Institute for study of the Earth's interior, Misasa.

We obtained preliminary results using this cell for the garnet sample. The thermal diffusivity showed lower value (~15 %) and the thermal conductivity was slightly high value compared with the previous results using the large cell, although their pressure derivatives consist with the previous ones. The precision of measurements will be improved by well-controlled machining of the cell assembly and by refining the data acquisition system. Heat capacity data with far precision are required for discussing the equations of state in the Earth's interior. For this purpose assessment by a finite-element method is a promising tool to optimize the cell assembly.

キーワード: 熱拡散率, 熱伝導率, 比熱, 高圧力, マントル鉱物

Keywords: thermal diffusivity, thermal conductivity, heat capacity, high-pressure, mantle minerals

## プレートジャンクションにおけるマントル流動とスラブの変形 The mantle flow and the deformation of subducting slab at the plate junction

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Recent seismological studies suggest the importance of the plate junction on the mantle flow and the deformation of subducting slab. As an example of this, we consider the junction of the southwestern Kurile arc and the northeastern Japan arc in this presentation. The observations of S-wave splitting in this region show that the fast polarization direction in the mantle wedge is approximately the same as the maximum dip direction of the subducting slab, which suggests 3D mantle flow. The angle of subduction shows some variation along the strike of the trench. It is smallest at the plate junction and it becomes larger beneath the southwestern Kurile arc where oblique subduction occurs. We shall explore the origin of these features by numerical modeling.

In numerical simulation, we use the previously-developed numerical model of subduction zone in a spherical coordinate system with a minor modification to include the non-linear rheology (i.e., dislocation creep). The numerical model is set so that it is similar to the geometry of the plate boundaries in the region considered. We estimate seismic anisotropy based on the theory of LPO development.

Our results show that the flow in the mantle wedge is 3D, whereas that in the subslab mantle (i.e., the mantle below the subducting slab) is almost 2D. Our results also show that the geometry of the subducting slab is qualitatively the same as the observations. It may be explained by considering the torque balance acting on subducting slab, that is, the torque due to the dynamic pressure and that due to the gravity of the subducting slab. We find that the pattern of seismic anisotropy obtained in the numerical simulation and the observations are similar in the mantle wedge, which suggests that the 3D mantle flow as seen in our results may exist in this region.

キーワード: プレートジャンクション, 沈み込み帯, マントル流動, 沈み込むスラブの変形, 地震波速度異方性  
Keywords: plate junction, subduction zone, mantle flow, deformation of subducting slab, seismic anisotropy

## ガイド波を用いて推定した海洋リソスフェアの地震学的構造 Seismic structure of the oceanic lithosphere inferred from guided wave

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Seismological observation using Broad-Band Ocean Bottom Seismometers (BBOBSs) was conducted in the northwestern Pacific from 2007 to 2008 and from 2010 to 2011. In the BBOBS data, unusual phase generated by events in the subducting Pacific plate were recorded universally. The phase shows some prominent features; large negative travel time anomaly ( $\sim 10\%$ ), high-frequency content ( $> 10$  Hz), and long coda for both P and S waves and the effect is much stronger for P wave. These features indicate that the unusual phase is guided wave traveling mainly in the oceanic lithosphere. The guided wave was previously called as Po/So waves and was studied actively from the 1970s to 1990s. It is now generally believed that these phases travel efficiently through the oceanic lithosphere. However, the mechanism of generation and propagation of the phases are still controversial.

We conduct travel time analysis of the guided wave. Both the guided wave and the direct wave are contained in each record and the guided wave is observed as a later phase in most case. We pick the onsets of the guided wave and the direct wave manually in high-pass filtered record with the corner frequencies of 10 Hz and 0.5 Hz, respectively. The travel time interval of the two phases changes systematically depending on the focal depth, the epicentral distance, and the azimuth. The apparent velocity of the guided P-wave varies from 7.8 to 8.6 km/s depending on the azimuth. The azimuth of the maximum velocity is north-south direction. These results are consistent with the previous explosion experimental studies and indicate that the guided wave travel horizontally in the oceanic lithosphere.

From the analysis of waveform observed at the eastern seaboard of northern Japan and numerical FDM simulation of seismic wave propagation, Furumura and Kennet [2005] demonstrate that the guided wave travelling in the subducting plate is produced by multiple forward scattering of high-frequency seismic waves due to small-scale heterogeneity in the plate structure. We apply this method to demonstrate the guided wave observed by the BBOBS array. This will help us to understand generation and propagation mechanism of the guided wave and the seismic structure of the oceanic lithosphere.

## SOIL PRIME MINERALS MAPPING USING LINEAR SPECTRAL UNMIXING TECHNIQUE IN MULTISPECTRAL IMAGERY DATA SOIL PRIME MINERALS MAPPING USING LINEAR SPECTRAL UNMIXING TECHNIQUE IN MULTISPECTRAL IMAGERY DATA

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Generally, soil characteristics are obtained via field observation. However, completely relies on field survey is not effective due to various cost and time issues. In addition, information taken via field survey is lack of spatial context, and thus it is difficult to have overall and comprehensive view of the soil dynamics. Therefore, in this paper, we presented an alternative method of soil mapping by utilizing widely available multispectral data.

The aim of this research is map soil characteristic in a mixed volcanic and carbonate mineral-dominated formation named Kebobutak formation. In tropics, the main issue for soil mapping would be the variation of land cover which led to the abundance of mixed pixels. As a resolve, we applied pixel unmixing method on multispectral data to obtain the fraction of soil characteristics on EO-1 ALI (Advanced Land Imager) image. ALI image was selected because it has several additional bands which benefited in the process of incorporating spectral library data for soil mapping. Soil spectra from spectral library were down-sampled to match the spectral resolution of ALI image prior to unmixing process. The results of unmixing were classified via rule-based classification to obtain tentative soil map. Finally, the tentative soil map was assessed using field data to produce final soil map which shows the distribution of soil characteristic in spatial context.

キーワード: mixed pixel, unmixing, soil characteristic, unmixing, ALI, spectral library

Keywords: mixed pixel, unmixing, soil characteristic, unmixing, ALI, spectral library