多結晶ダイヤモンドYakutiteの鉱物結晶学的特徴とその起源
Mineralogical/crystallographic features of polycrystalline diamond, Yakutite

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Yakutite is a type of polycrystalline diamonds occurred from alluvial deposits in Northern Yakutia of Russia. It is characterized by a massive morphology and black color and appears to be similar to carbonado, another type of polycrystalline diamond. There are only a few previous studies on Yakutite and its origin (formation process and environment) and mineralogical/crystallographic characteristic have still remained unclear. In this study, I examined the microtexture of Yakutite samples by means of electron microscopy as well as x-ray diffractometry and Raman spectroscopy to understand what actually Yakutite is in material point of view.Raman spectra collected from Yakutite show a characteristic profile in which only a small and very wide diamond Raman peak at ~1330 cm^{-1} is observed together with a significant background increase toward the higher frequency side probably due to strong fluorescence signal from sample itself. The result suggests that the constituent diamond crystals in Yakutite are extremely small like the case of synthetic nano-polycrystalline diamond (NPD). The result of micro-focus XRD revealed the presence of varying degrees of lattice preferred orientation of diamond crystals and coexistence of lonsdaleite. Most samples show the co-axial relation between lonsdaleite 100 and diamond 111, suggesting that Yakutite is a product of direct conversion (martensitic transformation) from well-crystalline graphite.TEM observation showed that Yakutite consists of extremely small diamond grains of 5-50 nm which constructs weak lineation (layered-structure) along a particular direction. Electron diffraction also showed the coexistence of lonsdaleite with the co-axial relation to diamond (lonsdaleite 100 // diamond 111). Such a microtexture is well comparable to that of impact diamond from Popigai crater that is located at Northern West of Yakutia and produces a large amount of natural poly-crystalline diamond (Ohfuji et al., 2015). The distance between the locality of Yakutite and the Popigai crater is 350-500 km, which seems to be within the outreach of the long-distance ejecta from the crater. Therefore, Yakutite is an impact diamond that is originated from the large meteoritic impact at Popigai.

キーワード：ダイヤモンド、相転移、隕石衝突
Keywords: Diamond, Phase transition, Meteoritic impact

密度汎関数法を用いた氷XVの構造の研究
Revisit to the structure of Ice XV: a DFT study

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There are open questions in the study of ice XV, the ordered phase of ice VI. The previous studies give inconsistent results between permittivity measurement (Johari & Whalley, 1976), neutron diffraction study (Saltzmann et al. 2009), and theoretical studies (Kuo & Kuhs, 2006; Knight & Singer, 2005). Permittivity measurements and theoretical study suggest that ice XV is ferroelectric, whereas neutron diffraction study suggests that ice XV is anti-ferroelectric. To obtain the consistent result, we classified 45 possible hydrogen configurations using a newly developed invariant, and then performed neutron Rietveld analyses and DFT calculations for every 45 possible configurations. The Quantum Espresso (Giannozzi et al. 2009) was used for the DFT calculations (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). Quantum Espresso is a package for the calculation of electronic structure properties using a plain-wave basis set and pseudopotentials. We used Perdew-Burke-Ernzerhof type non-empirical exchange-correlation functionals (Perdew et al, 1996) for this study. PBE type Xc/Corr energy form gives similar energy tendency (del Ben et al., 2014) with approximations from wave function theory such as a MP2 (Head-Gordon et al. 1988) and RPA (Macher et al., 2014). The pseudopotentials are derived using Troullier-Martins Method (Troullier and Martins, 1991). The enthalpies of 45 possible configurations for ice XV were calculated within an unit cell with the kinetic energy cutoff of 70 Ry and the Brillouin zone k mesh of 5 x 5x 6. The cell and atomic parameters were optimized using BFGS quasi-Newton method (Broyden, 1970; Fletcher, 1970; Goldfarb, 1970; Shanno, 1970) at atmospheric pressure. The phonons were calculated using density functional perturbation theory (Baroni et al., 2001). To correct the effect of zero-point motions of atoms, we added calculated phonon energy ($=1/2\Sigma_n \omega_n$) to the enthalpies from structural optimizations for each configuration. The effect of ferro-electricity were corrected by the Ewald construction, the same as the previous work about ice XV (Del Ben et al., 2014).
A consistent result was obtained about the structure of ice XV that the experimentally obtained ice XV have *Pmmn* space group, that is, the structure of ice XV is partially ordered structure. Our DFT calculations with surface effect corrections suggest that the energy difference between 45 possible patterns is between 0.05 eV (20 K in the reduced temperature). Moreover, the energy differences among several lower energy configurations are within 0.01 eV. Such a small energy difference gives us an interpretation of our experimental result that the ice XV has a *Pmmn* space group as time-space averaged structure.

キーワード：氷、密度汎関数法
Keywords: Ice, Density Functional Theory
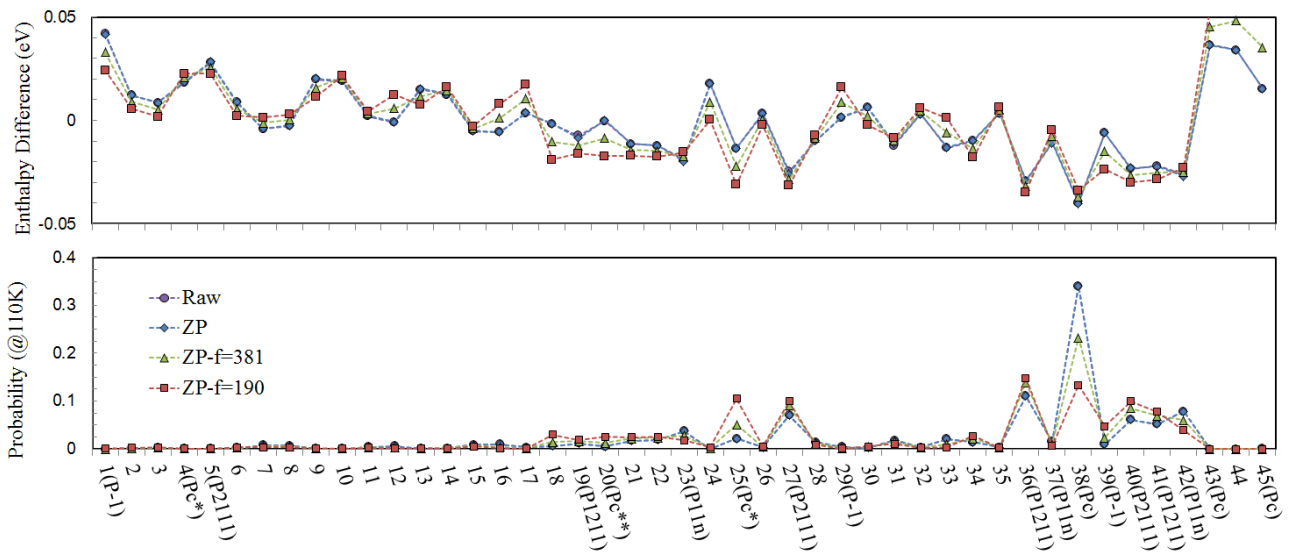
LA-ICP-MSを用いた高圧鉱物の微量元素二次元分析
Imaging Analysis of trace elements for high pressure minerals using LA-ICP-MS

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超高圧実験で得られる試料の主成分元素測定にはEPMAが用いられるが、濃度0.1wt%以下の微量元素の分析には、レーザーアブレーション誘導結合プラズマ質量分析計(LA-ICP-MS)や、二次イオン質量分析計(SIMS)が用いられる事が多い。これらの測定では、直径数十ミクロン程度の一定範囲をレーザーやイオン・ビームにより掘り進めながら測定し、微量元素濃度を求めていた。近年、試料上にレーザーを走査しながらICP-MS測定を行う二次元分析が行われるようになった。この方法は、もっぱら微量元素の二次元分布を定性的に解析する目的に用いられているが、測定データの解析法を工夫する事により、定量的な分析値を得る事も可能である。本研究では、超高圧実験で得られた試料をLA-ICP-MSで二次元測定を行い、高圧鉱物結晶内の微量元素分布状態を調べるとともに、二次元測定データから定量値を求め、高圧鉱物と珪酸塩メルト間の微量元素分配係数の推定も試みた。

出発物質には希土類元素などを約200ppm程度添加したカンラン岩組成の試料を用いた。超高圧実験には、東京工業大学の川井型マルチアンビル装置を用いて、17GPa以上の圧力で試料の融解実験を行った。大きな高圧鉱物結晶を得るために、実験では加圧後、目的温度よりも100度程度高温まで一旦加熱し、その後10分かけて目的温度まで徐冷し、30分から1時間目的温度で保持した後、急冷回収した。回収試料は研磨した後に、EPMAを用いて主成分元素濃度を測定した。微量元素分布測定には、エキシマレーザーと四重極型質量分析計を組み合わせた、京都大学のLA-ICP-MS装置を用いた。アブレ-ションは、10から20ミクロンのビーム径で行った。

珪酸塩メルトと共存するリキダス相は、17GPaではWadsleyite+Garnetであったが、圧力を上げるとGarnet+Ferropericlaseとなり、23GPa以上ではBridgmanite+Ferropericlaseであった。Ferropericlase以外の高圧鉱物は、50ミクロン以上の比較的大きな結晶が得られた。これらの試料をLA-ICP-MSを用いて微量元素の二次元分布を調べたところ、100ミクロンを超える大きなGarnet結晶などの場合には、実験温度を下げて結晶を成長させた事に伴う、微量元素の濃度変化が認められた。LA-ICP-MSの二次元データから、組成が均一な領域を分離して微量元素の定量値を計算し、珪酸塩メルトの組成と比較して分配係数を求めたところ、通常の方法により得られる値とほぼ同じ結果を得る事が出来た。

キーワード：高圧鉱物、微量元素、二次元分析
Keywords: high pressure minerals, trace elements, imaging

高圧下におけるFeS-NiS二成分系メルトの密度測定
Density measurements of the FeS-NiS binary melts at high pressure

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Planetary cores consist mainly of iron, nickle and some light elements. Sulfur is thought to be a primary lightening element in the metallic core of the small planets, satellites and planetesimals. Planetary magnetism arises from a dynamo driven by convection in the liquid core. Physical properties of sulfur-bearing Fe liquids are, therefore, fundamental to understand the dynamics of liquid core in the planetary interior. Here we report the results of density measurements of FeS-NiS binary sulfide melts at high pressure by means of X-ray absorption technique. Experiments were conducted at BL22XU of SPring-8, at which the cubic-type multi-anvil press is equipped and highly brilliant monochromatic X-ray is available. We determined the densities and the expansivities of NiS, $(Fe_{0.3}Ni_{0.7})S$, $(Fe_{0.5}Ni_{0.5})S$ and $(Fe_{0.7}Ni_{0.3})S$ composition liquids at about 2GPa and 1273-1673 K. Density of (Fe,Ni)S liquid increases with Ni content. Compositional dependence of density allow us to evaluate the partial molar volumes of liquids FeS and NiS. The partial molar volumes of liquids FeS and NiS are consistent with those at 1 atmospheric pressure (Kress, 2008). On the other hand, the extrapolated densities of liquid FeS is 8-10% lower than the EoS determined by Nishida et al (2011). Our new data would contribute to understand compressional behavior as well as thermochemical properties of Fe-Ni-S liquid alloys under pressure.
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キーワード：硫化物メルト、密度、部分モル体積、惑星核
Keywords: sulfide melt, density, partial molar volume, planetary core

$Mg_{14}Si_5O_{24}$ anhydrous phase Bの低温熱容量と標準エントロピーの決定
Determination of low-temperature heat capacity and standard entropy of $Mg_{14}Si_5O_{24}$ anhydrous phase B

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$Mg_{14}Si_5O_{24}$ anhydrous phase B (Anh-B) は、マントル中においてオリビンや輝石のSiO_2成分が流体相に選択的に溶解し、残渣がMgO成分に富むような場合に、$5Mg_2SiO_4$ forsterite (Fo) + 4MgO = $Mg_{14}Si_5O_{24}$ (Anh-B) の反応により存在することが予想されている。Anh-Bの熱力学的安定性を検討するために必要となるエントロピーは、実験的に決定されていなかった。そこで、本研究では熱容量測定を行うことにより低温熱容量を決定し、標準エントロピーを求めた。また、得られた低温熱容量に基づく格子振動モデル計算から高温熱容量の推定も行った。

川井型マルチアンビル高圧発生装置を用いて、出発物質のMg_2SiO_4 Fo:MgO = 5:4（モル比）混合物を15 GPa, 2073-2273 Kで3時間保持した後、急冷回収することによりAnh-Bの高圧合成を行った。回収試料は、微小部X線回折測定およびSEM-EDSにより単相であることを確認した。低温熱容量は、熱緩和法を応用したカンタムデザイン社製PPMS装置を用いることにより、2-307 Kの温度範囲において約2 Kの温度間隔で測定された。試料ステージとの熱接触を良くするため、円柱状の試料の片側底面が平らになるようにラッピングフィルムで研磨した。熱量測定に用いた試料の重量は、合計10.988 mgであった。

低温熱容量は、各測定温度において約0.3%の測定精度で測定された。得られた300 K付近での熱容量は、我々の示差走査熱量測定による値と誤差範囲内で一致しており、測定結果が妥当であったことを示している。実測された熱容量(Cp)を用いて、0から298 Kまでの範囲においてCp/Tを積分することにより、格子振動寄与による298 Kでの標準エントロピーは544.17(1) J/mol.Kと決定された。この値は、Ottonello et al. (2010)の第一原理計算から求められた561.2 J/mol.Kよりは小さく、またGanguly and Frost (2006)により酸化物のエントロピーから推定された547.3 J/mol.Kと良い一致を示す。さらに、得られた低温熱容量を再現するようにキーファーモデルを用いて格子振動のフォノン状態密度をモデル化し、格子振動モデル計算を行うことにより、実測できない800 K以上の高温領域での熱容量を推定した。300-2000 Kの熱容量は、$Cp(T)=6.624 \times 10^2 + 2.123 \times 10^4 T^{-0.5} - 4.827 \times 10^6 T^{-2} + 2.221 \times 10^9 T^{-3} - 1.061 \times 10^{-1} T - 3.643 \times 10^5 T^{-1}$と求められた。

キーワード：アンハイドラスフェイズＢ、熱容量、エントロピー、熱力学的安定性、格子振動モデル計算
Keywords: anhydrous phase B, heat capacity, entropy, thermodynamical stability, lattice vibrational model calculation

テラヘルツ顕微ラマン分光法と鉱物科学への応用
Terahertz micro-Raman spectroscopy and its application to mineral sciences

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ラマン分光法におけるテラヘルツ領域とは、相対波数で約200 cm^{-1}以下を指す。この領域はトリプルモノクロメーターを持つラマンシステムで古くから測定されてきた。しかし、20年くらい前から、より安価でコンパクトな「ラマン(ノッチ)フィルター＋シングルモノクロメーター＋冷却CCD検出器」の測定系が広く普及した。これに使われるフィルターはテラヘルツ領域をほとんど測定できない。そのため、最近の研究ではテラヘルツ領域はまず測定されない。これは、その場測定のような明るい光学系が必要な際に顕著である。テラヘルツ領域は結晶相の同定には必須ではないが、ガラスではボソンピークが出現し、相転移ではソフトモードが主に存在するなど、系のダイナミクスに関連する情報が得られる重要な領域である。この不幸な状況はONDAX社が新しいノッチフィルターを開発したことで変わり、シングルモノクロメーターを使って5 cm^{-1}程度まで測定可能となった(doi: 10.1063/1.3520137)。著者らのところではこのフィルターを導入して、既存の自家製顕微ラマンシステムに取り付けて、テラヘルツ領域が測定できるようにしている。本講演では、そのシステムの詳細と、いくつかの応用例を示す。

我々の測定系は後方散乱配置であり、通常測定ではSemrock社のラマンエッジフィルターを使い、100 cm^{-1}程度まで測定できる。ただし、強度を重視する場合は、レーザービームを試料に送る部分のビームスプリッターをSemrock社のダイクロイックビームスプリッターで置き換えている。これで散乱強度が3倍ほど稼げるが、このビームスプリッターの性能のため200 cm^{-1}以下が測れなくなる。テラヘルツ領域の測定では、それらのフィルター類を外して、ONDAX社のフィルター(SureBlock, 488 nm用)を取り付ける。1枚でOD4程度なので、ラマンピーク観察にはフィルター2枚が必要である。フィルターは光軸に対して数度傾ける必要があり、ソーラボ社のキネマテックマウントに取り付けている。レイリー散乱の強度を最小にするように角度を微調整する。透過率が良くないので、フィルター2枚で感度は約1/3落ち、ビームスプリッター部での低下を含めて、200 cm^{-1}以上測定用設定と比べて最大1桁ほど感度が落ちることになる。

この測定系でまず硫黄を測定した。硫黄には27 cm^{-1}にラマンピークがあることが知られており、性能の評価には最適である。アンチストークスおよびストークス側でこのピークを確認できた。著者のウェブページでそのスペクトルを公開している。シリカガラスを測定すると、ボソンピークが確認された。以前、我々は$AlPO_4$においてmoganite相を報告しており、高温その場ラマン測定(> 100 cm^{-1})も行っているが、その試料を測定したところ、テラヘルツ領域で2本のピークを新たに見つけた。moganite相も石英相同様に高温で転移があるので、これらがソフトモードの可能性もあり、興味深い。高温その場実験を予定している。

さらにアミノ酸の1つである、アラニン結晶を測定した。アラニン分子はキラリティを持つが、ラマン分光法では分子のキラリティを区別できない(Raman Optical Activity法ではできるが)。結晶化した場合は事情が少し異なり、ラセミ化したものと、してないものでは結晶の対称性が異なる。そのためラマンの選択則も異なり、その場合にはラマン分光法でも区別がつく。その違いは分子間の振動に主に反映されるので、テラヘルツ領域に差異が期待される。そこで、D-, L-, DL-アラニン結晶をそれぞれ測定して比較した。確かにDL-アラニンとD-, L-アラニンではテラヘルツ領域に違いがあり、区別ができることがわかった。ラセミ化の温度依存性などへの実験的な応用が考えられる。

キーワード：顕微ラマン分光法、テラヘルツ、鉱物、アラニン、ラセミ化
Keywords: Micro-Raman spectroscopy, terahertz, mineral, alanine, racemization

ハイドロガーネット，加藤石 $Ca_3Al_2(H_4O_4)_3$，の高圧下での構造特性
High-pressure structural behavior of hydrogrossular, katoite $Ca_3Al_2(O_4H_4)_3$

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Nominally anhydrous minerals (NAMs) in the Earth's mantle are important because they may potentially introduce a large amount of water in the Earth mantle thus significantly modifying its elastic properties. Calcium aluminum garnet, grossular $Ca_3Al_2(SiO_4)_3$, with the largest divalent cation Ca^{2+} and the smallest trivalent cation Al^{3+} exhibits a complete solid solution with katoite, $Ca_3Al_2(O_4H_4)_3$, which is the Si-free end member of the hydrogrossular. Katoite is known as a typical model for the hydrogarnet substitution ($Si^{4+} \leftrightarrow 4H^+$) in garnets and other silicates. The replacement Si^{4+} by $4H^+$ results in profound changes in the physical properties and thermodynamic stability of garnet structure. We carried out high-pressure Raman spectroscopy, high-pressure single-crystal synchrotron X-ray diffraction study, and high-pressure neutron diffraction study to clarify the physical and structural properties of katoite at the mantle condition. Raman spectra collected at ambient conditions clearly showed the OH stretching vibration at 3652 cm^{-1}. Translational OH motion and mixed translational/librational motions of O_4H_4 were observed at 537 cm^{-1} and 332 cm^{-1}, respectively. It is noteworthy that with increasing pressure the OH stretching vibration mode exhibited a negative pressure shifts above 5 GPa, which is responsible for the hydrogen bonding formation in the O_4H_4 cluster. In addition, the pressure dependence of the full width half maximum (FWHM) of the OH stretching mode was also changed at the pressure, which is interpretable as a result of peak-splitting derived from cubic-tetragonal transformation. The results of high-pressure single-crystal X-ray diffraction and high-pressure neutron diffraction studies exhibited a discontinuous volume change occurs between 5 and 6 GPa, which supports the cubic (space group *Ia*-3 *d*) to tetragonal (space group *I*-43*d*) phase transformation.

高温高圧下における炭化ケイ素の相関係と常温での岩塩型高圧相の圧縮挙動
Phase relations in SiC under high pressure and temperature and compression behavior in rock-salt-type phase

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Although planets in the solar system are oxygen-rich compared to the carbon, the exoplanets may have fundamentally different chemistry. For example, recently found super-Earth, 55 Cancri e is orbiting around the host star, which has particularly high C/O ratio. According to the mass-radius relations (McArthur et al., 2004; Winn et al., 2011; Demory et al., 2011), the interior of 55 Cancri e is expected to be carbon-rich similarly with the host star, and is possibly constructed from iron, silicon-carbide (SiC) and carbon (Madhusudhan et al., 2012). However, the physical property of SiC is so far poorly understood under high pressure conditions, although it is essentially important to know the internal structure of the super-Earth.

 SiC is known to have polytypes such as 3C and 6H at ambient condition. It is reported that zincblende type 3C phase undergoes phase transition to rock salt type phase under high pressure. However, the phase transition pressures are inconsistent between theoretical prediction and experimental results. *Ab initio* calculation showed that the 3C phase transformed into the rock salt type phase at 66 GPa (Chang et al., 1987; Karch et al., 1996). In contrast, the previous experimental study observed the phase transition at 100 GPa or higher (Yoshida et al., 1993).

 In this study, we have examined the phase relations of SiC under high pressure and temperature conditions by a combination of laser-heated diamond-anvil cell and *in-situ* X-ray diffraction (XRD) measurements at BL10XU of SPring-8. In addition to the phase relations, the compression behavior of rock salt type phase was firstly determined by means of experimental method. The XRD data were obtained up to around 100 GPa and 3500 K. The results showed that the rock salt type phase is stable above about 74 GPa and 2000 K, which is significantly lower pressure than the previous study without annealing. Obtained results showed that the rock salt type phase is 19.4 % denser than 3C phase at about 74 GPa. Such large increase of density may have a strong effect on the estimation of the internal structure of super-Earth, such as 55 Cancri e.

キーワード：炭化ケイ素、炭素惑星、スーパーアース、高圧相転移、X線回折、レーザー加熱式ダイヤモンドアンビルセル
Keywords: silicon carbide, carbon planet, super-Earth, high-pressure phase transition, X-ray diffraction, laser-heated diamond-anvil cell

タングステンカーバイドアンビルと組み合わせた川井型マルチアンビルプレスによる44 GPa、2000 KにおけるLiNbO$_3$型 Mg$_3$Al$_2$Si$_3$O$_{12}$の合成

Synthesis of LiNbO$_3$-type Mg$_3$Al$_2$Si$_3$O$_{12}$ at 44 GPa and 2000 K using Kawai-type multianvil press with tungsten carbide anvils

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Garnet is one of the major constituent minerals of the upper mantle. In particular, pyrope is one of the most abundant components. Pyrope transforms to aluminous bridgmanite (Al-Brm) + corundum at about 25 GPa and Al$_2$O$_3$ content in Brm increases with increasing pressure (e.g. Kubo and Akaogi, 2000; Liu et al. submitted). Finally, Al-Brm with pyrope composition is synthesized over 40 GPa and 2000 K (Liu et al. submitted). Recently, Ishii et al. (2016) reported that recovered sample synthesized at 44 GPa and 2000 K has LiNbO$_3$ (LN)-type structure. Although there are synthesis reports of LN phase with (Mg,Fe,Ca,Mn)Al$_2$Si$_3$O$_{12}$ natural garnet (Funamori et al., 1997; Miyajima et al. 1999), synthesis with composition of pyrope end-member is first time and this structure refinement has never been made. Therefore, we made the Rietveld refinement of LN phase with pyrope composition. We also introduce high-pressure generation technique for synthesis over 40 GPa with a Kawai-type multianvil press (KMAP) in this study.

We used a 15-MN KMAP with DIA-type guide blocks carefully optimized to make a cubic compression space formed by first-stage anvils. WC anvils (TF05, Fujilloy Co., Ltd) of 1.5 mm truncation with 1.0 degree tapering were adopted for generating pressure over 40 GPa, combining a semi-sintered MgO + 5wt.%Cr$_2$O$_3$ octahedron as a pressure medium. Pressure at 2000 K was estimated with Al$_2$O$_3$ content in aluminous Brm by Liu et al. (submitted). Sintered ilmenite-type Mg$_3$Al$_2$Si$_3$O$_{12}$ (py-Ak) was synthesized as starting material at 26 GPa and 1200 K (Kubo and Akaogi, 2000) to minimize the pressure drop for volume change by phase transition. Sample was put in Re furnace surrounded by a LaCrO$_3$ thermal insulator. Al$_2$O$_3$ rods were placed at the both end of the sample in a heater and these were separated with Re disks. A microfocus X-ray diffractometer and an FE-SEM-EDS were used to analysis phase and composition of recovered sample. Synchrotron XRD data for Rietveld analysis were collected rotating sample at ambient conditions in SPring-8 (BL10XU). Rietveld refinement of recovered sample was performed using the RIETAN-FP/VENUS package (Izumi and Momma, 2007).

R factors for structure refinement were converged to reasonable values (R_{wp}, R_B and R_F<5). Lattice parameters of this phase with space group of R3c were determined as a = 4.8196(3) Å, b = 4.8195(3) Å, c = 12.6877(8) Å, V = 255.2(1) Å^3.

温度効果によるクリストバライトへの炭素固溶
The effect of high temperature on carbon solubility in cristobalite

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Silicates is one of the major and important components in the Earth's crust and mantle. Because an enormous amount of carbon is stored in the Earth's interior, it can be suggested that the silicates must be exposed to carbon under high-pressure and high temperature conditions (Sen et al. 2013). Recently, Santoro et al. (2014) demonstrated that carbon atoms can be substituted with silicon in cristobalite at P = 16-22 GPa and T > 4000K. Furthermore, the first-principles calculation showed the possibility that a continuous solid-solution can be formed between SiO_2 and CO_2 in a metastable cristobalite phase at ambient pressure (Aravindh et al. 2007). However, the effect of temperature on carbon solubility in silica has not been confirmed yet. Accurate knowledge of the carbon solubility in silica under high temperature can help us to understand the interaction between carbon and silicate minerals in the Earth's interior. In this study, we investigated the carbon solubility and structure change of cristobalite under high temperature condition.

First, we prepared amorphous silica and graphite as starting materials. Powder amorphous silica and graphite were mixed sufficiently by an agate mortar and pestle. Second, the mixture was vacuum-enclosed in a quartz tube and heated at 1300°C for 3 days. Then, it was removed from the furnace and quenched at room temperature. The sample was carefully examined by powder XRD, EPMA, and IR spectroscopic analysis.

Regardless of the Si : C ratios of starting materials, all mixtures were crystalized into cristobalite. The result of the EPMA suggested that carbon was incorporated into cristobalite. The intensity of CKα was apparently increased with the carbon content. The amount of carbon in cristobalite was < 0.4 wt%. The powder XRD analysis revealed that all peaks corresponding to cristobalite were shifted to the lower angles, indicating the increases of unit cell and volume with the carbon content. Furthermore, cristobalite incorporating carbon in the structure was reheated in a quartz tube at 1300°C for 3days. The results of powder XRD showed that all of the peak positions came back to the original positions, which suggested that the carbon in crystobalite was resubstituted with oxygen atom. Therefore, these results support the following equation:

$$SiO_2 + xC \leftrightarrow Si(C_xO_{2-x}) + (x/2)O_2 \ (0 \leq x \leq \alpha)$$
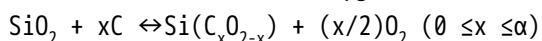
Here, αis the solubility limit.

Consequently, it can be concluded that carbon can be substituted with oxygen in cristobalite at high temperature. In addition, we will report quantitative experimental results of temperature dependence on carbon solubility in cristobalite in detail.

キーワード：炭素固溶、珪酸塩鉱物、粉末XRD測定、EPMA測定
Keywords: carbon solubility, silicate mineral, powder XRD, EPMA

粒子画像解析による砂粒子の粒径や形状分布の粒子数依存性に関する実践的調査
A Practical Investigation on Particle Number Dependence of Particle Size and Shape
Distributions of Sand Particles by Automated Particle Image Analysis.

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[Introduction]
Particle size distribution (PSD) is one of the most important soil parameters often used in soil, mineral, geological, and geomorphological laboratories. To characterize of particles , an Image Analysis (IA) based on manual microscopic techniques is one of the effective ways to determine the morphological characteristics of particles ,such as their size and shape. However, one of the major drawbacks of manual microscopic analysis is the near impossibility of measuring a statistically significant number of particles, such as measuring tens to hundreds of thousands of particles, as recommended in ISO 13322-1,2. Recent advances in computer technology have allowed for the development of a new automated particle image analysis (APIA) approach that uses digital imaging technology to allow for the acquisition of 2D particle projection images of a statistically significant number of particles. This technique has allowed for the calculation of a wide range of morphological parameters, such as the size and shape of particles, as well as allowing for the identification and quantification of the most subtle of differences within tens to hundreds of thousands of particles. This study had suggested a practical investigation of particle number dependence of particle shape distribution of soil particle by APIA.
[Method]
APIA analyses were conducted on a Morphologi G3SE as automated image analysis system (Malvern Instruments, Worcestershire, UK). Sample was subsequently dispersed with an SDU using a short duration pulse of compressed air. Measurements were collected automatically using standard operating procedures (SOPs), which clearly define the software and hardware settings used during the measurement process. The measurement sample was dispersed on a glass plate, which was used as a sample carrier to minimize environmental exposure within the enclosed sample chamber unit.

キーワード：粒子径および形状、画像分析、計測数
Keywords: Particle Size and Shape, Image Analysys, Partcile Number

高圧下でのFe-Si合金の磁性・構造転移
Magnetic and Structural transition of Fe-Si alloy under high pressure

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The Earth's core is consider to be divided into the liquid outer core and solid inner core based on seismological observations. The Earth's core is mainly composed of Fe although the density of the core is smaller than that of pure iron under the core conditions. Therefore, the core has been considered to contain light elements, such as H, S, Si, C, and O. In particular, Si is one of the most important light elements in the core. Although the phase relations and compression behaviors in the Fe-Si alloy have been studied at high pressure and temperature in order to investigate properties of the inner core, magnetic properties of the alloys have not been studied well. In order to clarify the relationship between the magnetic transition and the structural transition of the Fe-Si alloy, we made simultaneous measurements of X-ray diffraction and synchrotron Mössbauer spectroscopy the Fe-Si alloy up to 40 GPa at room and high temperature.
The starting materials of Fe-Si alloys used for the measurements had compositions of $Fe_{0.95}Si_{0.05}$ or $Fe_{0.88}Si_{0.12}$ enriched with ^{57}Fe. The mixture powder were heated in the $Ar-H_2$ atmosphere by a double sided laser heating system and the molten samples were quenched to room temperature by shutting the laser. Mössbauer spectra and XRD patterns were obtained at the beamlines, BL10XU and BL11XU of SPring-8 up to 40 GPa at room and high temperature. Our Mössbauer data together with X-ray diffraction data revealed that the magnetic transition started to transform from magnetic to non-magnetic phase at around 15 GPa for $Fe_{0.95}Si_{0.05}$ and 14 GPa for $Fe_{0.88}Si_{0.12}$. This transition was likely simultaneous transition with the bcc to hcp transition. The magnetic and structural transition pressures increased as increasing Si amounts in the Fe-Si alloys. In addition, Mössbauer spectra and XRD patterns were obtained from room temperature to 700 K at about 7 GPa. As the temperature raised, the internal magnetic fields became small and bcc structure started to transform to fcc structure at 870 K and 8.0 GPa and only fcc structure was observed at 920 K and 8.0 GPa.

キーワード：Fe-Si合金、メスバウア分光、磁性転移、構造転移
Keywords: Fe-Si alloy, Mossbauer spectroscopy, Magnetic transition, Structral stransition