

## Silicate-C-O-H-N fluids and melts at upper mantle temperatures, pressures, and redox conditions

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The speciation of C-O-H-N volatiles and silicate components in fluids and solubility and solution mechanisms of C-O-H-N volatiles in aluminosilicate melts have been determined experimentally, mostly *in situ* with the sample at high temperature and pressure corresponding to those of the upper mantle, as a function of melt composition and redox conditions. In silicate-O-H systems, molecular H<sub>2</sub>O and OH groups linked to the silicate network exist in silicate and aluminosilicate-saturated fluids and in water-saturated melts.

The delta H of the water speciation equilibrium, H<sub>2</sub>O+O=2OH, is ~30 kJ/mol. The delta H of hydrogen bonding is ~10 and ~20 kJ/mol for melt and fluid, respectively. Hydrogen bonding is not detected above about 500 deg C. Silicate speciation in fluid and in melt comprises similar Q-species with delta H of the solution reaction ~400 kJ/mol. In silicate-C-O-H systems, under oxidizing conditions (such as that controlled by the magnetite-hematite, MH, buffer, for example) the CO<sub>2</sub> solubility in melts, where it exists as molecular CO<sub>2</sub> and CO<sub>3</sub> groups, is in the 1-4wt% range between ~1 and 3 GPa and upper mantle temperatures. Its solution mechanism is CO<sub>2</sub>+Q<sup>n</sup>=CO<sub>3</sub>+Q<sup>n+1</sup>. This equilibrium probably shifts to the right with temperature and left with pressure [1]. Alkalis and alkaline earths dissolve in C-O-H fluid as complexes with CO<sub>3</sub>. Silicate is not detectable in CO<sub>2</sub> fluid. Methane, CH<sub>4</sub>, is the dominant C-species in melts at f<sub>H2</sub>≥MW (magnetite-wustite), whereas in fluids, more reducing conditions [iron-wustite (IW) buffer] are necessary to form detectable CH<sub>4</sub>. Methane solubility in melts is 10-30% of that of CO<sub>2</sub>. At f<sub>H2</sub>(IW) the dominant fluid species are CH<sub>4</sub>+H<sub>2</sub>+H<sub>2</sub>O. In coexisting melt, CH<sub>3</sub> groups linked to the silicate melt structure via Si-CH<sub>3</sub> bonding coexist with molecular CH<sub>4</sub> with a solution mechanism, CH<sub>4</sub>+Q<sup>1</sup>=CH<sub>3</sub>+Q<sup>0</sup>. The C(melt)/C(fluid) partition coefficient is in the 0.01-0.1 range with a delta H-value near 50 kJ/mol. In silicate-NOH systems, under oxidizing conditions [f<sub>H2</sub>(MH)] nitrogen exists principally as N<sub>2</sub>. Under reducing conditions, f<sub>H2</sub>(MW), the nitrogen oxidation state is lowered with NH<sub>2</sub><sup>+</sup> groups dominating in fluid and melt. At the more reducing f<sub>H2</sub>(IW) condition, NH<sub>3</sub>+NH<sub>2</sub><sup>+</sup> fluid coexisting with NH<sub>3</sub>+NH<sub>2</sub><sup>-</sup>+H<sub>2</sub>+H<sub>2</sub>O species in melt with the ammine groups bonded directly to Si<sup>4+</sup> (Si-NH<sub>2</sub>) and solution mechanism, NH<sub>3</sub>+Q<sup>1</sup>=NH<sub>2</sub>+Q<sup>0</sup>. The N(melt)/N(fluid) is ≤0.1 with a delta H near 50 kJ/mol. The nitrogen solubility under these conditions are 2-3 times greater than for oxidized nitrogen.

The f<sub>H2</sub>-dependent speciation C-O-H-N volatile components result in f<sub>H2</sub>-dependent thermodynamic and transport properties of fluids and melts in the interior of the Earth and terrestrial planets. Reduced and oxidized C-O-H-N species exist fluids and melts in the modern mantle, whereas reduced species dominated in the young Earth. In fluids, the solubility of nominally incompatible trace elements can increase by orders of magnitude upon its saturation with silicate components. Trace element and stable isotope partitioning between fluids and melt can change by >100% for the same reason. Dissolved C-O-H-N volatile components in melts can have similar effects. Silicate solute in C-O-H-N fluids also governs the fluid and melt equation of state. For example, dissolved silicate in fluid can increase its density by ≥20% compared with pure H<sub>2</sub>O at 1 GPa.

[1] Guillot, B. and Sator, N. (2011). *Geochim. Cosmochim. Acta*, 75, 1829.

## 沈み込むスラブ中での炭酸塩鉱物の電気伝導度 Electrical conductivities of carbonates in the subducted slab

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The behavior of carbonate minerals under high pressures is important in our understanding of the geochemical cycle of carbon in the deep mantle. Magnesium and calcium carbonate minerals dominate the Earth's interior. Magnesite,  $MgCO_3$ , is a naturally occurring carbonate mineral and is stable over a wide range of pressure and temperature. In contrast, calcium carbonate ( $CaCO_3$ ) occurs in three structural forms: calcite, aragonite, and vaterite. Calcite is stable under ambient conditions, and adopts several different modifications (calcite I-V), whereas aragonite is thermodynamically stable at high pressures and high temperature corresponding to the upper mantle conditions. Dolomite ( $MgCaC_2O_6$ ) is stable up to the mantle pressures. Therefore, the behavior of magnesite, aragonite, and dolomite are important for an understanding of the circulation of carbon from the crust to the upper mantle. Recent advances in geophysical observations have allowed to map the electrical conductivity of the Earth's mantle. Electrical conductivity measurements on carbonates at high pressures and high temperatures can contribute towards an estimation of the distribution of carbonate rocks in the deep mantle. In this study, we have determined the electrical conductivities of three carbonates up to 6 GPa and 1000 K using in situ complex impedance spectroscopy in a multi-anvil high-pressure apparatus. These measurements allowed us to quantify the effects of pressure, temperature, and chemical composition. The electrical conductivity of magnesite increased with increasing pressure. The activation enthalpy also increased with increasing pressure. The effect of pressure was interpreted as being the activation volume in the Arrhenius equation. The negative activation volume and relatively large activation energy observed in this study suggests that the hopping of large polarons is the dominant mechanism for the electrical conductivity over the pressure and temperature range investigated [1]. In the case of aragonite, a decrease in the electrical conductivity with increasing pressure was observed. The calculated activation enthalpy increased with increasing pressure. The positive activation volume observed in this study suggests that ionic conduction is the dominant mechanism over the pressure and temperature range investigated [2]. The electrical conductivity of aragonite was higher than that of magnesite. The electrical conductivity of dolomite was similar to the value of magnesite. According to our data, the electrical conductivities of carbonates can be described as a function of pressure, temperature, and chemical composition. Our new data can contribute to interpret the electrical conductivity map of the Earth's interior.

[1] Mibe & Ono (2011) *Physica B*, 406, 2018-2020.

[2] Ono & Mibe (2013) *Eur. J. Mineral.* (in press).

キーワード: 電気伝導度, 炭酸塩鉱物, スラブ, 高圧実験

Keywords: Electrical conductivity, Carbonate, Slab, High pressure experiment

## Viscosity of CO<sub>2</sub>-bearing silicate melts at high pressure Viscosity of CO<sub>2</sub>-bearing silicate melts at high pressure

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Viscosity is an important property of magma (silicate melt), because it controls the transportation of magma in the planetary interior. Traditionally, viscosity at high pressure was measured in quenching experiments. At the beginning a metallic sphere was placed at the top of a sample chamber. The falling velocity was determined from the falling distance during the molten period of sample. The movement of a metallic sphere in a sample chamber was recorded in X-ray radiography image. We have used this technique to determine the pressure, temperature and compositional dependence of the viscosity of silicate melts. The main goal of our study is to determine the effect of dissolving carbon dioxide on the viscosity of silicate melts at high pressure. It has been known that volatiles are dissolved in natural magmas and affects the physical properties. However, very few studies have been performed to investigate the effect of carbon dioxide on the viscosity of silicate melts at mantle pressures. In the present study, the viscosity of carbon-dioxide bearing CaMgSi<sub>2</sub>O<sub>6</sub> and NaAlSi<sub>2</sub>O<sub>6</sub> composition melts have been determined up to 5 GPa.

We installed an X-ray radiography system at the NE7A station at High Energy Accelerator Research Organization (KEK) in Tsukuba, Japan. A charge-coupled device (CCD) camera with a YAG:Ce fluorescence screen was used to obtain the X-ray absorption contrast image. High-pressure was generated using a Kawai type multi-anvil apparatus, which was driven by a DIA type guide block in the MAX-III system. The pressure was determined by using an equation of state for MgO. A pure-Ge solid state detector was used to collect the X-ray diffraction data of the pressure standard by energy-dispersive method. The starting mixture was synthesized from reagents at 1 atm. A powder mixture of oxides and carbonates were fused and quenched to make a glass. Carbonate powder was finally added as a source of carbon dioxide.

Structural study has suggested that the CaMgSi<sub>2</sub>O<sub>6</sub> composition melt is depolymerized. The viscosity of pure CaMgSi<sub>2</sub>O<sub>6</sub> melt increases with increasing pressure. By the addition of 1.0 wt % of carbon dioxide produces about 50% decrease under pressure. NaAlSi<sub>2</sub>O<sub>6</sub> composition melt has polymerized structure. In our previous study, we observed the decrease of viscosity of the pure NaAlSi<sub>2</sub>O<sub>6</sub> melt with elevating pressure. In this study, we measured the viscosity of NaAlSi<sub>2</sub>O<sub>6</sub> + 0.5 wt% CO<sub>2</sub> melt. The viscosity of CO<sub>2</sub>-bearing NaAlSi<sub>2</sub>O<sub>6</sub> melt decreases by about one order of magnitude. Our results suggest that the viscosity of the polymerized silicate and aluminosilicate melts are relatively reduced by the addition of CO<sub>2</sub>, because CO<sub>2</sub> depolymerizes the SiO<sub>4</sub> and AlO<sub>4</sub> networks.

キーワード: マグマ, 粘度, 高圧, CO<sub>2</sub>, 揮発性成分, 放射光

Keywords: magma, viscosity, high pressure, CO<sub>2</sub>, volatile element, synchrotron radiation

## ナノ多結晶ダイヤモンドの合成と応用 Synthesis and applications of nano-polycrystalline diamond

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ダイヤモンドは最も硬い物質として知られているが、高温高圧実験やCVD法により合成することが可能である。高温高圧下での純粋なダイヤモンド多結晶は2003年に最初に報告され、これが特異なナノ組織と高い硬度を持つことが明らかにされた。我々はこのようなナノ多結晶ダイヤモンド(NPD)の大型化を試み、最近1cm程度までのNPD合成に成功している。本公演では、NPD合成の現状と、その高圧実験、工業的製品、また新たな多結晶合成への応用について述べる。

キーワード: ダイヤモンド, 高温高圧合成, 高圧発生, 工業的応用, 多結晶, 鉱物物性

Keywords: diamond, high-pressure high-temperature synthesis, high-pressure generation, industrial application, polycrystal, mineral physics

## Carbon isotope fractionation during carbonated mantle melting: Implications for deep carbon cycle

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Carbon, the fourth most cosmic abundant element in the solar system, has a key role in the melting phase relations and redox conditions of mantle rocks and can move within the mantle as carbonate-rich melts and volatiles (Dasgupta et al., 2013; Stagno et al., 2013). Carbonate carbon and organic carbon, the two solid forms of carbon in the surface of the Earth, is recycled to the mantle by subduction processes. The mass balance between the surface and mantle carbon inventories has been a topic of hot debate (Dasgupta et al., 2013), where the carbon isotopic composition serves as an efficient tool to understand the carbon cycle, both in the shallow and deep Earth environments. Recently, the presence of light carbon isotope-bearing diamonds was considered to provide evidence for deep cycling of surface carbon of the organic matter origin (Walter et al., 2011), however recent experimental results in the Fe-C system suggests an alternate possibility of light carbon can exist in the core (Satish-Kumar et al., 2011). Therefore, it is essential to understand the carbon isotope fractionation processes taking place in the mantle during carbonated mantle melting conditions in order to clearly interpret the movement of carbon in the deep Earth. Here, we present results on experimental determination of partitioning of carbon isotopes at high-pressure and high-temperature conditions, analogous to melting of carbonated mantle in the presence of graphite/diamond, and discuss the carbon mobility in the mantle.

High-pressure experiments were performed in the Mg-Si-C-O system using a Kawai type multi-anvil high-pressure apparatus at the Institute for Study of the Earths Interior, Okayama University, Misasa, Japan. Starting materials comprise of natural enstatite, synthetic magnesite, San Carlos olivine and pure graphite, that were mixed in the molar ratio 3:2:1:3. This mixture is assumed as simplified carbonated harzburgite in a upper mantle, with excess carbon. Experiments were carried out at pressures of 5 and 10 GPa at varying temperature conditions between 1100 C and 1800 C. Retrieved samples from HPHT experimental runs were mounted in epoxy and cut into two halves where one half was used for petrographic observations and the other half for carbon isotope measurements. Run products were mechanically and/or chemically separated and carbon isotope measurements were carried out using a conventional gas source isotope ratio mass spectrometer (IRMS).

Preliminary results indicate that runs at 5 GPa and above 1500 C have melted and the chemical composition of the melt varied widely, such as C-rich melt or Si-rich melt. Carbon isotope results show considerable partitioning between graphite/diamond and carbonate melt at temperatures and pressures corresponding to upper mantle conditions. We discuss the carbon isotope systematics during melting of carbonated mantle and implications for deep carbon cycle based on our experimental results.

References: Dasgupta et al., (2013) *Nature*, doi:10.1038/nature11731; Satish-Kumar et al., (2011) *Earth Planet. Sci. Lett.* 310, 340-348; Stagno et al., (2013) *Nature*, doi:10.1038/nature11679; Walter et al., (2011) *Science*, 334, 54-57

キーワード: Carbon isotope fractionation, Mantle melting, Graphite, Diamond

Keywords: Carbon isotope fractionation, Mantle melting, Graphite, Diamond

## 230 GPa までにおける $\text{Fe}_3\text{C}$ の融解関係および安定性: 地球内核における炭素への応用

### Melting relations and stability of $\text{Fe}_3\text{C}$ up to 230 GPa: Implication for the carbon in the Earth's inner core

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The carbon cycle in the interior of the Earth (Deep Carbon Cycle) is one of the outstanding topics in the Earth science. The Earth's core is considered a carbon reservoir as a part of Deep Carbon Cycle. The Earth's core is regarded as an Fe-Ni alloy but the density of the core is lower than the pure Fe density at pressures and temperatures corresponding to the core conditions. Therefore, the Earth's core is supposed to contain light elements and carbon is one candidate of the light elements to explain the density deficit of the Earth's core. Until present day, many studies on physical and chemical properties of Fe-carbides have been carried out at high pressure. Especially, the recent studies about melting of  $\text{Fe}_3\text{C}$  were reported by Nakajima et al. (2009) and Lord et al. (2009). Nakajima et al. (2009) reported melting temperatures of  $\text{Fe}_3\text{C}$  up to around 30 GPa based on the textual observation, the chemical analysis, and in situ X-ray diffraction experiments using a Kawai-type multi anvil apparatus. Lord et al. (2009) reported melting temperatures of  $\text{Fe}_3\text{C}$  up to 70 GPa was determined by the temperature plateau during heating against increasing laser power using a laser-heated diamond anvil cell. However, there are obvious discrepancies between the melting curves of  $\text{Fe}_3\text{C}$  reported by Nakajima et al. (2009) and Lord et al. (2009). In this study, the melting temperatures of  $\text{Fe}_3\text{C}$  were determined based on in situ X-ray diffraction experiments. This study aims to reveal the uncertainty of the melting temperature of  $\text{Fe}_3\text{C}$  and discuss the behaviours of carbon in the Earth's core.

We have performed experiments using a laser-heated diamond anvil cell combined in situ X-ray diffraction experiment at BL10XU beamline, SPring-8 synchrotron facility. The melting of the sample was determined by a disappearance of the X-ray diffraction peaks as described in previous works. We determined the melting relations of  $\text{Fe}_3\text{C}$  up to 200 GPa by in situ X-ray diffraction experiments. We also confirmed that  $\text{Fe}_3\text{C}$  is stable as a subsolidus phase at least up to 237 GPa and 4100 K. Incongruent melting ( $\text{Fe}_3\text{C} \Rightarrow \text{Fe}_7\text{C}_3 + \text{liquid}$ ) temperatures agree with Nakajima et al. (2009) below 30 GPa and Lord et al. (2009) from 50 to 70 GPa. The solidus temperature extrapolated to the ICB pressure, 330 GPa, is 5500 K. Our results suggest that  $\text{Fe}_3\text{C}$  is a potential candidate of the carbon reservoir in the Earth's inner core. However, if the core has a carbon-rich composition and the inner core crystalized by cooling of the outer core from above 5500 K, the inner core is indicated to be composed of  $\text{Fe}_7\text{C}_3$ .

Keywords: Deep carbon cycle, Earth's inner core, Fe-Carbide, In situ X-ray diffraction experiment, Diamond anvil cell

## 沈み込み帯からのマントル起源炭素と硫黄のフラックス Mantle carbon and sulfur fluxes in subduction zone

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Carbon and sulfur dioxide have been discharging for a long time from the Earth's mantle to the atmosphere through volcanic and hydrothermal activity. In contrast to noble gases, they do not accumulate in the atmosphere but are chemically trapped as compounds in oceanic sediment and terrestrial deposits. Some of them may be recycled again into the mantle. Subduction-zone volcanism is a key area to study these volatile transfers to the mantle and/or the recycling. The mantle C flux at mid-ocean ridge (MOR) was assessed from the spreading rate of oceanic plates and their C content [1] and from the MOR-<sup>3</sup>He flux and CO<sub>2</sub>/<sup>3</sup>He ratio in basalt glasses [2]. On the other hand, the degassing rate at convergent plate margins was estimated by the flux observation in arc volcanoes [3] and the ARC-<sup>3</sup>He flux and CO<sub>2</sub>/<sup>3</sup>He ratio in volcanic gases [4]. Recently MOR-<sup>3</sup>He flux has been revised to 530 mol/y by an ocean general circulation model [5], which is about half of the previous value. Based on the new value and argument of global <sup>3</sup>He flux [6], ARC-<sup>3</sup>He flux could be corrected to 110 mol/y. From the literature, we have selected 26 arc volcanic gas and steam well data whose temperatures are higher than 200°C. Their C is well explained by the mixing of three components, MORB, Sediment and Limestone [7]. Since the average CO<sub>2</sub>/<sup>3</sup>He ratio of these data is 1.9±1.0×10<sup>10</sup>, ARC-C flux would become 2.1±1.1×10<sup>12</sup> mol/y, which is consistent with 1.9×10<sup>12</sup> mol/y by the most recent estimate [8]. The mantle S flux of 0.1~2.6×10<sup>11</sup> mol/y at MOR has been reported by a new experimental crushing and extraction method of MORB [9], which is significantly smaller than the old value of 2.7×10<sup>12</sup> mol/y [10]. On the other hand, the ARC-S flux of 3.15×10<sup>11</sup> mol/y was estimated by the SO<sub>2</sub> flux from volcanoes [8]. We discuss here the ARC-S flux based on the ARC-<sup>3</sup>He flux and SO<sub>2</sub>/<sup>3</sup>He ratio in high temperature volcanic gases.

Reference [1] Javoy et al., 1982. *Nature* **300**, 171-173 [2] Marty and Jambon, 1987. *EPSL* **83**, 16-26 [3] Hilton et al., 2002. *RiMG* **47**, 319-370 [4] Sano and Williams, 1996. *GRL* **23**, 2749-2752 [5] Bianchi et al., 2010. *EPSL* **297**, 379-386 [6] Torgersen, 1989. *Chem Geol* **79**, 1-14 [7] Sano and Marty, 1995. *Chem Geol* **119**, 265-274 [8] Fischer, 2008. *Geochem J* **42**, 21-38 [9] Kagoshima et al., 2012. *Geochem. J.* **46**, e21-e26 [10] Alt et al., 1985. *Init. Rep. DSDP* **83**, 283-287

キーワード: マントル, 揮発性元素, 同位体, 放出量

Keywords: mantle, volatile, isotope, flux

## 継続的噴煙活動による全球火山ガス放出量

## The global volcanic gas flux from subduction zones by continuous degassing

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Global volcanic volatile fluxes from subduction zones by the continuous degassing are estimated based on the compilation of the SO<sub>2</sub> fluxes and the gas compositions. Previously Andres and Kasgnoc (1998) compiled the measured SO<sub>2</sub> fluxes and estimated that the global SO<sub>2</sub> flux by the continuous degassing is 9.7 Mt/a in which 9.2 Mt/a is from subduction zones. As the SO<sub>2</sub> flux by explosive eruptions is about 1 Mt/a, the continuous degassing is the major emission source of volcanic gases to the Earth's surface (Shinohara, 2008). The previous estimate, however, is likely significantly underestimated because the compilation did not include several large flux volcanoes, such as Popocatepetle, Ambrym and volcanoes in Kamchatka. By compiling the recent SO<sub>2</sub> flux datasets, the global SO<sub>2</sub> flux and that from the subduction zones are estimated to be 18 and 15 Mt/y, respectively. Both estimates are about twice of the previously estimated values.

Volcanic volatile fluxes can be estimated by multiplying the SO<sub>2</sub> flux with the concentration ratios of the volcanic gases. Previous studies estimated the concentration ratio of the volcanic volatiles by compiling fumarolic gas composition data, because volcanic gas compositions were available only for the accessible fumaroles. The fumarolic gas degassing is commonly small in flux and often studied during waning stage of the eruptive activity. Recent development of the Multi-GAS techniques enabled to measure volcanic gas composition discharged from the open-vents, that are the major degassing sources of the continuously degassing. The recent compilation indicates that the volcanic gas composition of the open-vent degassing with the large SO<sub>2</sub> flux is different from the high-temperature fumarolic gases. For example, the previous studies estimated the average CO<sub>2</sub>/SO<sub>2</sub> ratio of the Japanese volcanic gases is 2.2 or 6.5, however, the average ratio obtained based on the measured composition of the large flux continuously degassing volcanoes is 0.9. The large ratios estimated by the previous studies are due to the contribution of the fumarolic gases of Usu and Showashinzan volcanoes, which are high in temperature but quite small in fluxes and with the CO<sub>2</sub>/SO<sub>2</sub> ratios larger than 10. The estimated average composition of Japanese volcanic gases are H<sub>2</sub>O/SO<sub>2</sub>= 50, CO<sub>2</sub>/SO<sub>2</sub>=0.9 and Cl/SO<sub>2</sub>=0.2 mol ratios.

The number of the volcanic gas composition measurements of the open-vent degassing is still limited at volcanoes other than in Japan, and the estimated of a precise average composition is difficult. The observed composition ranges from the average composition for the Japanese volcanoes to CO<sub>2</sub>-rich composition, similar to the global estimate by the previous studies. The volcanic gas compositions are different at the different subduction zones; Japan and Kamchatka have relatively small CO<sub>2</sub>/SO<sub>2</sub> ratio around one, whereas Italian volcanoes have large ratio over six. In contrast, the H<sub>2</sub>O/SO<sub>2</sub> ratios and the CO<sub>2</sub>/Cl ratios of the open-vent degassing are around 50 and 5, respectively. Although more detailed data set is necessary to the precise estimate, a middle value of the composition range is considered as the average composition; H<sub>2</sub>O/SO<sub>2</sub>=50, CO<sub>2</sub>/SO<sub>2</sub>=2 and Cl/SO<sub>2</sub>=0.5. Based on this composition and the SO<sub>2</sub> flux, the global volcanic volatile flux by the continuous degassing is estimated as H<sub>2</sub>O=200, CO<sub>2</sub>=21, SO<sub>2</sub>=15 and Cl=4.4 Mt/a. Because of the small H<sub>2</sub>O/SO<sub>2</sub> and CO<sub>2</sub>/SO<sub>2</sub> ratios, the estimate H<sub>2</sub>O and CO<sub>2</sub> fluxes are about four times less than by the previous studies, such as Hilton et al. (2003) and Fischer (2008).

キーワード: 火山ガス, 沈み込み帯, 放出量, 継続的噴煙活動

Keywords: Volcanic gas, Subduction zone, volatile flux, continuous degassing



## 超高压变成作用起源ダイヤモンド中の深部マントル起源希ガスとその意義 Deep-mantle-derived noble gases in metamorphic diamonds: evidence of mantle plume involvement in UHP metamorphism

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Metamorphic diamonds from the Kokchetav massif in northern Kazakhstan are considered to have crystallized from C-O-H fluid during ultra-high-pressure metamorphism of metasedimentary rocks subducted to 190-280 km depth [1]. Noble gas isotopes offer great potential to constrain the origin of diamond-forming media. Previous studies have revealed that secondary processes during the diamond residence in the host rock drastically modified the original noble gas signature of the diamonds [2]. Nanometric solid/fluid inclusions in the microdiamonds, which represent the former diamond-forming fluid [1], are potential candidates to preserve the noble gas trapped during the diamond crystallization. Sumino et al. (2011) [3] analyzed noble gas isotopic compositions of the Kokchetav metamorphic microdiamonds using two gas extraction techniques: in vacuo crushing and stepwise heating. The latter selectively extracts noble gases from inclusions with less noble gas extraction from the diamond lattice.

Most <sup>3</sup>He was extracted by diamond crushing what indicates that <sup>3</sup>He occurs within inclusions trapped during diamond formation. The estimate of the inclusion-hosted <sup>3</sup>He/<sup>4</sup>He of  $(3.3-6.5) \times 10^{-5}$  is significantly higher than that of the MORB-source mantle ( $1.1 \times 10^{-5}$ ), but close to the highest value observed in OIBs (ca.  $7 \times 10^{-5}$  [4]) containing primordial noble gases derived from deep mantle. Neon isotope ratios obtained using stepwise heating also support the presence of a plume-like component [3].

Results show the involvement of plume-like, primordial-enriched noble gases in the Kokchetav microdiamond formation, implying metasomatism of the continental lithosphere by a plume prior to its subduction [5], or interaction of the continental slab and a fragment of the very deep mantle, in the latter of which the fragment might have been delivered to the mantle wedge of the subduction channel by large-scale mantle convection originating from a deeper lower mantle source. If the former is the case, the plume-derived noble gases could be ubiquitous in continent-continent convergent margins where continental crust was subducted such as in Hindu Kush and Burma [5]. Further noble gas investigation of diamonds from other ultrahigh-pressure metamorphic terranes is required in order to confirm which one of the two possibilities is correct, namely the metasomatism of subducting continental lithosphere by a plume or the large-scale mantle convection in a subduction channel.

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キーワード: 希ガス, ダイヤモンド, マントルブルーム, 超高压变成作用, コクチェタフ超高压变成帯

Keywords: noble gas, diamond, mantle plume, ultrahigh-pressure metamorphism, Kokchetav ultrahigh-pressure massif

## Diamond in Almahata Sitta Ureilite Diamond in Almahata Sitta Ureilite

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Almahata Sitta, originating from asteroid 2008 TC<sub>3</sub>, is the first meteorite that was observed and its trajectory was determined before the fall [1]. Almahata Sitta 2008 TC<sub>3</sub> is a polymict asteroid, consists mainly of coarse-grained and fine-grained ureilite with less abundant chondritic fragments [2-3]. The ureilitic fragments contain carbonaceous materials such as graphite and diamond. There are three major models as a diamond formation mechanism in ureilite; i.e., 1) formation from a fluid or melt in the deep interior of an ureilite parent-body [e.g., 4], 2) formation through chemical vapor deposition (CVD)[e.g., 5] and 3) shock-induced transformation of graphite at the moment of planetesimal collision [e.g., 6]. We found a huge single diamond crystal from one of Almahata Sitta coarse-grained ureilite samples. Here, we report the occurrence and nature of the unique diamond in the Almahata Sitta coarse-grained ureilite, and discuss its possible formation mechanism.

The coarse-grained ureilite, Almahata Sitta MS-170 consists mainly of olivine (Fa<sub>18-21</sub>) and low-Ca pyroxene, with less abundant troilite, kamacite, magnetite, schreibersite (Fe<sub>3</sub>P) and diamond-graphite assemblages. Most diamond-graphite assemblages exist between the olivine grains. The olivine grain adjacent to the diamond-graphite assemblages usually shows a reduction texture; i.e., olivine dissociates into enstatite and kamacite. Because of its hardness, diamond appears above the polished surface, easily seen under an optical microscope and SEM. The main diamond Raman band stays within narrow range (1333.5 cm<sup>-1</sup>, sigma = 1.7, n = 53), implying that the diamond is well-crystallized. High-magnification BSE images show that many diamonds have hexahedron- or octahedron-like habits, which corresponds to idiomorphic {001} or {111} diamond, respectively, although not always idiomorphic. TEM images and EBSD analysis show that most diamonds are single crystals because several diamond fragments have similar crystallographic orientations. One of the biggest single crystal diamond we found is ~100 micro m or more in a dimension. We could not find a specific crystallographic orientation between graphite and diamond. The isotope distribution images obtained with a NanoSIMS show heterogeneous nitrogen abundance and delta<sup>13</sup>C among individual diamond grains and even within the grains. Almahata Sitta is a less shocked ureilite (S0). The idiomorphic huge single diamond was not formed from graphite through martensitic phase transformation mechanism under high-pressure and -temperature condition induced by a dynamic event. Nitrogen sector zoning texture implies that the diamond grew very slowly. It is likely that the diamond was formed by chemical vapor deposition (CVD) process or formed from a C-H-O fluid at the deep interior of an ureilite parent-body. Nonetheless, some deformation textures were observed by TEM in the diamonds, which is due to a later dynamic event after primary diamond formation.

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