SCG09-01   :101A   :5   20   14:15-14:45

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

Mysen Bjorn[1][*],   [2],   [2],   [2]
Bjorn Mysen[1][*], tokio tomita[2], Eiji Ohtani[2], Akio Suzuki[2]

[1]Geophysical Laboratory, Carnegie Instn. Washington, USA., [2]Dept. Earth Planet. Mater. Sci., Graduate School of Science, Tohoku University, JAPAN
[1]Geophysical Laboratory, Carnegie Instn. Washington, USA., [2]Dept. Earth Planet. Mater. Sci., Graduate School of Science, Tohoku University, JAPAN

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_2O 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, $H_2O+O=2OH$, 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_2 solubility in melts, where it exists as molecular CO_2 and CO_3 groups, is in the 1-4wt% range between ~1 and 3 GPa and upper mantle temperatures. Its solution mechanism is $CO_2+Q^n=CO_3+Q^{n+1}$. 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_3. Silicate is not detectable in CO_2 fluid. Methane, CH_4, is the dominant C-species in melts at $f_{H2} \geq MW$ (magnetite-wustite), whereas in fluids, more reducing conditions [iron-wustite (IW) buffer] are necessary to form detectable CH_4. Methane solubility in melts is 10-30% of that of CO_2. At f_{H2}(IW) the dominant fluid species are $CH_4+H_2+H_2O$. In coexisting melt, CH_3 groups linked to the silicate melt structure via $Si-CH_3$ bonding coexist with molecular CH_4 with a solution mechanism, $CH_4+Q^1=CH_3+Q^0$. 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_{H2}(MH)] nitrogen exists principally as N_2. Under reducing conditions, f_{H2}(MW), the nitrogen oxidation state is lowered with NH_2^+ groups dominating in fluid and melt. At the more reducing f_{H2}(IW) condition, $NH_3+NH_2^+$ fluid coexisting with $NH_3+NH_2^-+H_2+H_2O$ species in melt with the ammine groups bonded directly to Si^{4+} ($Si-NH_2$) and solution mechanism, $NH_3+Q^1=NH_2+Q^0$. 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_{H2}-dependent speciation C-O-H-N volatile components result in f_{H2}-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 $\geq 20\%$ compared with pure H_2O at 1 GPa.

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

SCG09-02   :101A   :5   20   14:45-15:00

Electrical conductivities of carbonates in the subducted slab

[1]*,   [2]
Shigeaki Ono[1]*, Kenji Mibe[2]

[1]   ,[2]
[1]JAMSTEC, [2]ERI, Univ. of Tokyo

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, MgCO3, is a naturally occurring carbonate mineral and is stable over a wide range of pressure and temperature. In contrast, calcium carbonate (CaCO3) 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 (MgCaC2O6) 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).

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

SCG09-03   :101A   :5   20   15:00-15:15

Viscosity of CO2-bearing silicate melts at high pressure
Viscosity of CO2-bearing silicate melts at high pressure

1*

Akio Suzuki[1*]

1

[1]Tohoku University

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 places 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 $CaMgSi_2O_6$ and $NaAlSi_2O_6$ 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 sate 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 $CaMgSi_2O_6$ composition melt is depolymerized. The viscosity of pure $CaMgSi_2O_6$ melt increases with increasing pressure. By the addition of 1.0 wt % of carbon dioxide produces about 50% decrease under pressure. $NaAlSi_2O_6$ composition melt has polymerized structure. In our previous study, we observed the decrease of viscosity of the pure $NaAlSi_2O_6$ melt with elevating pressure. In this study, we measured the viscosity of $NaAlSi_2O_6$ + 0.5 wt% CO_2 melt. The viscosity of CO2-bearing $NaAlSi_2O_6$ 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_2, because CO_2 depolymerizes the SiO_4 and AlO_4 networks.

                :   ,   ,   , CO2,   ,
Keywords: magma, viscosity, high pressure, CO2, volatile element, synchrotron radiation

SCG09-04   :101A   :5   20   15:15-15:30

Synthesis and applications of nano-polycrystalline diamond

Tetsuo Irifune[1*], Toru Shinmei[1], Hiroaki Ohfuji[1], Yoshinori Tange[1], Futoshi Isobe[1], Takeshi Arimoto[1], Norimasa Nishiyama[2], Takehiro Kunimoto[3]

[1]Geodynamics Reserach Center, Ehime University, [2]Deutsches Elektronen Synchroton, [3]JASRI, SPring-8

CVD
2003
NPD   1cm   NPD
NPD

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

SCG09-05　　　　　　　　:101A　　　　　　　　　:5　　20　　15:30-15:45

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

Shogo Mizutani[1], Satish-Kumar Madhusoodhan[2*], Takashi Yoshino[3]
Shogo Mizutani[1], Satish-Kumar Madhusoodhan[2*], Takashi Yoshino[3]

[1]Department of Geosciences, Shizuoka University, Japan, [2]Department of Geology, Niigata University, Japan, [3]ISEI, Okayama University, Misasa, Japan
[1]Department of Geosciences, Shizuoka University, Japan, [2]Department of Geology, Niigata University, Japan, [3]ISEI, Okayama University, Misasa, Japan

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

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

SCG09-06   :101A   :5   20   15:45-16:00

230 GPa Fe_3C :

Melting relations and stability of Fe_3C up to 230 GPa: Implication for the carbon in the Earth's inner core

[1*], [1], [2], [1], [1], [1], [3], [3]
Suguru Takahashi[1*], Eiji Ohtani[1], Takeshi Sakai[2], Masaaki Miyahara[1], Seiji Kamada[1], Izumi Mashino[1], Naohisa Hirao[3], Yasuo Ohishi[3]

[1], [2], [3]
[1]Tohoku University, [2]GRC, Ehime University, [3]JASRI, SPring-8

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 Fe_3C were reported by Nakajima et al. (2009) and Lord et al. (2009). Nakajima et al. (2009) reported melting temperatures of Fe_3C 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 Fe_3C 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 Fe_3C reported by Nakajima et al. (2009) and Lord et al. (2009). In this study, the melting temperatures of Fe_3C were determined based on in situ X-ray diffraction experiments. This study aims to reveal the uncertainty of the melting temperature of Fe_3C 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 Fe_3C up to 200 GPa by in situ X-ray diffraction experiments. We also confirmed that Fe_3C is stable as a subsolidus phase at least up to 237 GPa and 4100 K. Incongruent melting ($Fe_3C => Fe_7C_3$ + 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 Fe_3C 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 Fe_7C_3.

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

SCG09-07 :101A :5 20 16:15-16:30

Mantle carbon and sulfur fluxes in subduction zone

Yuji Sano[1*], Takanori Kagoshima[1], Naoto Takahata[1], Teruyuki Maruoka[2], Tobias Fischer[3], Bernard Marty[4]

[1]University of Tokyo, [2]University of Tsukuba, [3]University of New Mexico, [4]Centre national de la recherche scientifique

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-^{3}He flux and $CO_2/^3$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-^{3}He flux and $CO_2/^3$He ratio in volcanic gases [4]. Recently MOR-^{3}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 ^{3}He flux [6], ARC-^{3}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^oC. Their C is well explained by the mixing of three components, MORB, Sediment and Limestone [7]. Since the average $CO_2/^3$He ratio of these data is $1.9+/-1.0 \times 10^{10}$, ARC-C flux would become $2.1+/-1.1 \times 10^{12}$ mol/y, which is consistent with 1.9×10^{12} mol/y by the most recent estimate [8]. The mantle S flux of $0.1\sim2.6 \times 10^{11}$ 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^{12} mol/y [10]. On the other hand, the ARC-S flux of 3.15×10^{11} mol/y was estimated by the SO_2 flux from volcanoes [8]. We discuss here the ARC-S flux based on the ARC-^{3}He flux and $SO_2/^3$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

Keywords: mantle, volatile, isotope, flux

SCG09-08 　　　　　　:101A　　　　　　　　　　:5　20　16:30-16:45

The global volcanic gas flux from subduction zones by continuous degassing

[1*]

Hiroshi Shinohara[1*]

[1]

[1]Geological Survey of Japan, AIST

Global volcanic volatile fluxes from subduction zones by the continuous degassing are estimated based on the compilation of the SO_2 fluxes and the gas compositions. Previously Andres and Kasgnoc (1998) compiled the measured SO_2 fluxes and estimated that the global SO_2 flux by the continuous degassing is 9.7 Mt/a in which 9.2 Mt/a is from subduction zones. As the SO_2 flux by explosive eruptions is about 1 Mt/a, the continuous degassing is the major emission source of volcanic gases to the Erath'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_2 flux datasets, the global SO_2 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_2 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_2 flux is different from the high-temperature fumarolic gases. For example, the previous studies estimated the average CO_2/SO_2 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_2/SO_2 ratios larger than 10. The estimated average composition of Japanese volcanic gases are H_2O/SO_2= 50, CO_2/SO_2=0.9 and Cl/SO_2=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_2-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_2/SO_2 ratio around one, whereas Italian volcanoes have large ratio over six. In contrast, the H_2O/SO_2 ratios and the CO_2/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_2O/SO_2=50, CO_2/SO_2=2 and Cl/SO_2=0.5. Based on this composition and the SO_2 flux, the global volcanic volatile flux by the continuous degassing is estimated as H_2O= 200, CO_2=21, SO_2=15 and Cl=4.4 Mt/a. Because of the small H_2O/SO_2 and CO_2/SO_2 ratios, the estimate H_2O and CO_2 fluxes are about four times less than by the previous studies, such as Hilton et al. (2003) and Fischer (2008).

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

SCG09-09   :101A   :5   20   16:45-17:00

Deep-mantle-derived noble gases in metamorphic diamonds: evidence of mantle plume involvement in UHP metamorphism

[1*], Larissa F. Dobrzhinetskaya[2],   [1], Ray Burgess[3]
Hirochika Sumino[1*], Larissa F. Dobrzhinetskaya[2], Hiroyuki Kagi[1], Ray Burgess[3]

[1]   ,[2]   ,[3]
[1]GCRC, Grad. Sch. Sci., Univ. Tokyo, [2]Department of Earth Sciences, UC Riverside, [3]SEAES, Univ. Manchester

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 ^{3}He was extracted by diamond crushing what indicates that ^{3}He occurs within inclusions trapped during diamond formation. The estimate of the inclusion-hosted ^{3}He/^{4}He of (3.3-6.5) x 10^{-5} is significantly higher than that of the MORB-source mantle (1.1 x 10^{-5}), but close to the highest value observed in OIBs (ca. 7 x 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.

[1] Dobrzhinetskaya et al. (2006) EPSL 243, 85-93. [2] Verchovsky et al. (1993) EPSL 120, 87-102. [3] Sumino et al. (2011) EPSL 307, 439-449. [4] Stuart et al. (2003) Nature 424, 57-59. [5] Seno and Rehman (2011) Gondowana Res. 19, 327-333.

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

SCG09-10   :101A   :5   20   17:00-17:15

Diamond in Almahata Sitta Ureilite
Diamond in Almahata Sitta Ureilite

[1]*,   [1], El Goresy Ahmed[2], Yang-Ting Lin[3], Lu Feng[3], Jian-Chao Zhang[3], Philippe Gillet[4],   [5],
[1],   [6]

Masaaki Miyahara[1]*, Eiji Ohtani[1], Ahmed El Goresy[2], Yang-Ting Lin[3], Lu Feng[3], Jian-Chao Zhang[3], Philippe Gillet[4], Toshiro Nagase[5], Jun Muto[1], Masahiko Nishijima[6]

[1]Department of Earth Sciences, Tohoku University, [2]Bayerisches Geoinstitut, Universitat Bayreuth, [3]Chinese Academy of Sciences, [4]Ecole Polytechnique Federale de Lausanne, [5]Center for Academic Resources and Archives, Tohoku University, [6]Institute for Materials Research, Tohoku University
[1]Department of Earth Sciences, Tohoku University, [2]Bayerisches Geoinstitut, Universitat Bayreuth, [3]Chinese Academy of Sciences, [4]Ecole Polytechnique Federale de Lausanne, [5]Center for Academic Resources and Archives, Tohoku University, [6]Institute for Materials Research, Tohoku University

Almahata Sitta, originating from asteroid 2008 TC_3, is the first meteorite that was observed and its trajectory was determined before the fall [1]. Almahata Sitta 2008 TC_3 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_{18-21}) and low-Ca pyroxene, with less abundant troilite, kamacite, magnetite, schreibersite (Fe_3P) 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^{-1}, 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^{13}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 dy-namic 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.

References:
[1] Jenniskens P. et al., 2009, Nature 458:485-488. [2] Bischoff A. et al., 2010, Meteorit.Planet.Sci. 45:1638-1656. [3] Zolensky M. et al., 2010, Meteorit. Planet. Sci. 45:1618?1637. [4] Urey H.C., 1956, Astrophys. J. 124:623-637. [5] Fukunaga K. et al., 1987, Nature 328:141-143. [6] Nakamuta Y. & Aoki Y., 2000, Meteorit. Planet. Sci. 35:487-493.

SCG09-P01   :   :5   20   18:15-19:30

6GPa   900-1400C   2
Phase diagrams of binary carbonate systems at 6 GPa and 900-1400C

, [1],   [2*],   ,   [1],   ,   M[1],   ,   D[1],
,   N[1]

SHATSKIY, Anton[1], Eiji Ohtani[2*], SHARYGIN, Igor[1], BORZDOV, Yuri M[1], LITASOV, Konstantin D[1], PALYANOV, Yuri N[1]

[1]   , [2]
[1]V.S. Sobolev Institute of Geology and Mineralogy SB RAS, [2]Graduate School of Science

In this study we conducted HP-HT experiments at 6 GPa and 900-1400oC in binary carbonate systems K2CO3-MgCO3, K2CO3-CaCO3, Na2CO3-MgCO3, Na2CO3-CaCO3 using multianvil apparatuses at Tohoku University (Sendai, Japan) and IGM SB RAS (Novosibirsk, Russia). Based on obtained results we plotted phase diagrams for studied systems which shown in Fig. 1.

:   ,   , 2   ,
Keywords: Phase diagram, Carbonate, Binary system, High pressure and temperature

SCG09-P02   :   :5   20   18:15-19:30
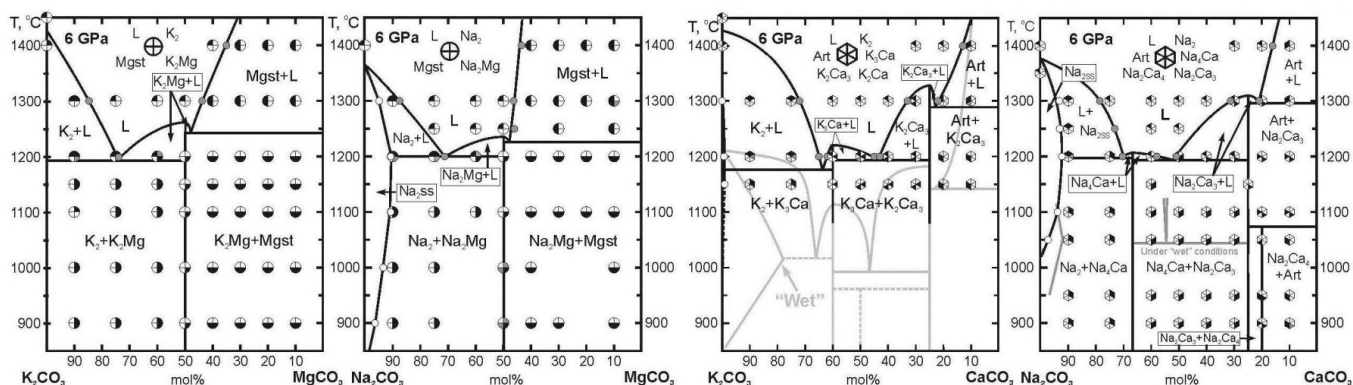
Solubility of Carbon in metallic liquid under high pressure in the natural carbonaceous chondrite system

[1]*,   [1],   [1]

Yuki Asahara[1]*, Eiji Ohtani[1], Akio Suzuki[1]

[1]

[1]Tohoku university

In order to explain of the density deficit of the core of the earth, the core is considered to contain some amounts of light elements. Oxygen, sulfur, silicon, carbon, and hydrogen are the possible candidates. It has been considered that the core composition was established by chemical differentiation processes in the magma ocean on the early stage of the earth. To clarify the core composition, the partitioning behavior between silicate- and metallic-liquids of the candidate elements; oxygen, sulfur, and silicon, has been investigated by many workers. However, there are not so many studies on carbon and hydrogen because of the difficulty of chemical analyses. The volatile depleted primitive materials similar to carbonaceous chondritie group have been considered as the building blocks of the earth. We choose Allende meteorite (CV3) as a model composition of primitive earth and investigated partitioning behavior of carbon together with sulfur and oxygen between silicate- and metallic-liquids.

We used natural Allende meteorite as the starting material. The sample was crushed and grounded to fine powder for high pressure experiments. High pressure experiments were performed using 3000 ton Kawai-type multianvil apparatus installed at Tohoku University. WC-anvils with truncation edge length of 12 mm were used. Semi-sintered zirconia was used as the pressure medium, and graphite was used for a sample container and a cylindrical heater. In each experiment, the sample was first compressed to the desired pressure, then, the temperature was raised to the target temperature at a rate of 85 K/min. Recovered sample was cut with a diamond blade and polished for electron microprobe analyses. Microfocused X-ray diffractometry and electron microprobe analysis were used for phase identification and compositional analysis of run products.

The experiments were performed at the conditions of 5 GPa and 2073 K. We will present experimental results and discuss about core-mantle chemical differentiation processes on early planets.

Keywords: Carbon, carbonaceous chondrite, high pressure, solubility, high temperature

Fe-Ni-C
Sound velocity of liquid Fe-Ni-C alloy at high pressure and temperature

[1]*, [2], [1], [3], [3], [2], [2], [1]

Souma Kuwabara[1]*, Keisuke Nishida[2], Hidenori Terasaki[1], Ken-ichi Funakoshi[3], Yuji Higo[3], Masashi Ushioda[2], Moe Sakurai[2], Tadashi Kondo[1]

[1] , [2] , [3]

[1]Graduate School of Science, Osaka University, [2]Graduate School of Science and Engineering, Tokyo Institute of Technology, [3]Japan Atomic Energy Agency

Sound velocity is important to understand the composition of the Earth's and lunar core because it can be directly compared with seismological data.

Carbon is a plausible candidate as a light element in the core due to its high cosmic abundance and high affinity to liquid Fe [e.g., Wood, 1993]. However, the effect of carbon on the sound velocity (V_P) of liquid Fe-Ni alloy has not been investigated. In this study, we have measured the V_P of liquid (Fe-10wt.%Ni)-4wt.%C alloy at around 4.7 GPa and 1563-1788 K.

High-pressure experiment was performed using a 1500-ton multi-anvil apparatus (SPEED-1500) installed at BL04B1 of the SPring-8 synchrotron radiation facility. Experimental pressure was determined from the lattice constants of MgO and hBN. We have used a cylindrical graphite heater and temperature was monitored using a W5%Re-W26%Re thermocouple. V_P measurements were carried out by the pulse-echo-overlap method using a $LiNbO_3$ transducer for generating and receiving P-wave signals. Used frequencies of the wave signal were 37 and 21 MHz. The sample length was measured from an X-ray radiography image of the sample.

The observed V_P of liquid Fe-Ni-C decreases with increasing temperature. Comparing the V_P of Fe-C calculated from the previously reported densities and bulk moduli of liquid Fe and Fe-C [Anderson & Ahrens, 1994; Shimoyama et al., 2013; Terasaki et al., 2010], V_P of liquid Fe-C or Fe-Ni-C decrease with increasing carbon content.

: , ,
Keywords: Carbon, Eatth's outer core, Light element

SCG09-P04 : :5 20 18:15-19:30

N-O-H-D
In-situ determination of NOHD species in coexisting silicate melt and fluid

[1]*, Mysen Bjorn[2], [1], [1]
Tokio Tomita[1]*, Bjorn Mysen[2], Eiji Ohtani[1], Akio Suzuki[1]

[1] , , ,[2] , ,
[1]Dept. Earth Planet. Mater. Sci., Faculty of Science, Tohoku University, JAPAN., [2]Geophysical Laboratory, Carnegie Instn. Washington, USA

In-situ measurements of solubility and speciation of N-O-H-D volatiles in coexisting fluid and melt were made at high pressure and temperature to estimate the effect of N-O-H-D volatiles on physical properties of magma. The experiment was performed using a Bassett-type hydrothermal diamond anvil cell with Raman spectroscopy as a structural probe. Silicate composition was $(Na_2O-4SiO_2)90(Na_2O-4NaAlO_2)10$. Water is a liquid mixture of H_2O and D_2O ($H_2O:D_2O=50:50$ in volume ratio). Nitrogen was supplied from $Ag(14/15=0.7/0.3)N_3$. Pressure was measured with one-phonon Raman shift of carbon-13 diamond [1]. The in-situ measurements were conducted in the pressure and temperature range of 425-800 ?C and 100-1300 MPa, respectively. Temperature was initially raised up to 800 ?C and then decreased to the desired values. Experiments were conducted in two different redox conditions. Oxidizing conditions were obtained by using no buffer and reducing condition controlled with the Mo-MoO2 buffer based on the reaction $Mo+2H_2O=MoO_2+2H_2$. In the reducing condition, fO_2 was near that of the iron-wustite buffer. In the experiments under oxidizing conditions, only molecular N_2 was observed in coexisting silicate melt and NOH fluid. The $14N_2$ and $15N_2$ can be clearly distinguished. However, the isotope partitioning between fluid and melt is uncertain because of the low nitrogen solubility in the melt. For experiments under reducing conditions, nitrogen in the fluid was reduced to NH_3 coexisting with $H_2O+H_2(+D_2O+D_2)$. In coexisting melt, both molecular NH_3 and NH_2 groups were observed in the pressure and temperature range investigated. The ammine groups bonded directly to Si^{4+} to $Si-NH_2$ bonding. In the spectra of fluid, there is evidence for both NH_3 and probably ND_3 in addition to H_2O, D_2O, H_2, and D_2. Partitioning of D and H between the coexisting phases was determined spectroscopically. $SiNH_2$ groups were also detected in melt and probably generated by the reaction, $Si-O-Si+NH_3=Si-NH_2+H-O-Si$. This reaction depolymerizes the network of SiO_4 tetrahedra and will affect, therefore melt properties that depend on silicate polymerization (melt viscosity, diffusion, mineral/melt partitioning).

From these data, it is clear that nitrogen in the Earth's interior cannot be modeled simply as a N_2 molecule, whether in melt or fluid. The reduced nitrogen species have a different solubility, different solution mechanisms and probably different nitrogen and hydrogen isotopic behaviors. These results do, therefore affect modeling of earth degassing based on assumed behavior of nitrogen.

[1] Mysen, B. O., Yamashita, S., (2010). Geochimica et Cosmochimica Acta 74, 4577-4588

Keywords: fluid, speciation, distribution, silicate melt, diamond anvil cell, in-situ