

Kinetics of carbide rim growth and the diffusion of carbon in the Earth's upper mantle

STAGNO, Vincenzo^{1*}

¹Geodynamics Research Center, Ehime University (Japan), ²Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo 152-8550, Japan

The speciation of carbon in the interior of the Earth is mainly controlled by temperature, pressure and the oxygen fugacity (f_{O_2}) buffered by the surrounding abundant Fe-bearing silicates. Within a peridotitic mineral assemblages the f_{O_2} is thermodynamically predicted to decrease with the depth until the precipitation of Fe-Ni metal alloy occurs at about 250-300 km down in the mantle. In addition, the application of a recently calibrated oxybarometer for eclogites suggests that subducted carbonates will be reduced to diamonds at about 200-250 km depth. Therefore, at such conditions the speciation of subducted carbon will be mainly affected by the local Fe(Ni)/C ratio, with diamond, Fe₃C and C-bearing Fe-Ni alloys being the most likely stable phases. To date, however, no experiments are available 1) to constrain the transport of carbon by diffusion in iron metal at pressures and temperatures of the Earth's upper mantle and 2) to test the formation of carbide phases at the interface between diamonds/graphite and Fe metal.

We performed multi-anvil experiments between 3 and 10 GPa and temperatures of 700-1200 °C with the aim of measuring C diffusion in γ -Fe. Glassy carbon, graphite rods and synthetic diamonds were used as diffusants, placed directly in contact with pure iron rod with a thickness of 800-1400 μ m. FE-SEM was used for accurate analyses of the Fe-C interface and concentration profiles of carbon in iron were measured by electron microprobe.

Results show that the diffusion coefficient for carbon in iron metal ($\sim 3 \times 10^{-11}$ m²s⁻¹) and the activation energy (~ 62 kJ/mol) are similar to previous data from much lower pressures. The activation volume ($\sim 1.5 \times 10^{-6}$ m³/mol) obtained from isothermal runs is in agreement with that determined for other elements for which the interstitial diffusion mechanism in iron has been established. In addition, experiments revealed the formation of carbide as reaction rim between the diffusant and Fe metal. Time series experiments were, therefore, performed to investigate the growth kinetics of iron carbide (Fe₃C) rim. Results allow to improve our understanding of the C storage in the Earth's interior. In addition, our data provide an experimental constraint on the formation of carbide phases during subduction, with implications for the deep carbon cycle and the C isotopic signature of eclogitic diamonds.

Keywords: carbide, diffusion, diamonds, eclogites, oxygen fugacity, high pressure

Ferromagnesite as a Potential Deep-Mantle Carbon Carrier

LIN, Jung-fu^{1*}

¹Department of Geological Sciences, The University of Texas at Austin

Physical and chemical properties of the potential deep-carbon carriers such as carbonates can play a significant role in our understanding of the deep-carbon storage as well as the global carbon cycle of the planet. Iron-bearing magnesite, ferromagnesite [(Mg,Fe)CO₃], has been commonly proposed to be a major carbon carrier in the Earth's mantle. Studying its elasticity and phase diagram under relevant P-T conditions of the deep mantle is thus important for our understanding of the deep-carbon storage in the Earth's interior. Here I will discuss our recent research results on single-crystal elasticity, the spin transition, and the high-pressure structural transition in the (Mg,Fe)CO₃ carbonate system in the deep mantle [1-4]. Based on Brillouin experimental results and thermal elastic modelling, magnesite exhibits extremely high compressional wave (V_p) anisotropy of approximately approximately 48 percent and shear wave (V_s) splitting of approximately 40 percent along an expected geotherm of the cold subducting slab. These anisotropies are much larger than those of major constituent minerals in the Earth's upper mantle including olivine, pyroxene, and garnet. The modeled aggregate V_p and V_s velocities in moderately carbonated peridotite and eclogite containing approximately 10 wt. percent magnesite (approximately 5 wt. percent CO₂) show minimal effects of magnesite on the seismic profiles of these rock assemblages at upper mantle conditions, suggesting that the presence of magnesite is likely difficult to be detected seismically in the mantle. However, due to its unusually high V_p and V_s anisotropies, magnesite-rich rocks with strong preferred orientations may exhibit sufficient V_p and V_s anisotropies that can have significant influences on seismic anisotropies of the regionally carbonated upper mantle [2]. Using synchrotron X-ray diffraction and Raman spectroscopy coupled with a diamond anvil cell, we have also studied the phase stability and compressional behavior of ferromagnesite at lower-mantle P-T conditions. An electronic spin transition of iron in the (Mg,Fe)CO₃ system occurs at approximately 40 GPa and can significantly affect its elasticity, phase stability, and chemistry at high P-T [3-4]. Our high-pressure results further show that rhombohedral ferromagnesite transforms into an orthorhombic high-pressure phase following the spin transition of iron at mid-lower mantle P-T conditions [1]. The high-pressure orthorhombic phase is found to be in the low-spin state that can become a stable deep-carbon carrier at deeper parts of the lower mantle below 2000 km in depth. These findings suggest that deep-mantle carbonates can exhibit unique physical and chemical properties than that at shallower mantle conditions, affecting our understanding of the deep carbon cycle at extreme environments.

References:

1. J. Liu, J. F. Lin, and V. B. Prakapenka, High-pressure orthorhombic ferromagnesite as a potential deep-mantle carbon carrier, *Scientific Reports*, 5, 7640.
2. J. Yang, Z. Mao, J. F. Lin, and V. B. Prakapenka, Single-crystal elasticity of the deep-mantle magnesite at high pressure and temperature, *Earth Planet. Sci. Lett.*, 392, 292-299, 2014.
3. J. Liu, J. F. Lin, Z. Mao, and V. B. Prakapenka, Thermal equation of state and spin transition of magnesiosiderite at high pressure and temperature, *Am. Miner.*, 99, 84-93, 2014.
4. J. F. Lin, J. Liu, C. Jacobs, and V. B. Prakapenka, Vibrational and elastic properties of ferromagnesite across the electronic spin-pairing transition of iron, *Am. Miner.*, 97, 583-591, 2012.

Keywords: Ferromagnesite, Carbonate, Mineral Physics, High Pressure, Deep Carbon Cycle, Lower Mantle

Equation of state of Fe_3C under high pressure and temperature with implications for carbon in the Earth's core.

TAKAHASHI, Suguru¹ ; OHTANI, Eiji^{1*} ; HIRAO, Naohisa² ; OHISHI, Yasuo²

¹Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku University, ²Japan Synchrotron Radiation Research Institute, SPring-8

The densities and sound velocities of the Earth's interior have been known based on the seismological observations, as well-known as Preliminary Reference Earth Model (PREM). Although the Earth's core is regarded as an Fe(-Ni) alloy, its density is lower than that of Fe, and sound velocities of the core could not be explained by those of pure Fe at the core conditions. Therefore, the Earth's core is supposed to contain light elements to explain the density deficit and differences of sound velocities between Fe and the Earth's core. Carbon is one of the most important candidates for light elements in the Earth's core. In this study, we focused on the compression behavior of Fe_3C , which is one of the Fe-carbide. We aimed to discuss the possibility of Fe_3C as the constituent of the Earth's inner core.

We performed in-situ X-ray diffraction experiments using the diamond anvil cell at BL10XU beamline of SPring-8 facility to obtain pressure and volume relations of Fe_3C . We obtained P - V profiles of Fe_3C at 70~180 GPa, and ~2300 K. The equation of state (EOS) of Fe_3C at high temperature conditions was determined using P - V - T relationships. Compressional data were fitted by the 3rd-order Birch-Murnaghan EOS at 300 K and the Mie-Grüneisen-Debye EOS at high temperature conditions. The parameters of $V_0 = 152.13(8)$, $K_0 = 265.1(6)$, $K'_0 = 3.66(1)$, $\theta_0 = 246(84)$, $\gamma_0 = 1.06(7)$ and $q = 1.5(2)$ were obtained. The density of Fe_3C at inner core condition (assuming 329 GPa and 5000 K) calculated from the EOS was compatible with PREM profiles. Our results indicate that Fe_3C could be dominant in the Earth's inner core.

Keywords: Earth's core, Fe_3C , Equation of state, PREM, Density

Carbon isotope compositions in sublithospheric diamonds

HARTE, Ben^{1*}

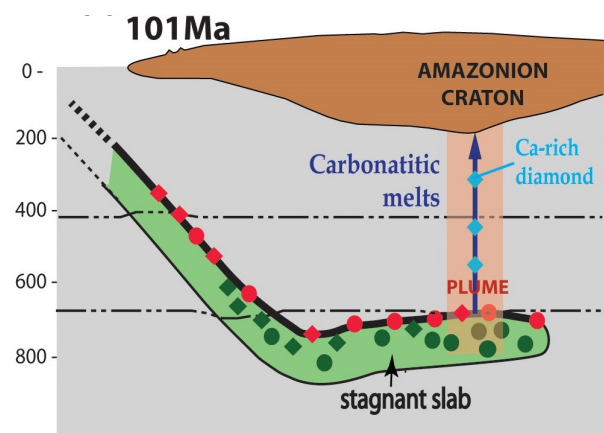
¹CSEC, Earth Sciences, School of Geosciences, University of Edinburgh, Scotland, UK.

Studies of silicate and oxide mineral inclusions in diamonds have provided evidence of a small number of diamonds formed at depths of approximately 250 to 800 kms in the Earth's mantle. The major source of these diamonds is kimberlites of Cretaceous age from Juina province, Brazil; but small numbers of similar diamonds have been found on most of the world's continents. On the basis of their inclusions, the diamonds have been divided into three major groups (ref 1) as follows: (a) *majoritic garnet suite* (basic bulk compositions and relatively Ca-poor); (b) *perovskite and periclase suite* (dominantly ultrabasic Mg-rich bulk compositions); (c) *Ca-rich suite* (with Ca-Si-Ti minerals, carbonates and some aluminous silicates). The estimated principal depths of formation these groups are respectively in the ranges of: (a) 250-500 km; (b) 650- 750km; (c) 300-550 km.

The Carbon isotope compositions of the diamonds hosting the above suites of inclusions show some marked differences. Majoritic suite inclusions of group (a) have $\delta^{13}\text{C}$ in the range of -5 to -24 ‰. The ultrabasic inclusions of group (b) have $\delta^{13}\text{C}$ compositions in the range -3 to -7 ‰. However, some rare inclusions of basic composition from the same depth range as the ultrabasic inclusions have $\delta^{13}\text{C}$ extending to -24 ‰ (ref 2), as with the majoritic suite. In group (c) the diamonds largely range in $\delta^{13}\text{C}$ from -3 to -25 ‰. The highly negative $\delta^{13}\text{C}$ values have been considered to indicate carbon of organic origin and therefore suggest derivation from subducted ocean floor protoliths (refs 3, 4, 5, 6). Other evidence of initial ocean floor protoliths is shown by Eu anomalies in some majoritic inclusions, and the occurrence of some highly aluminous phases in group (c). A very small number of diamonds with $\delta^{13}\text{C}$ close to 0 (zero), may indicate a marine carbonate source.

The nature of the ultrabasic protoliths yielding diamonds with $\delta^{13}\text{C}$ values of -3 to -7 is particularly interesting. These carbon isotope values are regarded as typical of the mantle. But what is the petrological history of this mantle? Given the evidence of an ocean floor origin for the protoliths of the other inclusion suites, it is suggested that the mantle protolith for the ultrabasic inclusions also formed part of the oceanic lithosphere before being subducted. Unlike basic rock compositions forming the ocean crust, the ultrabasic rocks of the oceanic mantle lithosphere were probably too far below the ocean floor to acquire organic carbon - thus they retained their primitive mantle carbon signatures, although they may have undergone hydration.

With subduction, the oceanic lithosphere may give rise to a stagnant slab lying close to the upper/lower mantle boundary (refs 1 and 7). During descent of the slab, dehydration reactions may give rise to fluids/melts from which the diamonds of groups (a) and (b) crystallised (ref 4). In the accompanying image for the Juina diamonds at 101 Ma, the formation of diamonds of groups (a) and (b) is indicated by the red and green diamond shapes respectively. Once formed these are represented by the solid circular shapes and transported with the stagnant slab. Diamonds with Ca-rich inclusions (group c) are suggested to form in association with carbonatitic melts (ref 5), which also transport all diamonds towards the continental lithosphere of the Amazonion craton.



Carbon isotopes in a Juina diamond with carbonate inclusions

PINTI, Daniele^{1*} ; ISHIDA, Akizumi² ; TAKAHATA, Naoto² ; SANO, Yuji²

¹GEOTOP-Universite du Quebec a Montreal, Canada, ²Atmosphere and Ocean Research Institute, The University of Tokyo

Juina super-deep diamonds are formed at the transition zone, between the upper and the lower mantle. They contain numerous mineral inclusions such as carbonates. Although rare, the occurrence of carbonates in the transition zone or even the lower mantle suggests that the Earth's global CO₂-cycle has an ultra-deep extension. Some authors have pointed out carbonate inclusions as an evidence of the involvement of subduction-related fluids in the formation of these super-deep diamonds, and in general of eclogitic-type diamonds. Here we present new data obtained on three FIB-TEM prepared foils of a Juina diamond that contains a carbonate inclusion. Carbon isotopic signature ($\delta^{13}\text{C}$ in ‰) was measured together with N content in these foils and calibrated against a carbonado standard (GM02) with a $\delta^{13}\text{C}$ of -29.2 ‰, using a NanoSIMS 50 at the University of Tokyo. The $\delta^{13}\text{C}$ of a synthetic diamond used for anvil cell experiments and a natural diamond of type IA have been also measured (and conventional mass spectrometry analyses are under way) to use them as new internal standards and crosscheck the results.

A total of 14 raster analyses (1 x 1 μm) were carried out on the three foils, using a Cs⁺ beam. We used 2 detectors on different 3 magnetic fields, so we could estimate and compare three ¹³C/¹²C ratios. N amount was also determined. Instrumental mass fractionation (IMF effect) was calculated using the data of GM02. Quasi-simultaneous arrival (QSA) effect was taken into account and data corrected consequently, because of the large amount of secondary ions observed (above 100,000 cps). Counting was between 35 and 80 cycles, depending to the variable thickness of the foils (ca. 150 nm) to avoid that the Cs⁺ beam pierces the foil and measures C from the TEM carbon grid.

Results showed $\delta^{13}\text{C}$ values in the Juina diamond ranging from -9.1 ± 3.8 ‰ to -0.43 ± 2.82 ‰ with an average $\delta^{13}\text{C}$ value of -4.2 ‰ and a median value of -4.0 ‰. The diamond sample contains also a small amount of nitrogen with an average concentration of 62 ppm, similar to previously reported concentrations measured by SIMS. These results suggest a peridotitic origin for the diamond, possibly Type IaB, which is the most abundant class among the Juina diamonds. The origin of this diamond calls for alternative processes to explain the genesis of carbonate inclusions.

Keywords: Carbon cycle, Carbon isotopes, Diamonds, Carbonate, Juina, Transition zone

Mantle processes inferred from Os isotopic compositions and micro lectures of carbonado diamonds

KAGI, Hiroyuki^{1*} ; SHIRAIISHI, Noriko¹ ; SENDA, Ryoko² ; SUZUKI, Katsuhiko² ; ASANO, Natsuko³ ; OHFUJI, Hiroaki³

¹Graduate School of Science, The University of Tokyo, ²JAMSTEC, ³Geodynamics Research Center, Ehime University

Carbonado, a type of natural polycrystalline diamond, has characteristics distinct from those of typical natural diamonds: for example, no genetic relations to kimberlites, low carbon isotopic ratios, and the lack of mantle-derived mineral inclusions, and so on. Based on these characteristics, several diverse hypotheses have been proposed on the origin of carbonado. At present, no conclusive evidence has been proposed to settle the controversy. The most important point we have to remind is that carbonado had been heavily altered after the crystallization of diamonds and the grain boundaries of micro-diamonds in carbonado may have lost the intrinsic information on the formation of diamonds consisting of carbonado.

In this study, we tried to extract geochemical and mineralogical information from inside of diamond grains and grain boundaries, independently. We conducted Os isotopic analysis and electron microscopic observation on carbonado samples collected from placer deposits in the Central African Republic. We obtained very different results between inside of diamond grains and grain boundaries both on the Os isotopic values and mineralogy of inclusions. The origin of carbonado will be discussed based on the intrinsic information obtained from the inside of diamond grains.

Keywords: carbonado, Os isotopic compositions, platinum group elements, mineral texture, inclusions, diamonds

Oligomerization and carbonization of polycyclic aromatic hydrocarbons at pressures to 16 GPa

CHANY SHEV, Artem¹ ; LITASOV, Konstantin^{2*} ; SHATSKIY, Anton² ; FURUKAWA, Yoshihiro³ ;
YOSHINO, Takashi⁴ ; OHTANI, Eiji³

¹Novosibirsk State University, Novosibirsk, Russia, ²VS Sobolev Institute of Geology and Mineralogy, Novosibirsk, Russia,
³Graduate School of Science, Tohoku University, Sendai, Japan, ⁴Institute for Study of the Earths Interior, Okayama University,
Misasa, Tottori, Japan

We have examined the stabilities of different polycyclic aromatic hydrocarbons (PAHs) at pressures up to 16 GPa and temperatures to 1273 K. Experiments were performed using a large-volume multi-anvil apparatus. Quenched products were analyzed by matrix-assisted laser desorption/ionization (MALDI) and Raman spectroscopy. The MALDI measurements revealed the considerable oligomerization of PAHs at 7 GPa and 773 to 873 K and insignificant PAH oligomerization at 16 GPa and 300 K. At 7 GPa and 773 K, oligomers with atomic masses up to 3400 Da and higher were found, while only a small number of dimers of the starting PAHs were detected at 16 GPa and 300 K. PAH decomposition at 7 GPa occurred from 873 to 973 K, and the decomposition products consisted of nanocrystalline graphite. We also obtained solid-liquid-(C+H₂) triple points by in situ X-ray diffraction and X-ray radiography and found that they are located at relatively low pressures of 1-2 GPa for naphthalene, acenaphthene, pyrene, and coronene. Previously determined melting lines to 4-5 GPa were thus subjected for revision. The determined decomposition temperatures of the PAHs (873-973 K) are much lower than Earth's geotherms and the subduction slab P-T profiles at 6-7 GPa; therefore, PAH inclusions in mantle-derived minerals, which can be crystallized at 6 to 7 GPa and 1600 to 1700 K, should be secondary phases and could be formed by the successive polycondensation of simple hydrocarbon molecules under natural catalysts during eruption processes at sub-ambient pressures and temperatures. We also rebutted the high-temperature stability of PAHs suggested by previous shock compression experiments and theoretical predictions. However, metastable formation of PAHs in shock experiments at high PT-conditions may still be possible.

Keywords: high pressure, polycyclic aromatic hydrocarbons, carbon, oligomerization

Spatial distribution of hydrogen production zone and organic carbon in the oceanic crust

ANDO, Yumi^{1*} ; OKAMOTO, Kazuaki¹

¹Graduate school of education, Saitama University

Hydrothermal activity in the Archean-Ridge system has been considered to play a major role to maintain the oldest biosphere in early Earth. In the present ridge-system, hydrogen production in the serpentinized peridotite layer, is considered as major energy source. However, low temperature hydrothermal zone in the lower crust layer in the ridge has been recognized as hydrogen producing zone. Then what is the hydrogen source in the oceanic lower crust? Accreted oceanic plateau is one of the best sample to describe hydration process due to deep-sea-hydrothermal alteration because it is easy to observe huge outcrops and collect samples systematically in whole section. We have collected rock samples from the Mikabu high P/T rocks in Toba area, central Japan and from Ootoyo area, central Shikoku, Japan because there are large scale trench cliffs in the mine. Here, we report mineral composition surrounding organic carbon that was found in metabasaltic rocks from Ootoyo area. The metabasalt underlies metachert, and exhibit extensive plagioclase veins. Carbonaceous material and FeS are concentrated near the veins. Serpentinization of olivine gabbro was recognized in the metabasalt layer as lensoid body. In the Toba area, wehrlite and hornblende gabbro are dominant as the oceanic lower crustal material, subsequently suffered high P/T metamorphism. Abundant serpentine with magnetite are along olivine grain boundaries. Cr-spinel and epidote are occasionally recognized. That is, hydrogen was produced due to hydration reaction in the intruded wherlite from the lower crust of the large plateau. Thus the graphite probably from organic carbon in the metabasalt suffered high P/T subduction zone metamorphism. In order to know the fate of the graphite in deep subduction zone, we have observed the Sanbagawa eclogite (Tonaru eclogite) accompanying copper-iron sulfides (so called Besshi mine type Cu-Fe sulfides). In the eclogite, Cu-Fe sulfides contain silicate with graphite as inclusion. The graphite crystallization temperature calibrated using laser Raman peak shift, is estimated as 300-340 °C. It is obviously lower than that of the metamorphic temperature of the eclogite 550-600 °C. It clearly suggests that graphite was probably from the micro-bacteria with Cu-Fe sulfides in the hydrothermal zone in the Mid-oceanic ridge system. In summary, the lower crust might be significant zone producing hydrogen, and provide bacteria cluster above, and subsequently the organic carbon would be recycled down deep in the mantle via subduction zone.

Keywords: deep subduction zone, organic carbone

Hydrocarbon gas efflux from an active deep-water mud volcano constrained by seismic velocity profiles

KIOKA, Arata^{1*}; OTSUKA, Hironori¹; TSUJI, Takeshi²; ASHI, Juichiro¹

¹Dept. Ocean Floor Geosci., Atmos. Ocean Res. Inst., UTokyo, Japan, ²CO2 Stor. Res., Int'l. Inst. Carbon-Neutral Energy Res., Kyushu Univ., Japan

Mud volcanoes are considered to be one of the largest geological sources emitting hydrocarbon gases into the atmosphere. Numerous studies have revealed their origins and compositions from offshore mud volcanoes. The gas is composed dominantly by methane and is of mixed biogenic and thermogenic origin. Methane emissions from each mud volcano have high temporal variability of their intensities as found at cold seeps. A recent long-term observation in a submarine mud volcano sheds light on that larger volume of methane gas than expected is escaped from deep-water mud volcanoes. However, estimates on the gas volume fraction inside submarine mud volcanoes have been challenging because of difficulties of in-situ measurements without secure deep-drilling. Herein we provide a new scheme to link gas concentration and seismic velocity in gas-charged fluidized mud conduits of a submarine mud volcano. This model enables to estimate the methane concentration in the mud conduits of the offshore mud volcano using the seismic velocity profile derived from reflection and/or refraction seismic data. The scheme is universally applicable using the seismic data and provides useful and robust estimations of gas concentration in the conduits of offshore mud volcanoes. These estimations can be forwarded to assess stationary methane fluxes from deep-water mud volcanoes. Moreover, addressing these problems helps an assessment of potential methane concentration inside the mud volcanoes, which contributes to unpuzzle roles of offshore mud volcanism on subsurface carbon cycling as well as an urgent issue into the Missing methane. The application to an active mud volcano in the Kumano mud field of the Nankai unveils that the methane fraction in its conduits reaches a higher value than expected.

Keywords: Submarine mud volcanoes, methane gas fraction, seismic velocity

Fluid emission along the Nankai Trough: Insights from noble gases in the sediment pore water

TOMONAGA, Yama^{1*} ; ASHI, Juichiro¹ ; TAKAHATA, Naoto¹ ; YAGASAKI, Kazuhiro¹ ; TOYODA, Shin² ; SANO, Yuji¹

¹Atmosphere and Ocean Research Institute, The University of Tokyo, ²Department of Applied Physics, Faculty of Science, Okayama University of Science

Noble-gas geochemistry is known to change in response to the terrigenous fluid emission triggered by major seismic events, as observed, for instance, in the recent case of the Tohoku-Oki earthquake occurred in 2011. Therefore, characterizing the terrigenous fluid emission in tectonically active regions is a prerequisite to understand future geochemical changes.

In the present contribution we report the results of the noble-gas and carbon isotope measurements conducted in water and sediment samples collected along the Nankai Trough using the ROV HyperDolphin during RV Natsushima cruises NT13-08 and NT14-07.

In general, sediment cores acquired at active cold seeps at the splay fault off shore Kumano are characterized by the presence of crustal He and the respective He concentration gradients are highly variable. Sediment cores collected at shallower water depths show relatively low He concentration gradients and high ³He/⁴He ratios suggesting the presence of mantle He.

The fluid transport dynamics in the investigated area are discussed in the light of the new insights provided by the spatial distribution of the fluxes and the isotope signature of terrigenous He provided by the present study.

Keywords: He fluxes, subduction zones, terrigenous fluids, transport processes

Geochemical characteristics of submarine hydrothermal plumes near Tokara Islands

WEN, Hsinyi^{2*}; SANO, Yuji¹; TAKAHATA, Naoto¹; ISHIDA, Akizumi¹; TANAKA, Kentaro¹; TOMONAGA, Yama¹; KAGOSHIMA, Takanori¹; SHIRAI, Kotaro¹; ISHIBASHI, Jun-ichiro³; YOKOSE, Hisayoshi⁴; TSUNOGAI, Urumu⁵; YANG, Tsanyao F.²

¹Atmosphere and Ocean Research Institute, The University of Tokyo, Japan, ²Department of Geosciences, National Taiwan University, Taiwan, ³Department of Earth and Planetary Sciences, Faculty of Science, Kyushu University, Japan, ⁴Graduate School of Science and Technology, Kumamoto University, Japan, ⁵Graduate School of Environmental Studies, Nagoya University, Japan

Recently a new submarine volcano has been discovered near the Tokara Islands (South of Kyushu, Japan) by a multi-beam echo sounder survey. However, only a few geochemical data are available for the investigated area. Therefore, the aim of this study is to characterize the volatile geochemistry of shallow hydrothermal system of volcano in the adjacent region of Tokara Islands. Seawater sampling was carried out by CTD-CMS hydrocasts during the RV Shinsei Maru KS-14-10 research cruise (25th June – 5th July, 2014) in the region stretching from Kagoshima bay to Daiichi-Amami Knoll. In the vicinity of Tokara Islands (Daiichi-Amami Knoll and Ko-Takara Shima), higher turbidity and lower pH values together with excess ³He were observed at the same depth, suggesting the presence of a strong hydrothermal signal. ³He and CH₄ fluxes in this region are estimated to be 0.99-2.6×10⁴ atoms/cm²/sec and 6-60 ton/year, respectively. There is a positive relationship between the excess ³He and the excess ⁴He/²⁰Ne ratio relative to the air saturated seawater value at the ambient temperature, suggesting binary mixing between atmospheric and volcanic noble gases. The end member for Wakamiko (in Kagoshima bay) samples shows subduction-type mantle He signature with about 7 R_A, while that for Tokara Islands indicates more crustal He share with a value of about 4 R_A (R_A is the atmospheric ³He/⁴He ratio of 1.382×10⁻⁶). The estimated end-member of the carbon isotopic composition of CH₄ in Daiichi-Amami Knoll and Ko-Takara Shima are -29.25 ‰ PDB and -23.53 ‰ PDB, respectively. Based on the measured δ¹³C_{CH₄} values and CH₄/³He ratios, it is possible to estimate the origin of methane. There show mixing between East Pacific Rise type abiogenic and thermogenic methane in Tokara Islands, while Wakamiko samples may have been fractionated through rapid microbial oxidation in the water column.

Keywords: helium, methane, flux, Tokara Islands, shallow submarine hydrothermal plumes

Origin of carbon and other volatile elements on Earth in the light of the Rosetta cometary mission

BERNARD, Marty^{1*} ; ALTWEGG, Kathrin² ; ROSINA, Team²

¹CRPG-CNRS, ²Physikalisches Institut, University of Bern

The origin of carbon, water, nitrogen and noble gases on Earth is debated between several cosmochemical sources including the protosolar nebula, and volatile-rich bodies such as "wet" asteroids (up to 15 % equivalent water and a few % C) or comets (up to 50 % water ice). Terrestrial noble gases have been interpreted as originating from the solar nebula or from the solar wind. However, the H and N stable isotope compositions of the atmosphere and the oceans are consistent with an asteroidal, rather than solar or cometary, contribution. For the latter, this inference is based on D and ¹⁵N enrichments in comets. However, this view was recently challenged by the discovery of a Jupiter Family comet (JFC) having a ocean-like D/H ratio. The ESA Rosetta mission is presently analyzing the morphology, the physical parameters, and the composition of Comet 67P/Churirov-Gerasimenko (67P/CG). On board of the spacecraft, the Rosina instrument (PI. K. Altwegg, Univ. Bern, Switzerland) consisting of double focusing and time of flight mass spectrometers is analyzing gases released by the comet [1, 2]. The analysis of noble gases, stable isotopes, and volatile elements sheds constraints on the formation environment of this body, and seem to indicate a limited, but not necessarily negligible, contribution of 67P/CG-type material to the Earth's oceans and atmosphere and organics. In particular, the high Ar content of the comet and its implication for terrestrial noble gases will be discussed at the meeting.

[1] Altwegg et al., (2015), Science 347, 126952-1; [2] Hassig et al., (2015); Science 347, aaa0276-1

Keywords: carbon, volatile elements, Comet67P/CG, Rosina

Carbon in lunar mantle

NAKAMURA, Ryosuke^{1*} ; YAMAMOTO, Satoru² ; MATSUNAGA, Tsuneo² ; ISHIHARA, Yoshiaki³

¹AIST, ²NIES, ³JAXA

If the Moon was created from Earth's mantle by the so-called "Giant Impact", all the volatile component must have been lost from the very hot proto-lunar disk where even silicate is vaporized. Some special form of carbon (graphite, diamond, etc), however, could have survived in the harsh environment. Then, carbon monoxide (CO) could be produced in more reductive lunar mantle (Sato 1979). In fact, many lunar mare basalt samples show vesicular structures, indicating the presence of volatile components in the parent magma.

Another evidence of volatile inside moon is pyroclastic glass in Apollo samples. Volatile-induced pressure is required to produce them even under low gravity and no atmosphere on the Moon. The global survey by spectral profiler (SP) onboard Kaguya has discovered that Sinus Aestuum is the largest pyroclastic deposit on the Moon (Yamamoto et al. 2014). From the spatial extent and thickness, we deduce the total amount of volatile gas which have rapidly brought the parent magma to the surface. Assuming that the gas consists of only CO, we will estimate the carbon content in the lunar mantle.

Keywords: Earth, Moon, mantle, carbon, Remote sensing, Kaguya