

MIS002-01

Room:104

Time:May 27 14:15-14:45

Evidence for Deep Carbon Cycle: UHPM carbonates, microdiamonds, aqueous fluid and mantle metasomatism

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In calculated P-T grids for dolomite-bearing carbonate system, CaO-MgO-SiO₂-CO₂-H₂O (Ogasawara et al. 1995), a large "no-reaction" P-T space (excepting phase transitions) exists at high-P and low-T side, and its extent is affected by fluid conditions as XCO₂. This suggests that along P-T path of cold subduction the chance of "no reaction" in subducted carbonate rocks is high and carbonate rocks can survive up to great depths in the mantle. Deep carbonate subduction process can play as an important carrier of CO₂ as carbonates from Earth's surface to the mantle. The potential of CO₂ influx could be affected by aqueous fluid infiltrated in subducted materials. Such speculation based on the thermodynamic results was a trigger of my study on Ultrahigh-Pressure (UHP) metamorphic carbonate rocks and microdiamonds.

UHPM carbonate rocks have preserved variable information about not only P-T conditions, but chemical systems and related reactions within deeply subducted continental materials, and are the direct evidence for deep carbon cycle from Earth's surface to deep upper mantle. The occurrences of those precious materials including metamorphic diamonds are very rare in world UHPM terranes; the representative example is a diamond-bearing dolomite marble in the Kokchetav Massif, northern Kazakhstan. The Kokchetav microdiamonds are concentrated in a carbonate rock, impure dolomite marble; the highest diamond concentration domain in garnet showed about 2700 carat/ton. Microdiamonds in this marble formed at two different stages and the second stage diamond could formed from a multicomponent aqueous fluid (not from graphite). Garnet-biotite gneiss is the second highest diamond concentration. Protolith of this diamond-bearing dolomite marble is late-Proterozoic platform sediments (impure dolostone) on the basis of the local geology and the stable isotope data on the carbonates. This indicates that limestones and dolostones can subduct into the great depths at least to the low-P limit of diamond stability field. A similar UHP carbonate rock, Ti-clinohumite-bearing dolomitic marble whose assemblage aragonite-dolomite-Ti-clinohumite was stable at extremely low XCO₂, occurs at the same area, but diamond was unstable in this marble. Such strong contrast between two dolomite-bearing UHP carbonate rocks can be explained by the H₂O-rich fluid condition and its heterogeneity under UHP metamorphism. Another important evidence is exsolved coesite from supersilicic titanite discovered in titanite-bearing calcite (after aragonite) marble. Reintegrated precursor composition showed that excess Si in octahedral site, 0.145 gave corresponding minimum-P as 6 GPa; this impure limestone subducted to the depths over 200 km. Exsolved coesite in titanite also discovered in "skarn-like" garnet-clinopyroxene rock that suggests strong metasomatism at UHP conditions. These two exsolved-coesite-bearing rocks lack diamond except for a thin diopside-rich layer in the calcite marble (only 61 grains and no second stage growth).

Such features of the Kokchetav UHPM carbonate rocks strongly suggest that entire decomposition of carbonates is difficult during deep continental subduction and carbonate can survive at depths over 200 km although the metasomatism within subducted materials by H₂O-rich fluid ("Intraslab UHP Metasomatism") occurs at great depths. Abundant carbonate could be stored in the mantle than we expected before. Deep carbonate subduction is the most important carbon carrier into the mantle and makes strong compositional heterogeneity of the mantle. To clarify the fate of deeply subducted carbonates could be an important next step for Deep Carbon Cycle project.

Keywords: UHP Metamorphism, deep carbonate subduction, metamorphic diamond, dolomite, exsolved coesite from supersilicic titanite, Intraslab UHP Metasomatism

MIS002-02

Room:104

Time:May 27 14:45-15:00

Deep carbon reservoir inferred from natural polycrystalline diamonds, carbonado

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Carbonado is a natural polycrystalline diamond aggregate and the characteristics are very different from those of typical mantle-originated diamonds. The carbon isotopic compositions is significantly depleted in C-13 and no mantle-originated mineral inclusions have been found. Moreover, fluencies form radioactive nuclides were found from radiation damage and fissionogenic noble gasses. Based on those observations, some of researchers proposed crustal origin of carbonado diamond, which suggested diamond formation from biogenic carbon under a thermodynamically metastable condition with high-energy particles. On the other hand, residual pressures as high as 1GPa were detected inside of carbonado diamonds and the mantle-origin is also remained as a potential origin.

We recently carried out TEM observations on FIB-fabricated carbonado samples. The obtained fine structure showed that fluid inclusions as primary origin were trapped within a grain of diamond. The experimental results strongly suggests that the carbonado grew under the presence of fluids at a P-T condition where diamond is thermodynamically stable. Given that carbonado is originated from the mantle, this suggests that there may be a large carbon reservoir depleted in C-13 in the mantle or C-13 depletion occurred during the formation process of carbonado diamonds. In the presentation, we will discuss the relation between carbon reservoir in the mantle and the origin of carbonado based on our recent spectroscopic, isotopic and TEM observations.

Keywords: diamond, carbonado, mantle, carbon isotope

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MIS002-03

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Ultra-Deep Drilling to the Oceanic Mantle: towards understanding the deep carbon cycle

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The Integrated Ocean Drilling Program (IODP), an international scientific research program supported by 24 countries, advances scientific understanding of the Earth by monitoring, drilling, sampling, and analyzing seafloor environments. One final goal of IODP is full penetration of oceanic crust and the first sample return from the Earth's mantle in history, known as MoHole project. We here emphasize that MoHole could contribute greatly to understanding the whole-mantle-scale carbon cycle. One reason for believing so is recent discovery of diamond and other ultra-high-pressure minerals from podiform chromitites in ophiolites, i.e., fossil oceanic crust/mantle. A possible scenario of these diamond-bearing chromitites is that they were originally formed at the Moho transition zone via melt/harzburgite reaction, transported to the lower mantle and recycled to the uppermost mantle by convection. The recovery of diamond from the in situ oceanic mantle, together with characterization of carbon and other volatiles in high-pressure phases, should provide new insights into geochemical evolution of the solid Earth.

Keywords: IODP, MoHole, oceanic mantle, diamond, deep carbon cycle

MIS002-04

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Time:May 27 15:15-15:30

The occurrence of a carbon in ureilite of Almahatta Sitta TC₃

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Asteroid 2008 TC₃ exploded in air in the Earth around northern Sudan on October 7, 2008. Its remnants were recovered immediately and called Almahatta Sitta TC₃. Almahatta Sitta TC₃ is a first asteroid we could trace its passage during prior to falling on the Earth after tracing its path in the space by astronomic observation. Almahatta Sitta TC₃ consists mainly of coarse-grained and fine-grained ureilite fragments, OC, EH and EL chondrites. Both ureilites studied by us contain several carbon species. Here, we report the occurrence and nature of the carbon material in them.

The major constituent mineral of the coarse-grained ureilite is olivine (Fa₁₈₋₂₁). Minor low-Ca pyroxene, troilite and metallic Fe are also encountered. Raman spectroscopic analyses indicate that fine-grained diamond and graphite exists in the interstices of the olivine grains. The chemical compositions of olivine (Fa₄) surrounding the diamond + graphite assemblages are depleted in Fe compared with those of the olivine (Fa₁₈₋₂₁) in a host-rock. Many metallic Fe blebs are contained in the Fe-depleted olivine around the diamond + graphite assemblages. The Fe-depleted olivine and metallic Fe bleb assemblage would be reduction products of olivine by the carbon material.

The petrographic feature of the fine-grained ureilite is much more complicated than the coarse-grained ureilite. The fine-grained ureilite contains olivine, low-pyroxene and metallic Fe but appears to be a conglomerate of different fragments including carbon-bearing clasts. Graphite exists in clasts of metallic Fe. Fibrous graphite is observed on the surface of low-Ca pyroxene or olivine grain adjacent to the metallic Fe. The fibrous graphite might have grown when the metallic iron was molten. Few diamonds could be identified by Raman in few clasts in the fine-grained ureilite.

Keywords: graphite, diamond, ureilite

MIS002-05

Room:104

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Quantification of CO₂ dissolved in silicate glasses and melts using Raman spectroscopy: implications for geodynamics

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Understanding Earth degassing is fundamental in global studies of our planet history, as well as in studies of its recent climate. Degassing occurs mainly at Mid Ocean Ridges via exsolution of CO₂ vesicles in ascending tholeiite magma, and probably begins at some 30 km under the ridge. Therefore, a precise knowledge of how carbon solubility varies during ascent from the source region is mandatory, a process for which the effect of pressure remains poorly known. A pressure increase induces melt compression, known to diminish argon dissolution with respect to Henry's law at pressures above ~10 kbar, but this effect is poorly documented for carbon where things are complicated by the transformation of CO₂ into carbonate ion, CO₃²⁻. Early experimental investigations on carbon solubility in various silicate melts up to ~20-30kbar have shown that Henry's law is not followed at high pressures.

We have performed an experimental study of C dissolution in basaltic melts using high-pressure facility in Clermont-Ferrand (France). Analysis of dissolved C was performed using a micro-Raman spectroscopy. Dissolved carbon appears as clear bands due to carbonate ions (an intense peak at ~ 1100 cm⁻¹ and a doublet in the 1350-1600 cm⁻¹ region), molecular CO₂ being not detectable. Calibration of Raman spectroscopy for quantitative analysis was done by preparing standards at atmospheric pressure and analyzing them using a stable isotope mass spectrometer.

The results show that carbon concentration increases steadily with increasing pressure, a behavior consistent with (rare) previous studies on basaltic melts. We also have performed molecular dynamics simulations to investigate the dissolution of CO₂ in a silicate melt. The calculated solubility is consistent with the data, which help understanding how pressure acts on fluid and melt, and yield insight into the details of how CO₂ and CO₃²⁻ interact with the melt network. However, the fact that the carbon solubility in a MORB is continuously increasing with pressure is somewhat surprising, and will be discussed.

This work has shown that

- (i) Raman spectroscopy can be used to quantify C content in natural samples
- (ii) The C solubility measured in basaltic melt exhibits a behavior with pressure different from that exhibited by rare gases.
- (iii) Our results have important implications concerning the history of the atmosphere degassing and structure of the mantle.

Keywords: CO₂, Raman spectroscopy, silicate glasses and melts

MIS002-06

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Role of alkali carbonates in the mantle magmatism, metasomatism, and diamond formation

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There are much direct and indirect evidences of carbonatitic and hydrous melt/fluid segregation in the deep mantle in the past Earth's history. One particular example is the source regions of carbonatites, kimberlites, and lamproites some of which originate from more than 250 km depth. On the basis of experimental studies they appear to represent opposite ends of the volatile spectrum; carbonatites and kimberlites clearly require abundant CO₂ in the source, whereas lamproites require H₂O rich sources.

Another example is the natural diamond forming medium. Experimental data suggest that water-bearing alkali carbonates and CO₂-H₂O fluid are only species which are capable to initiate diamond crystallization at pressures and temperatures that correspond to those of natural diamond formation. Analysis of data on micro-inclusions in "fibrous" diamonds from different localities indicates that the diamond-forming media at the stage of inclusion entrapment constituted of super-critical fluid or melt with different ratios of carbonates and water. These integrated results strongly support the concept of diamond crystallization from either hydrous fluid or alkali carbonate melt.

In accordance with the current geotherms for the upper surfaces of subducted slabs and the phase equilibria computed for an oceanic metabasalt and subducted marine sediments the local abundance of water and carbonates in the mantle can be attributed to the subduction. However, for much of geological time (>500 m.y.) subduction geotherms have been too hot to allow carbonate and water subduction. This means that water-bearing silicates and carbonates rather underwent decomposition and melting at shallow depth leading arc magmatism than were transported into the deep mantle. In accordance with this and since the average mantle concentrations of carbon and hydrogen do not exceed 100 and 120 wt ppm respectively, the volatile segregation in a broad mantle region should be involved to explain the local abundance of CO₂ and/or H₂O. Enrichment of these fluids in incompatible trace elements (specifically, K, Rb, Sr, Ba, light REE, Ti, Nb, Zr, P, U, and Th) also implies their long infiltration history through the large volumes of mantle rocks. However, mechanisms and forces driving fluid transport and segregation in the deep mantle are poorly understood.

In this talk we would like to highlight following subjects.

- 1.PT conditions of carbonatite magma formation. Mantle solidus.
- 2.Mechanism of carbonate melts segregation.
- 3.Migration rate of carbonatite melt through solid no-porous silicate mantle.
- 4.Proto-kimberlite magma composition. Experimental constrain.
- 5.P-T conditions of natural diamond formation in presence of carbonatite melt.
- 6.Effect of carbonate-silicate ratio on kinetics of diamond formation.

Keywords: carbonatite melt, kimberlite, metasomatism, diamond, mantle

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MIS002-07

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Formation of hydrocarbons and graphite by polymerization of methane molecules under the Earth's mantle conditions.

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High-pressure and high-temperature experiments of olivine-methane-water and olivine-methane systems were performed using a laser-heated diamond anvil cell at a pressure range from 5.4 to 29.4 GPa and a temperature range from about 1600 to 2000 K corresponding to conditions of the upper mantle to the top of lower mantle. X-ray diffractometry, Raman spectroscopy, and transmission electron microscopy revealed that methane molecules polymerized under existence of olivine to form heavier hydrocarbon, graphite. A difference in the products was not observed between the present study and the previous studies of sole methane. The present result suggests there is no effect of olivine to polymerization of methane molecules. The present study demonstrates polymerization of methane occurs in the Earth's mantle and that is consistent with previous studies on finding some hydrocarbons in mantle-derived minerals.

Keywords: methane, olivine, hydrogen, polymerization, laser heated diamond anvil cell

MIS002-08

Room:104

Time:May 27 16:30-17:00

COH Solubility, solution behavior and $^{13}/^{12}\text{C}$ fractionation melt-fluid systems at mantle redox, P, and T conditions

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The solubility and solution mechanisms in melts and speciation in coexisting fluid of reduced and oxidized C-bearing volatiles in the system C-O-H have been determined as a function of melt composition (from haplobasalt to haploandesite) and redox conditions in the range from the MH to the IW buffer to upper mantle temperatures and pressures. Sample characterization was conducted with samples quenched from high temperature and pressure and with melt+fluid samples in-situ in hydrothermal diamond anvil cells. Raman, FTIR, and NMR spectroscopies were employed as structural tools for studies of glasses, melts, and fluids. Carbon solubility and carbon isotope fractionation between melt and fluid were determined mass-spectrometrically and interpreted with the aid of speciation of C-O-H in melt and in coexisting fluids (see also [1]).

Methane solubility increases from 0.2 wt percent to about 0.5 wt percent in the composition range between haploandesite and haplobasalt and increases by 150 percent between the IW and MH oxygen buffers at constant temperature and pressure. Carbon isotope fractionation between methane-saturated melts and (CH₄+H₂+H₂O)-fluid changes by 14 per mil with the melt compositions studied (haploandesite to haplobasalt). In the COH-silicate system at redox conditions of the NNO oxygen buffer and more oxidizing, carbon exists in melts as carbonate complexes and in the fluid as CO₂. Carbonate occurs in two forms, as CO₃-groups sharing one or more oxygen with the silicate melt network structure and as isolated CO₃-groups bonded to metal cations. Isolated CO₃-groups become more abundant the less polymerized the melt (more mafic melts). Reduced (C+H)-bearing species were detected in silicate melts at the redox conditions of the MW buffer and more reducing. From diamond cell (HDAC) experiments conducted in-situ from ambient temperature and pressure to 800 C and 1435 MPa under redox conditions near those of the IW buffer, the dominant fluid species in the fluid are CH₄, H₂, and H₂O. In coexisting melt, CH₃ - groups linked to the silicate melt structure via Si-CH₃ bonding occur together with molecular CH₄. There is no evidence of changes in hydrocarbon species or polymerization with temperature and pressure.

The melt composition-dependent solubility and change in carbon isotope fractionation is because of silicate composition-dependent changes of C-bearing species in the melt. The composition- and redox-dependent solution mechanisms of C-species in melts governs how melt properties can change with redox conditions. Redox melting in the interior of the Earth has been explained with the aid of the solution mechanisms of oxidized and reduced carbon in silicate melts. Further, effects of oxidized and reduced carbon on melt viscosity and on element partitioning between melts and minerals have been estimated from relationships between melt polymerization and dissolved carbon combined with existing experimental data that link melt properties and melt polymerization. With total carbon contents in the melts on the order of several mol percent, mineral-melt element partition coefficients and melt viscosity may change by several tens to several hundred percent as a function of redox conditions in the range of the deep crust and upper mantle of the Earth.

[1] Mysen, B. O., Cody, G. D., and Morrill, P. L. (2009) *Geochim. Cosmochim. Acta.* 73, 1699.

Keywords: carbon speciation, COH fluid, silicate melt, solubility, solution mechanism, isotope fractionation

MIS002-09

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Carbon in Planetary Cores

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Carbon is one of the candidates for the light elements in the core. Phase relations of the Fe-C system have been studied to the lower mantle conditions. These studies revealed that Fe₃C and Fe₇C₃ compounds can exist under the conditions. On the other hand, there are few data on the solubility of carbon in molten iron, and the effect of carbon on physical properties such as density and compressional wave velocity of molten iron at high pressure. Thus, we made experiments on partitioning of carbon and silicon between metallic iron and silicate under various oxygen fugacity conditions at high pressure. We made two sets of experiments. First is the density measurement of Fe-C liquid at high pressure using the sink-float test of a composite marker after quenching from high pressures and temperatures, and the in situ X-ray absorption imaging method. The second set of the experiments was to measure the solubility of carbon and silicon in molten iron coexisting with silicates at high pressure and temperature. The first result revealed that carbon can reduce density of the molten iron at high pressure, whereas it increases the velocity of molten iron. Thus, it can be a candidate of the light elements of the outer core. The second set of the experiments revealed that light elements dissolved into metallic iron change with the oxygen fugacity; i.e., under the extremely reducing conditions of fO₂, about -4.5 log units below the iron-wustite buffer, only a limited amount of carbon can be dissolved into molten iron, whereas silicon is the major light elements dissolved into metallic iron. On the other hand, carbon can be dissolved into molten iron under relatively higher oxygen fugacity conditions. Thus, carbon can be a light element of the core only when the oxygen fugacity during the core formation is relatively high.

Keywords: Carbon, Core, phase relation, density, velocity, Fe-C liquid

MIS002-10

Room:104

Time:May 27 17:15-17:30

Carbon isotope fractionation during the formation of the Earth's core

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Carbon, the fourth most abundant element in the solar system, is believed to be an important light element constituent in the Earth's core. The high carbon content of CI chondrites (3.2 wt.%) compared to bulk Earth estimates, the presence of graphite/diamond and metal carbides in iron meteorites, the high solubility of carbon into iron melts in the Fe-C system suggests the plausible presence of carbon in the Earth's core. However, the distribution of carbon isotopes in the core is not understood. We present here new experimental data in the Fe-C system and results on the equilibrium carbon isotope fractionation between graphite/diamond and iron carbide melt at 5 GPa and 10 GPa at a temperature range of 1200 to 2100 °C. Our results suggest that iron carbide melt will preferentially gather ¹²C than ¹³C, which is temperature dependent. It is intriguing that our results are consistent with the carbon isotope distribution observed between graphite and cohenite (Fe₃C) in iron meteorites. The temperature dependent fractionation between iron carbide melt and graphite/diamond finds potential application in determining the temperature of formation of meteorites and metallic core of planetary materials. Furthermore, we anticipate that the temperature dependent fractionation of carbon isotopes between iron carbide melt and graphite/diamond is an effective mechanism that created a ¹²C enriched core with large scale differences in the distribution of the carbon isotopes in the metallic core and bulk silicate Earth during the accretion and differentiation of early Earth. Our findings also have implications on the deep carbon cycle of the Earth, where the light carbon from the core might have transported to the mantle and crust through deep mantle plumes.

Keywords: core, carbon isotope fractionation, iron carbide, graphite, diamond

MIS002-11

Room:104

Time:May 27 17:30-17:45

Carbon isotopic variation during CO₂ fluxing in crustal magmatic systems

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#Introduction

Geochemical studies on glass inclusions trapped in phenocrysts suggest that shallow-stored crustal magmas often suffer the open-system addition of a CO₂-rich vapour from below, probably from a mantle-derived basaltic source (CO₂ fluxing) (e.g., Metrich and Wallace, 2008). This proposal was made because the CO₂/H₂O compositional ratio of the inclusions cannot be explained by conventional degassing models. The CO₂ fluxing is of importance in various geological settings. First, the fluxing may be the principal process that transfers carbon stored in the earth's interior to the atmosphere in the global carbon cycle. Second, the fluxing controls various igneous processes including crystallization and viscosity of a melt, because it reduces activity of water. Third, the fluxing may trigger a volcanic eruption, because it dramatically increases vapour fraction and thus decreases bulk density of the magma (Yoshimura and Nakamura, 2010). However, the mechanism of CO₂ fluxing is scarcely understood.

Recently, we have formulated the CO₂ fluxing as a reactive transport process and showed its fundamental properties. Such modelling enabled us to discuss the mechanism of vapour transport quantitatively (Yoshimura and Nakamura, submitted). In this study, we updated the model so that it might include carbon isotopic evolution ($\delta^{13}\text{C}$) of the melt and vapour.

#Reactive transport modelling

The model assumes that a CO₂-rich vapour with a fixed chemical and isotopic composition is continuously introduced into a water-rich, vapour-saturated melt column at a constant rate. The introduced vapour ascends upward at a constant velocity. Because this vapour is initially in chemical and isotopic disequilibrium with the melt, a volatile exchange takes place. The initial column is assumed to have the H₂O-CO₂ and $\delta^{13}\text{C}$ compositions formed by closed-system degassing, which evolved from the bottom magma to various extents dependent upon pressure.

The governing equations consist of advection equations for H₂O, ¹²CO₂ and ¹³CO₂, the solubility law of H₂O-CO₂ and an equation of isotopic equilibrium between ¹²CO₂ and ¹³CO₂. We assumed that the interaction is achieved instantaneously at each level of the column.

#Results and discussion

As was shown in Yoshimura and Nakamura (submitted), the melt gradually became CO₂ rich, while the vapour was diluted with H₂O that was discharged from the melt. Whilst the H₂O-CO₂ chemical exchange was still in progress, the isotopic equilibration was achieved in a very short duration. When the first packet of the introduced vapour reached the top of the column, nearly whole the melt column had a constant $\delta^{13}\text{C}$ value that is in equilibrium with the introduced vapour. The reason for such a quick isotopic equilibration is that the amount of ¹³CO₂ and ¹²CO₂ exchanged between the melt and vapour is extremely small compared with the amounts of each isotope originally contained in both phases. Such isotopic information will enable us to discuss more detailed mechanism and the source of CO₂, if $\delta^{13}\text{C}$ values in glass inclusions and volcanic gases are observed in the future.

Keywords: CO₂ fluxing, degassing, reactive transport

MIS002-12

Room:104

Time:May 27 17:45-18:00

The impact of Human intelligence on the global carbon cycle

Minik T. Rosing^{1*}

¹Rosing, M.T.

The human brain consumes about one fourth of the total energy spent by the human body or ~ 25 W. For the present human population this leads to an average global energy consumption of ~ 0.4 mW/m² for the collective human brain activity. However, Human thought has far greater consequences than the direct metabolic activity of the brain. The idea of thermodynamics has allowed humans to spend more energy than we can obtain through our own metabolism. We have overcome the constraints of maximum appropriation of the primary photosynthetic productivity.

On a global scale, photosynthetic organisms capture solar energy equivalent to about 250 mW/m² of Earth's surface 1. About 1 per mil of this is deposited in sediments and either returned to the mantle via subduction on relatively short geologic timescales or sequestered in the crust on long geologic timescales. The thermodynamic insights have allowed us to convert the stored photosynthetic energy to work and heat at a rate of ~ 30 mW/m² ref 2. This is equivalent to 1/3 of Earth total inner energy conversion expressed in volcanism, plate tectonics and geothermal heat, and 20 times greater than the physiological energy conversion of humankind. By analyzing the impact of human thought relative to the energy requirement of our physiology we can evaluate the impact of societal structure and culture on the global carbon cycle.

1. Field, C. B., Behrenfeld, M. J., Randerson, J. T. & Falkowski, P. Primary production of the biosphere: Integrating terrestrial and oceanic components. *Science* 281, 237-240 (1998).

2. Doman, L. E. in DOE/EIA-0484(2010) (ed U.S. Energy Information Administration) 9-21 (U.S. Energy Information Administration, Washington, DC, 2010).

Keywords: Global carbon, Human, photosynthesis, subduction, energy

MIS002-13

Room:104

Time:May 27 18:00-18:15

Carbon-bearing nano-grains in shallow and deep-related rocks

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The present results can be summarized as follows.

1) Diamond with large crystal planes collected on the surface of the crust is formed at deeper Mantle under high pressure condition with xenoliths grains of Fe, Mg, Si-rich grains, though such light element of carbon or carbon dioxides gas are difficult to move to deeper place of the Mantle after formation of planet Earth (except impact process).

2) From detailed in-situ investigation by the ASEM (Analytical Scanning Electron Microscopy), the Democratic Republic (RD) Congo diamond shows micro-xenoliths of halite and calcite of carbonates mainly supplied from shallow origin, which suggest carbon changes by shallow impacts.

3) In-situ ASEM analyses show that diamond from the Kimberlite in South Africa has foreign xenoliths micro-grains of Fe, Mg-rich silicates and Ca, Fe and Mg carbonates (without any Na and Cl).

4) Impact Libyan glasses formed at shallow impact near at shallow sea-water contains micro grains of calcite carbonates and halite solidified from sea-water environment, which are confirmed by in-situ ASEM analyses.

5) The same in-situ ASEM methods are also applied to carbon-bearing carbonatites and shungite samples to discuss the micrograins.

6) Direct evidence of carbon in the deep interior can be applied to see solidified mixed area of any iron meteorites, where the Kuga plessite regions have carbon-bearing grains obtained by the ASEM methods.

Keywords: carbon-bearing nano-grains, diamonds, carbonatite, shungite, impact, sea-water remnants

MIS002-P01

Room: Convention Hall

Time: May 27 10:30-13:00

Melting phase relations in the peridotite and eclogite systems coexisting with reduced C-O-H fluid at 3-16 GPa

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Melting phase relations of peridotite and eclogite systems coexisting with reduced C-O-H fluid has been studied at 3-16 GPa and 1200-1600°C. In order to perform these experiments the double-capsule technique with fO_2 control by outer Mo-MoO₂ or Fe-FeO buffer capsule was designed and developed for multianvil experiments at pressures above 3 GPa. This technique can be successfully used up to pressures of 20-21 GPa using conventional multianvil devices. The inner capsule contained silicate starting material with an addition of 8-10 wt% stearic acid, which served as a fluid source, whereas outer capsule contained talc, which served as a hydrogen transmitting medium to maximize fH_2 in the inner capsule.

Silicate phase assemblages resemble those in volatile-free lithologies, i.e. olivine/wadsleyite-orthopyroxene-clinopyroxene-garnet in peridotite and garnet-omphacite in eclogite. Melting was detected by appearance of quenched crystals of pyroxene, feldspar and glassy silica. Abundant voids indicate presence of fluid in all runs. The compositions of partial melt were estimated from mass-balance calculations. The partial melt from peridotite runs has CaO-poor (6-9 wt%) basaltic composition with 44-47 wt% SiO₂ and 1.1-1.6 wt% Na₂O (all oxides recalculated to 100% of dry residue). Eclogitic melts contain more SiO₂ (47-49 wt%) and are enriched in CaO (9-15 wt%), Na₂O (9-14 wt%), and K₂O (1.3-2.2 wt%). All runs contained graphite or diamond crystals along with porous carbon aggregate with microinclusions of silicate phases. Analyses of carbon aggregates by defocused electron microprobe beam reveal compositions similar with estimated partial melts.

The appearance of quench crystals was considered as an indication of melting and allows to estimate the solidus temperatures in the studied systems. The solidi have relatively steep slope in the pressure range between 3 and 16 GPa. Estimated solidus temperatures for peridotite + C-O-H fluid with fO_2 control by Fe-FeO buffer are 1200°C at 3 GPa and 1700°C at 16 GPa. The solidus of the system with fO_2 control by Mo-MoO₂ buffer was about 100°C lower. Estimated solidus temperatures for eclogite + C-O-H fluid with fO_2 control by Fe-FeO buffer are 1100°C at 3 GPa and 1600°C at 16 GPa. The solidus of the system with fO_2 control by Mo-MoO₂ buffer was 20-50°C lower. These solidus temperatures are much higher (300-500°C) than those for peridotite/eclogite systems with H₂O and CO₂. However, they are still 300-400°C lower than solidi of volatile-free peridotite and eclogite at studied pressures.

We did not measure fluid compositions in present experiments. The estimations of fluid compositions using known equations of state for real gases (e.g. Zhang and Duan, 2009) show that fluid is H₂O-rich (H₂O > CH₄) in case of Mo-MoO₂ buffer and CH₄-rich (CH₄ > H₂O) in case of Fe-FeO buffer. The role of H₂O in the fluid increases with pressure. The high melting temperature of silicate assemblages coexisting with essentially H₂O-bearing fluid can be explained by the effect of methane and hydrogen, which may inhibit dissolution of silicate components in reduced fluids even if their absolute amounts are subordinate.

The present results have important implication for modeling of mantle melting. The oxygen fugacity decreases with pressures from about Fayalite-Magnetite-Quartz buffer at shallow mantle of 20-50 km to about Iron-Wustite at 250-300 km according to fO_2 estimations from cratonic peridotite (Frost and McCammon, 2008). Subduction/upwelling processes would perturb mantle oxygen fugacity regimes and cause its local increase or decrease. We show significant increase of solidus temperatures in peridotite and eclogite coexisting with reduced CH₄-H₂O fluid relative to the systems with oxidized H₂O-CO₂ fluid. We argue that redox melting by change of oxidation state across a mantle section, a phase transition, or lithosphere-asthenosphere boundary can be dominant melting process in the deep Earth's interior.

Keywords: upper mantle, peridotite, eclogite, oxidation state, C-O-H fluid