

Natural diamond formed by chemical vapour deposition CVD

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More than 20 years ago Russian geologists reported diamond in bedrock in recent lavas from the active Avacha volcano within the Kamchatka Peninsula (Baikov et al., 1995). These diamonds are aggregates of micro- to nanocrystalline diamond a few hundred micrometre in size. In a recent paper these Kamchatka diamonds have been attributed as carbonado-like diamonds (Kaminsky et al., 2016). However, TEM studies on several of the diamond aggregates have demonstrated that these diamonds have been crystallized via gas phase condensation during volcanic activity. The characteristic microstructure of these diamonds, such as extremely dense twinning with partially very high dislocation density and very high porosity between grains suggests a CVD process for diamond formation. The pore space between diamond crystals is filled either with tridymite or amorphous SiO₂ and/or Si and SiC or with W-carbide and B-carbide. W-carbide and B-carbide as well as Si and SiC can easily crystallize in a CVD process, which is well known from the synthesis of these compounds.

These diamond aggregates form together with W-, B- and Si-carbide in local microenvironments by gas phase condensation where the necessary highly reducing conditions are provided.

Such kind of diamonds can be identified and discriminated from other natural diamonds by their unique microstructure and phase composition.

Baikov, A.I., Anikin, L.P., Dunin-Barkovsky, R.L., 1995. Find of carbonado in volcanic rocks of Kamchatka. Doklady Akademii Nauk SSSR 343 (1), 72–74 (in Russian).

Kaminsky, F., Wirth, R., Anikin, L.P., Morales, L., Schreiber, A., (2016) Carbonado-like diamond from the Avacha active volcano in Kamchatka, Russia. Lithos, 265, 222 –236.

Keywords: Diamond CVD Volcano

Application of a STXM analysis for diamond in ureilite

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A member of primitive achondrite, ureilite is an ultramafic rock, and contains considerable amount of carbon. Although most carbon in ureilite occurs as graphite, a small amount of diamond accompanies the graphite in some ureilite. The formation mechanism of diamond included in ureilite has been enigmatic for decades. Most diamonds in ureilite are from several nano-meters to micro-meters in size. A specific crystallographic orientation between graphite and diamond was observed in some ureilite. Based on these mineralogical features, most previous studies concluded that diamonds in ureilite were formed by a high-pressure condition induced by planetesimal collision occurred on a parent-body of ureilite [e.g., 1]. On the other hand, many coarse-grained diamonds (~100 micro-meter > across) were found in Almahata Sitta ureilite. Considering mineralogical and isotopic characteristics, it is possible that the coarse-grained diamonds included in Almahata Sitta ureilite formed from a fluid or melt in the deep interior of an ureilite parent-body or through CVD process in the solar nebula [2]. Recently, scanning transmission X-ray microscopy (STXM) has been applied for earth and planetary science field such as environmentology and astrobiology [e.g., 3]. X-ray absorption fine structure (XANES) can be obtained by STXM measurement. A bonding-state of element and chemical species can be clarified from XANES. FIB-assisted STXM measurement with a well-shaped X-ray beam (~30 nm) by a zone plate allows us to conduct functional group analysis and speciation at a specific interesting point. Functional group and speciation mapping images also can be taken by using a precious drive sample stage. The bonding-states of carbon and their 2-D distributions in the graphite-diamond assemblage of ureilite would be a clue for diamond formation mechanism. In addition, the bonding-state and chemical species of impure elements such as iron and nitrogen included in the graphite-diamond assemblage could constrain pressure, temperature and oxygen partial pressure conditions at a place where diamond formed. Accordingly, we have tried to adopt FIB-assisted STXM measurement for diamond in ureilite. A part of the coarse-grained diamond in Almahatta Sitta ureilite was excavated by FIB for STXM measurement, and became a foil. STXM measurement was carried at BL4U, UVSOR. Synthetic graphite and natural terrestrial diamond were also measured as a reference material. XANES of graphite, diamond and amorphous carbon (C-K edges) could be obtained from the foil successfully, and their 2-D distributions were constructed using a dedicated image processing application. The amorphous carbon portion is a deposition (made by a FIB-CVD) to reduce a damage on the foil during FIB thinning. Although the diamond appears to be a single crystal under a TEM image, several isolated (island-like) graphite portions (~100 x 200 nm across) were formed in the diamond. Some isolated graphite portions appear to be arranged along with a diamond {111} plane. The diamond was rimed with thin graphite layers (~100 nm > thickness). It is likely that the graphite is evidence for a transformation from diamond to graphite.

[1] Nakamuta et al., *JMPS*, 111, 252-269, 2016.

[2] Miyahara et al., *GCA*, 163, 14-26, 2015.

[3] Suga et al. under review.

Keywords: Diamond, Ureilite, STXM

Spin crossover of iron in (Mg,Fe)CO₃ ferromagnesite and beyond

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Ferromagnesite [(Mg,Fe)CO₃], an iron-bearing carbonate stable up to 100-115 GPa, is believed to be the major carbon carrier in the earth's lower mantle and play a key role in the earth's deep carbon cycle. Starting ~100 GPa, ferromagnesite goes through a complicated structural transition. The detail of this transition and the atomic structures of high-pressure (Mg,Fe)CO₃ phases are still highly debated. Here, we use the local density approximation + self-consistent Hubbard U (LDA+ U_{sc}) method to study the iron spin crossover in ferromagnesite with a wide range of iron concentration (12.5-100%). Our calculation shows that this mineral undergoes a crossover from the high-spin (HS) ($S = 2$) to the low-spin (LS) ($S = 0$) state at around 45-50 GPa, regardless of the iron concentration [1]. The intermediate-spin ($S = 1$) state is energetically unfavorable and not involved in spin crossover. The anomalous changes of volume, density, and bulk modulus accompanying the spin crossover obtained in our calculation are in great agreement with experiments. Our calculation also predicts that an abrupt change of the iron nuclear quadrupole splitting, from 2.8 mm/s to 0.3 mm/s, can be observed in Mossbauer spectra at 45-50 GPa as a signature of the HS-LS crossover. Based on these accurate results, I will also discuss why the LDA+ U_{sc} method is necessary to make reliable predictions regarding the structural transition of iron-bearing carbonates in the earth's deep lower mantle, a subject of great geophysical and geochemical interest.

[1] Han Hsu and Sheng-Chieh Huang, Phys. Rev. B **94**, 060404(R) (2016).

Keywords: spin crossover, carbonate, magnesite, first-principles, Mossbauer

New stable members at the phase diagram of CaCO₃ at pressures to 35 GPa

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We determined phase transitions in CaCO₃ at pressures up to 35 GPa and high-temperatures using in situ X-ray diffraction and synchrotron radiation combined with multianvil technique or diamond anvil cell. In addition to geological importance, this investigation has crystal-chemical and fundamental aspect as in this region enigmatic phase transitions from aragonite to disordered calcite or other phases takes place (Suito et al., 2001; Ishizawa et al., 2013). In present experiments we observed transition of aragonite to presumably disordered calcite phase at 1 to 5 GPa and 1273-1473 K, however at 8 GPa and higher temperature we observed transition to new phase, which we tentatively named disordered aragonite. At 14 GPa and 19 GPa we observed aragonite transition into two new different phases at 1773 K. At 30 GPa transition to new structure occurred at 1773-1873 K. An intermediate stable/metastable phase was also observed at 1373-1773 K and 30 GPa. The structures of the new phases were not refined at present, however, they were characterized using orthorhombic symmetry. At 30 GPa new phase may be similar with P2₁c-I phase, predicted by *ab initio* computations (Pickard and Needs, 2015). In addition, we determined melting line of phases in the CaCO₃ system, which is flat above 6-7 GPa and at 30 GPa it was 200 K lower than previously reported. In this study we significantly improved knowledge of CaCO₃ phase diagram, which may be important for thermodynamic calculations of chemical reactions involving carbonate phases relevant to the deep mantle. Indeed, additional refinement of new phases may be needed because it was not possible to quench them to ambient conditions.

Keywords: carbonate, high pressure, mantle, phase diagram

A Revised Budget for Sedimentary Carbon Subduction during the Cenozoic

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Carbon plays a central role in governing the climate and biosphere of Earth, yet quantification of carbon's long-term cycling from the mantle to the surface remains contentious. Sedimentary carbon represents a significant part of the budget and can be recycled to the mantle if underthrust in subduction zones. I estimate that ~60 Mt/yr is presently being subducted below the outer forearc, 80% in the form of carbonate carbon, significantly more than previously estimated (~20-25 Mt/yr). Sedimentary carbon represents around two thirds of the total carbon input at the trenches. An additional 7 Mt/yr is averaged over the Cenozoic as a result of passive margin subduction during continental collision (~83% CaCO₃). This revision brings the input and output budgets within the range of uncertainty. Degassing from arc volcanoes and forearcs totals ~55 Mt/yr. When carbon in hydrothermal veins in the altered oceanic crust and serpentinized upper mantle is accounted for a net flux to the mantle appears likely. The efficiency of carbon subduction is largely controlled by the carbonate contents of the sediment column, and is partly linked to the latitude of the trench since that controls carbonate production. Accretionary margins are the biggest suppliers of carbon to the mantle wedge, especially Java, Sumatra, Andaman-Burma and Makran, reflecting the inefficiency of offscraping, the thickness of the subducting sediment and the trench length. The Western Pacific trenches are negligible sinks of sedimentary carbon. Increases in deep-sea carbonate in the Oligocene and Mid Mesozoic had a large impact on the subduction budget, increasing it greatly compared to earlier times.

Keywords: Subduction, Carbon, Sediment geochemistry

CO₂ sequestration in ophicarbonates and listvenites from Chinese southwestern Tianshan: insight into the deep carbon cycling in subduction zones

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Subduction zones play a significant role in regulating the carbon fluxes in solid earth by carrying shallow carbonated oceanic rocks into the deep mantle. Carbonated serpentinite / serpentinitized mantle peridotite (ophicarbonate), in spite of not a very crucial part of the global carbon budget compared with the two others (carbonated sediments and carbonated basaltic oceanic crust) owing to its limited volume proportion, show great potential for CO₂ capture and storage (CCS). Ophicarbonates, in southwestern Tianshan (China) HP-UHP metamorphic belt, could be divided into two different types based on their inside carbonate phases (such as magnesite and dolomite). Field occurrence, petrography, major and trace element concentrations, carbonate C and O isotopic compositions and whole-rock Sr isotopic studies indicate distinct origins of the two types of ophicarbonates: (a) CO₂-bearing seawater hydrothermal alteration (S-ophimagnesite) and (b) high pressure COH-Ca fluids metasomatism (M-ophidolomite). High pressure COH fluids, produced by decarbonation reactions and (or) carbonate dissolution of subducted S-ophimagnesite during their peak metamorphic temperature (530~590°C), transfer upwards into the subduction channel and induce the blueschist-facies overprint in eclogites with the release of Ca. Then, the combined COH-Ca fluids in fluid channel, in turn, metasomatize slab - interface mantle rocks to form the M-ophidolomites and thermodynamic phase equilibrium modeling defines the pressure at 18.5~23.5kbar. This implies high pressure CO₂ sequestration in serpentinite could prevent the CO₂-bearing fluids from directly transporting upwards into the mantle wedge. In addition, the occurrence of through-going chrysotile + magnesite veins in serpentinites indicates that carbonic fluids could be mobilized at relatively low P and T conditions as well and the end product of metasomatism by these carbonic fluids is called listvenite, which refers to the fully carbonated serpentinite. Isotopic compositions (C, O and Sr) indicate that CO₂-bearing fluids responsible for the formation of listvenite may originate from the previous S-ophimagnesite and M-ophidolomite during their retrograde exhumation. We infer that the formation of listvenite (P≈5kbar, T≈350°C) are closely related to the process of a second serpentinitization with rodingization (P=4~8.5kbar, T=200-410°C) in southwestern Tianshan (China) based on the compilation of previous researches and our field observation, demonstrating that carbonate dissolution could occur not only at high pressure but also at a low pressure and temperature condition during the exhumation of the subducted slab. We stress that the content of initial carbon uptake in oceanic altered peridotite determined only by analogy of carbon content in exhumated ophicarbonates could be underestimated, because decarbonation and (or) carbonate dissolution exist extensively in ophicarbonates, even at low P and T conditions.

Keywords: ophicarbonate, listvenite, CO₂ sequestration, Tianshan, China