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 SiO_2 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.

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Keywords: Diamond CVD Volcano

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Application of a STXM analysis for diamond in ureilite
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.

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キーワード：Diamond、Ureilite、STXM
Keywords: Diamond, Ureilite, STXM

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Spin crossover of iron in $(Mg,Fe)CO_3$ ferromagnesite and beyond

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Ferromagnesite [$(Mg,Fe)CO_3$], 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 $(Mg,Fe)CO_3$ 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

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New stable members at the phase diagram of $CaCO_3$ at pressures to 35 GPa

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We determined phase transitions in $CaCO_3$ 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 $P2_1c$-I phase, predicted by *ab initio* computations (Pickard and Needs, 2015). In addition, we determined melting line of phases in the $CaCO_3$ 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 $CaCO_3$ 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

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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% $CaCO_3$). 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

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CO_2 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 / serpentinized 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 CO_2 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) CO_2-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℃), 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 CO_2 sequestration in serpentinite could prevent the CO_2-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 CO_2-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℃) are closely related to the process of a second serpentinization with rodingization (P=4~8.5kbar ,T=200-410℃) 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 subduted 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

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Phase relation in $MgCO_3$-SiO_2 system up to the lowermost mantle

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Diamond is an evidence for deep carbon in the Earth. Some diamonds are considered to have originated at various depth ranges from the mantle transition zone to the lower mantle (e.g., Brenker et al., 2007; Harte and Richardson, 2012). These diamonds from ‘super-deep’ regions have been paid attention because they are possible to carry significant information about the interior of the Earth (e.g., Pearson et al., 2014). We have to take account of an unusual environment to form such diamonds when interpreting information from super-deep diamonds. However, we do not have enough clues to speculate processes or environments of super-deep diamond formation.
Subduction has been considered to be related to diamond formation in the lower mantle (e.g., Harte, 2010), and a reaction of $MgCO_3$ and SiO_2 was suggested to form diamond in slabs descending into the lower mantle (Seto et al., 2008; Takafuji et al., 2006). Therefore, we determined the phase relations in an $MgCO_3$-SiO_2 system up to 152 GPa and 3100 K in order to reveal an origin of super-deep diamonds. Seto et al. (2008) suggested that a reaction between $MgCO_3$ magnesite and SiO_2 stishovite could react with each other in the lower mantle in hot slabs and might subduct to the lowermost mantle in cold slabs without any reactions. However, their experimental results were limited to the middle lower mantle conditions up to ~80 GPa. We extended the pressure range to the lowermost mantle and estimated their reaction up to the lowermost mantle.
We used a double-sided laser-heated diamond anvil cell (LHDAC) combined with in situ synchrotron X-ray diffraction at beamline BL10XU of Spring-8 in Hyogo, Japan. Starting materials were a natural magnesite and a reagent quartz. They were ground to >10 μm in diameter and mixed 1:1 by mole fraction using agate mortar. We loaded the powder mixture into a sample chamber in a tungsten gasket which was pre-compressed to 40–80 μm in thickness and drilled a 30–100-μm hole in diameter. Culet diameters of diamond anvils used were between 100 and 350 μm. A Size of a sample chamber was decided based on a culet diameter of anvils. Double-sided laser heating was conducted using a fiber laser equipped at BL10XU. We used Pt powder, foil or doughnut as a laser absorber. Experimental pressures were determined using a thermal equation of state of Pt (Fei et al., 2007) and thermal pressures were calculated using Mie-Grüneisen-Debye model (e.g., Fei et al., 1992). XRD patterns were analyzed using IPAnalyzer and PDIndexer software (Seto et al., 2010).
Magnesite reacted with stishovite or $CaCl_2$-type SiO_2 to form $MgSiO_3$ bridgmanite and maybe CO_2 above ~2000 K. These results almost corresponded to Seto et al. (2008) below 80 GPa. The phase relation was drastically changed above 80 GPa: diamond and bridgmanite were observed below 2000 K near 80 GPa and the reaction temperature seemed to gradually increase above 80 GPa. $MgCO_3$ was reported to transforms from magnesite to a high-pressure polymorph, phase II, above 82 GPa (Oganov et al., 2008). We actually observed $MgCO_3$ phase II above 80 GPa and at high temperature, and thus the phase transition of $MgCO_3$ might be related to the change of the phase relation.
We speculate a reaction between $MgCO_3$ and SiO_2 in a subduction process based on the present phase diagram. $MgCO_3$ and SiO_2 can react in hot or cold slabs up to 1900-km depth in the middle lower mantle, which forms high-pressure CO_2 polymorph or diamond. On the other hand, $MgCO_3$ and SiO_2 are possible to subduct up to the lowermost mantle in a very cold slab. Their reaction is expected at the lowermost

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mantle due to heating from the core in this case. Therefore, their reaction in a cold subduction can explain a formation process of some super-deep diamonds having an especially deep origin (e.g., Harte and Richardson, 2012; Hayman et al., 2005; Wirth et al., 2014).

キーワード：菱苦土石、珪酸鉱物、ダイヤモンド、レーザー加熱式ダイヤモンドアンビルセル、下部マントル
Keywords: magnesite, silica minerals, diamond, LHDAC, lower mantle

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High-pressure study of coronene: phase transitions, oligomerization, decomposition and thermal expansion

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Coronene $C_{24}H_{12}$ is a polycyclic aromatic hydrocarbon (PAH) consisting of six benzene rings. PAHs are believed to be the most abundant organic molecules in the Universe (Ehrenfreund and Charnley, 2000; Tielens, 2008) possibly due to electron delocalization over their carbon skeleton, which makes them remarkably stable (Ehrenfreund and Charnley, 2000). Coronene was found in hydrothermal (Echigo et al., 2007) and metamorphic rocks (Sawada et al., 2008) as well as in meteorites (e.g. Oro et al., 1971). Moreover, PAHs have been identified as inclusions in garnet, olivine, and diamond from mantle xenoliths in kimberlite pipes (e.g. Garanin et al., 2011; Kulakova et al., 1982). At 300 K and ambient pressure coronene possesses the space group $P2_1/a$ (Fawcett and Trotter, 1966). Two high-pressure phase transitions of coronene at 1.5 and 12.2 GPa were determined by Jennings et al. (2010). High-pressure phases were identified as monoclinic (1.5 *P* 12.2 GPa) and orthorhombic (*P* 12.2 GPa) crystal structures with space groups of $P2/m$ and *Pmmm*, respectively (Zhao et al., 2013).
Here we performed high-pressure experiments using multianvil apparatus and DAC. We observed phase transition ($P2_1/a$-$P2/m$) between 0 and 0.9 GPa. Compressibility parameters of coronene phase $P2/m$ were defined in the pressure range of 0.9-8.1 GPa at 300 K as K_0 = 13.0(3) GPa, K_0' = 7 at V_0 = 795.5 Å^3 using Vinet EOS (Vinet et al., 1987); the thermal expansion coefficient was found to be low at 2.0-7.5 GPa and 473-873 K (about 10^{-5} K^{-1}). The same low thermal expansion coefficient at P > 3 GPa was defined previously for naphthalene $C_{10}H_8$ (Likhacheva et al., 2014).
Coronene decomposition was determined in the pressure range of 2.0-15.5 GPa between 900-1000 K. Coronene decomposition products consist of nanocrystalline graphite, amorphous carbon and diamond with trans-polyacetylene lying along the grain boundaries. At lower temperatures (500-773 K) we observed significant oligomerization of coronene by MALDI measurements. Coronene oligomer formation occurs via PAH dehydrogenation and successive fusion of the initial hydrocarbon molecules through C-C bond formation. Based on our results and previous experimental study at ambient pressure (Talyzin et al., 2011) we have identified PT diagram of coronene phase transitions, oligomerization and decomposition parameters to 16 GPa and 1000 K (Fig. 1). Defined coronene phase diagram is extremely important for understanding the planet accretion by carbonaceous chondrites.

Fugure 1. PT-diagram of coronene with phase transitions, oligomerization and decomposition parameters. Shaded area is a coronene oligomerization field.

Keywords: aromatic hydrocarbons, carbon cycle, planetary interiors

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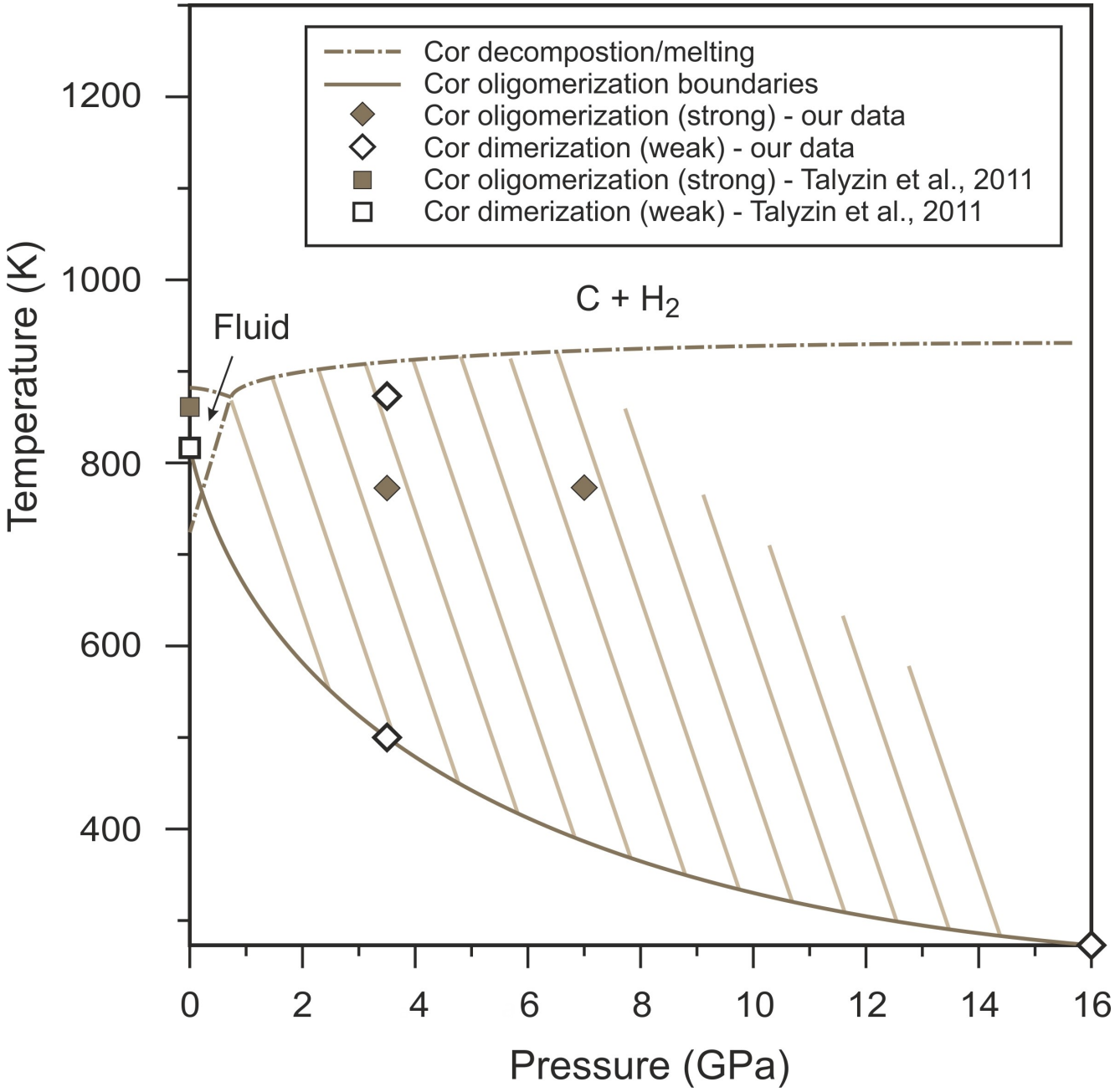

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Pressure-induced phase transitions of vaterite, a metastable phase of $CaCO_3$

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Calcium carbonate plays an important role in global carbon cycle. Calcium carbonate has three polymorphs, calcite, aragonite and vaterite. Vaterite is a meta stable phase and no systematic experiments on the behavior under high pressure have been condcuted so far. In this study, pressure-induced phase transitions of vaterite, a metastable phase of $CaCO_3$, were observed from Raman spectra and X-ray diffraction patterns at high pressure using diamond anvil cells at room temperature. Pressure dependence of Raman peaks assignable to the symmetric stretching vibration modes of carbonate ion indicated the phase transitions of vaterite. At 4.3 GPa, vaterite (vaterite I) transformed to a high-pressure form of vaterite (vaterite II). With increasing pressure, a part of vaterite II gradually transformed to calcite III, and the remainder of vaterite II transformed to another new phase (vaterite III). The phase transition from vaterite II to calcite III was irreversible, and calcite III back-transformed to calcite I during decompression. Moreover, at the pressures higher than 13.1 GPa, several diffraction spots were observed on an imaging plate, indicating another phase transition from vaterite III to a phase having coarse grains (vaterite IV). Our results indicate that vaterite undergoes more complex phase transitions at high pressure than other polymorphs of calcium carbonate, calcite and aragonite. These phase transitions of vaterite will open a window to understanding phase transitions of metastable minerals at high pressure.

キーワード：ファーテライト、炭酸カルシウム、高圧、相転移
Keywords: vaterite, calcium carbonate, high pressure, phase transformation

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Effect of alkalis on the reaction of clinopyroxene with Mg-carbonates at 6 GPa: Implications for partial melting of carbonated lherzolite

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The reaction between clinopyroxene and Mg-carbonate is supposed to define the solidus of carbonated lherzolite at pressures exceeding 5 GPa. To investigate the effect of alkalis on this reaction, subsolidus and melting phase relations in the systems $CaMgSi_2O_6$ + $2MgCO_3$ (Di + 2Mgs), $CaMgSi_2O_6$ + $NaAlSi_2O_6$ + $2MgCO_3$ (Di + Jd + 2Mgs), $CaMgSi_2O_6$ + $Na_2Mg(CO_3)_2$(Di + Na_2Mg), and $CaMgSi_2O_6$ + $K_2Mg(CO_3)_2$(Di + K_2Mg) have been examined at 6 GPa. The results are summarized in Fig. 1. The Di + 2Mgs system begins to melt at 1400 ˚C via the approximate reaction $CaMgSi_2O_6$ (clinopyroxene) + $2MgCO_3$ (magnesite) = $CaMg(CO_3)_2$ (liquid) + $Mg_2Si_2O_6$ (orthopyroxene) leading to essentially carbonate liquid (L) with composition of $Ca_{0.56}Mg_{0.44}CO_3$ + 3.5 mol% SiO_2. The initial melting in the Di + Jd + 2Mgs system occurs at 1350 ˚C via the reaction $2CaMgSi_2O_6$ (clinopyroxene) + $2NaAlSi_2O_6$ (clinopyroxene) + $8MgCO_3$ (magnesite) = $Mg_3Al_2Si_3O_{12}$ (garnet) + $5MgSiO_3$ (clinopyroxene) + $2CaMg(CO_3)_2$ (liquid) + Na_2CO_3 (liquid) + $3CO_2$ (liquid and/or fluid) yielding the carbonate liquid with approximate composition of $10Na_2CO_3$·$90Ca_{0.5}Mg_{0.5}CO_3$ + 2 mol% SiO_2. The systems Di + Na_2Mg and Di + K_2Mg start to melt at 1100 and 1050 ˚C, respectively, via the reaction $CaMgSi_2O_6$ (clinopyroxene) + $2(Na\ or\ K)_2Mg(CO_3)_2$ (solid) = $Mg_2Si_2O_6$ (orthopyroxene) + $(Na\ or\ K)_4CaMg(CO_3)_4$ (liquid). The resulting melts have alkali-rich carbonate compositions of $Na_2Ca_{0.4}Mg_{0.6}(CO_3)_2$ + 0.4 mol% SiO_2 and $43K_2CO_3$·$57Ca_{0.4}Mg_{0.6}CO_3$ + 0.6 mol% SiO_2. These melts do not undergo significant changes as temperature increases to 1400 ˚C retaining their calcium number, high Na_2O, K_2O and low SiO_2. We suggest that the clinopyroxene–Mg-carbonate reaction controlling the solidus of carbonated lherzolite is very sensitive to the carbonate composition and shifts from 1400 ˚C to 1050 ˚C at 6 GPa yielding K-rich carbonate melt if subsolidus assemblage contains $K_2Mg(CO_3)_2$ compound. Such a decrease in solidus temperature has been observed previously in the K-rich carbonated lherzolite system. Although a presence of eitelite, $Na_2Mg(CO_3)_2$, has a similar effect, this mineral cannot be considered as a potential host of Na in carbonated lherzolite as far as whole Na added into the system dissolves as jadeite component in clinopyroxene if bulk Al/Na 1. The presence of jadeite component in clinopyroxene has little impact on the temperature of the solidus reaction decreasing it to 1350 ˚C at 6 GPa.
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Fig. 1. Modal abundances of phases present as a function of temperature in the systems $CaMgSi_2O_6$ + $2MgCO_3$ (a), $CaMgSi_2O_6$ + $NaAlSi_2O_6$ + $2MgCO_3$ (b), $CaMgSi_2O_6$ + $Na_2Mg(CO_3)_2$ (c), and $CaMgSi_2O_6$ + $K_2Mg(CO_3)_2$ (d) at 6.0 GPa. Modes are in mol% were determined from the bulk compositions of starting mixtures and compositions of phases measured by electron microprobe.

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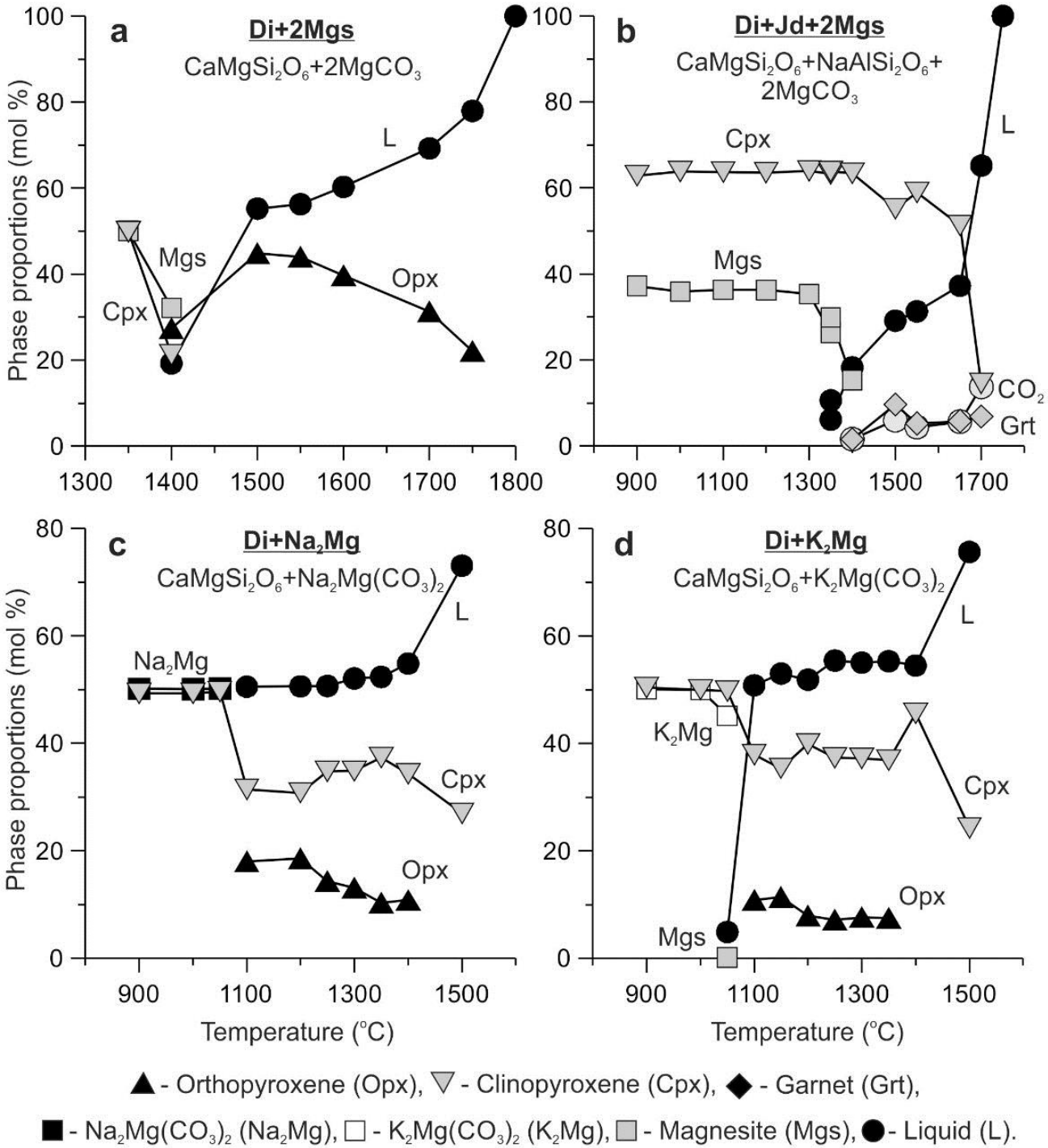
キーワード：アルカリ、単斜輝石、マグネシウム炭酸塩、高温高圧、ソリダス、相平衡
Keywords: Alkalis, Clinopyroxene, Mg-carbonates, High pressure and temperature, solidus, phase relations



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Existence of Carbon in the Earth’s inner core

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Carbon is an important candidate for light element in the Earth’s core. There have been contradictory results on the stability of Fe–C compounds, such as Fe_3C and Fe_7C_3 under the core conditions. We observed Fe_3C melts incongruently to form Fe_7C_3 and liquid at 4200 K and 200 GPa, Additionally, it was shown that the C content of the liquid coexisting with Fe_7C_3 decreases and the Fe–Fe_3C eutectic composition shifts toward the Fe-rich direction with increasing pressure. The present result revealed that Fe_3C and Fe_7C_3 are plausible constituents of the inner core, with a possible layering of Fe_7C_3 in the central region and Fe_3C in the outer region of the inner core formed during cooling of the core. We also conducted the equation of state and sound velocity measurements at high pressure and temperature by using XRD and IXS measurements at Spring-8. The results indicate that the sound velocity of the mixture of Fe-Fe3C is higher than the PREM inner core under the Earth’s core conditions. Thus, it is difficult to explain that the Earth’s inner core is composed of only a Fe–Fe_3C mixture. Since the inner core temperature is very close to the eutectic temperature of the Fe-Fe_3C system, pre-melting effect of Fe3C could be important to account for the sound velocity of the PREM inner core.

Keywords: Carbon, Fe3C, Melting relation, equation of state, Sound velocity

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Phase relations and liquid immiscibility in $KAlSi_3O_8$- and $CaMg(CO_3)_2$-bearing systems at 6 GPa: Implications for origin of fibrous diamonds

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The reaction between potassium feldspar (Kfs) and dolomite (Dol) could define the solidus of carbonated pelite below 7 GPa under nominally anhydrous conditions (Grassi and Schmidt, 2011). To investigate this reaction subsolidus and melting phase relations in the systems $KAlSi_3O_8$ + $CaMg(CO_3)_2$ (Kfs + Dol), $KAlSi_3O_8$ + $CaMgSi_2O_6$ + $NaAlSi_2O_6$ + $CaMg(CO_3)_2$ (Kfs + Di + Jd + Dol), and $KAlSi_3O_8$ + Na_2CO_3 + $CaMg(CO_3)_2$ (Kfs + Na_2 + Dol) have been examined at 6 GPa and compared with those established in dry carbonated pelite (DG2).

In the system Kfs+Dol at 1000 ˚C, the subsolidus assemblage consists of Kfs and Dol. Besides, Kfs contains numerous inclusions of $K_2Si_4O_9$ wadeite (K-wad), kyanite (Ky), coesite (Coe). At lower temperature 900 ˚C, Kfs and Dol are not stable and the assemblage includes K-wad, Ky, Coe, aragonite (Arg) and magnesite (Mgs). The system begins to melt at 1100 ˚C via reaction $6KAlSi_3O_8$ (Kfs) + $6CaMg(CO_3)_2$ (Dol) = $2(Ca_n,Mg_{1-n})_3Al_2Si_3O_{12}$ (Grt) + Al_2SiO_5 (Ky) + $11SiO_2$ (Coe) + $3K_2(Ca_{1-n},Mg_n)_2(CO_3)_3$ (L) + $3CO_2$ (F and/or L), where n ~ 0.3-0.4, leading to essentially carbonate liquid, L(C), with composition of $32K_2CO_3{\cdot}68(Ca_{0.63}Mg_{0.37})CO_3$ + 1-2 mol% SiO_2 + 0.5-1 mol% Al_2O_3. Kfs and Dol completely disappear at 1150 ˚C. Starting from 1300 ˚C, immiscible silicate melt, L(S), coexists with L(C). L(S) contains (in mol%): 64 SiO_2, 9 Al_2O_3, 2 MgO, 2 CaO, 11 K_2O, and 12 CO_2. The Grt + Coe + Ky + L(C) + L(S) phase assemblage remains stable up to 1500 ˚C.

Adding Di-Jd clinopyroxene in the Kfs + Dol system does not affect phase relations. At 1000 ˚C, the subsolidus assemblage is Kfs + CPx + Dol. Kfs is partially replaced by K-wad + Ky + Coe assemblage. Above the solidus at 1150 ˚C, Cpx, Grt, Ky, Coe coexist with L(C) [$34(K_{0.92}Na_{0.08})_2CO_3{\cdot}66(Ca_{0.62}Mg_{0.38})CO_3$ + 3 mol% SiO_2 + 1 mol% Al_2O_3]. L(S) appears at 1250 ˚C and contains (in mol%): 67 SiO_2, 7 Al_2O_3, 4 MgO, 4 CaO, 1 Na_2O, 7 K_2O, and 10 CO_2. The Cpx + Grt + Ky + Coe + L(C) + L(S) phase assemblage was established at 1250 and 1350 ˚C, whereas at 1500 ˚C only CPx remains in coexistence with L(C) and L(S). At 900 ˚C in the Kfs + Na_2 + Dol system, the subsolidus assemblage consists of Cpx ($Jd_{87-90}Di_{10-13}$), $(Na_{0.55}K_{0.45})_2Mg_{0.90}Ca_{0.10}(CO_3)_2$ (NaKMg), $(Na_{0.63}K_{0.37})_2(Ca_{0.93}Mg_{0.07})_3(CO_3)_4$ ($NaKCa_3$), Coe, and Mgs. As temperature increases to 1000 ˚C, NaKMg and $NaKCa_3$ disappear, while minor amount of Mgs and Coe remains. The sample consists of Cpx ($Jd_{78}Di_{22}$) and L(C) [$44(Na_{0.51}K_{0.49})_2CO_3{\cdot}56Ca_{0.57}Mg_{0.43}CO_3$]. Thus, an addition of Na_2CO_3 into the Kfs+Dol system yields formation of Cpx, NaKMg and $NaKCa_3$ at the expense of K-wad, Ky, Mgs, and Arg. Molar abundances of phases and their compositions change slightly with further temperature increase up to 1500 ˚C. Thus, Na_2CO_3 causes redistribution of K_2O into carbonate phases, whereas SiO_2 and Al_2O_3 are consumed on jadeite formation: Na_2CO_3 + $KAlSi_3O_8$ (Kfs or L(S)) = $NaAlSi_2O_6$ + SiO_2 + $NaKCO_3$ (L(C)). As a result, immiscible L(S) does not appear in this system.

In dry carbonated pelite (DG2), subsolidus assemblage established at 1000 ˚C is represented by Cpx, Grt, Ky, Coe, Dol, and $K_2Ti_{1-n}Si_{3+n}O_9$ wadeite. Two immissible liquids were established at 1350 and 1500 ˚C in coexistence with Cpx, Coe, Grt, Ky and CO_2 fluid. At 1350 ˚C, L(S) contains (in mol%): 56.6 SiO_2, 1.8 TiO_2, 8.3 Al_2O_3, 2.9 FeO, 1.3 MgO, 3.2 CaO, 1.4 Na_2O, 9.7 K_2O, and 15.0 CO_2, whereas L(C) composition is $(K_{0.74}Na_{0.26})_2(Ca_{0.58}Mg_{0.18}Fe_{0.24})_4CO_3$ + 4.2 mol% SiO_2 + 1.7 mol% TiO_2 + 1.4 mol% Al_2O_3.

The obtained immissible L(C) and L(S) resemble compositions of melt inclusions in fibrous diamonds worldwide. Thus, the K-aluminosilicate and K-Na-rich carbonatite melts entrapped by fibrous diamonds

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could be derived by liquid immissibility during partial melting of carbonated pelite subducted down to 180 km depth and heated to 1300 ˚C or higher temperature.
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Keywords: Phase relations, Liquid immiscibility, KAlSi3O8, CaMg(CO3)2, fibrous diamonds

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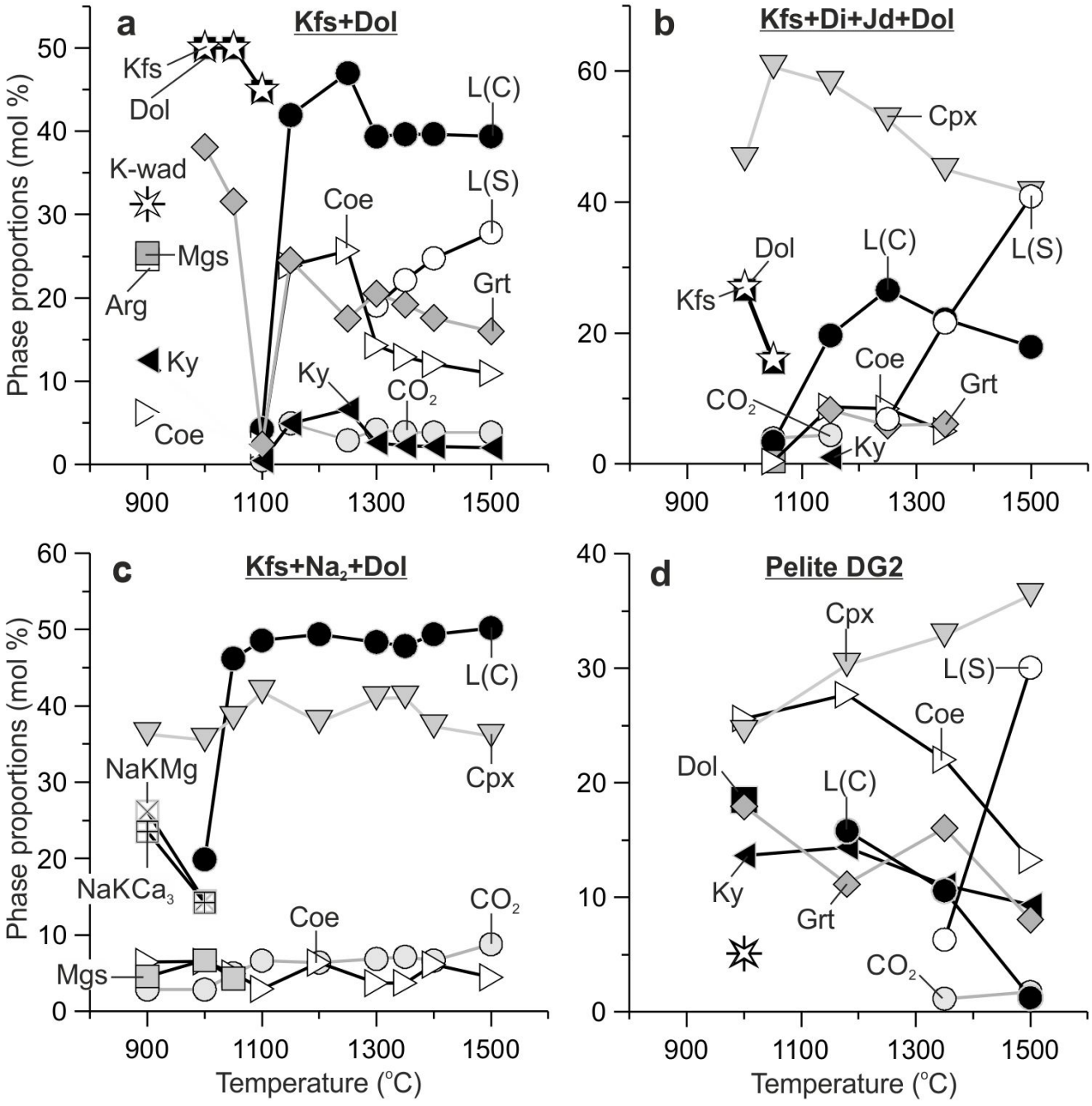

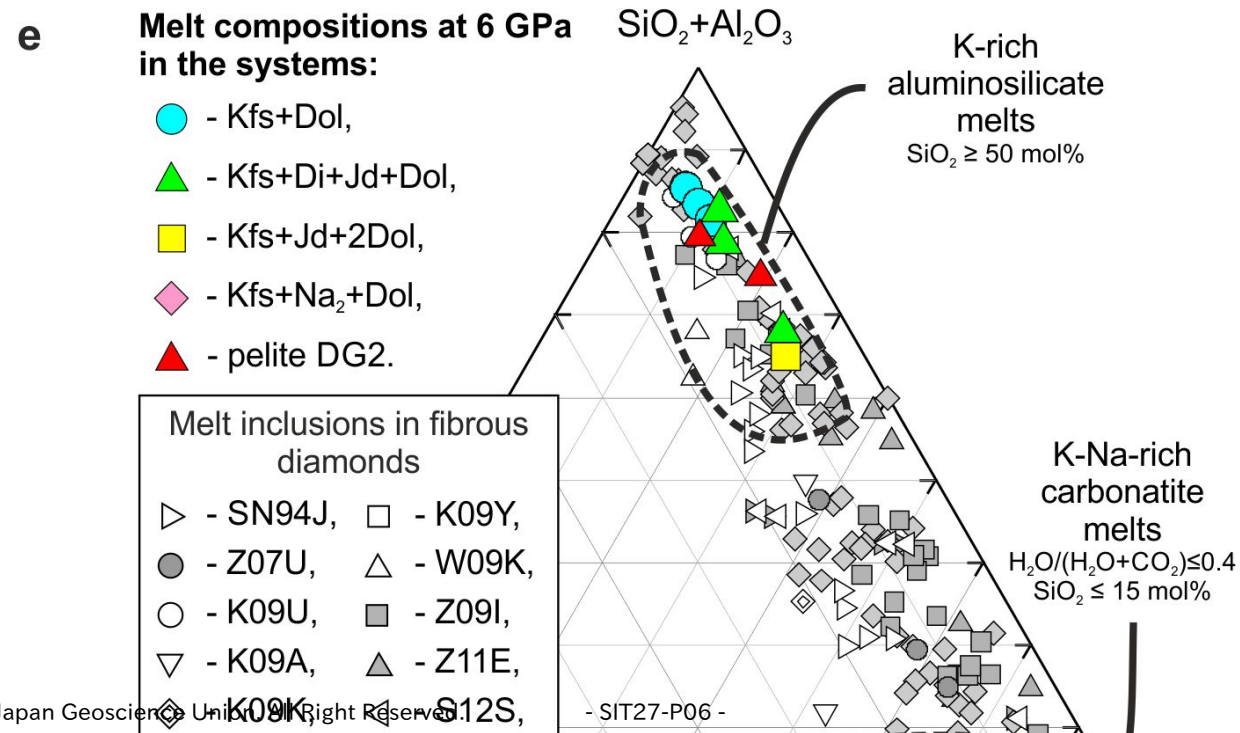

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