New Frontier in Studying Chemistry under Extreme Conditions: Applications of FIB Technology

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2014-04-15
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Application of a FIB system to ultra-high-pressure Earth and planetary sciences

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A FIB system allows us to conduct in-situ micro-meter size sampling for TEM, SEM, XRD, SIMS and STXAM analyses. We installed a FIB system for our laboratory in 2005. Our laboratory has applied FIB-assisted TEM observation, -FE-SEM observation and synchrotron XRD analysis for an ultra-high pressure synthetic sample recovered from a laser-heated diamond anvil cell (LHDAC) experiment and a natural high-pressure polymorph included in a heavily shocked meteorite. A conventional FIB sample preparation technique “lift-out method” was modified for the reliable analysis of a LHDAC sample. Our modified lift-out method allows us to thin the entire vertical section of the LHDAC sample. In addition, an EDS attached to scanning TEM (STEM) allows us to depict its complicate texture using an element distribution map besides a STEM image. We identified many kinds of natural high-pressure polymorphs from heavily shocked meteorites and Apollo samples through combined FE-SEM observation and FIB-assisted TEM and XRD analyses. These discoveries uncovered meteoroid impact histories occurred on an asteroid and planet, which have been overlooked so far.
The focused ion beam (FIB) of Ga+ ions is a relatively new technique in geosciences used for thin foil preparation. FIB indeed facilitates in situ lift out, milling and subsequent TEM examination of precise regions of interest on a large variety of samples, including recovered high-pressure samples. This technique has thus been logically extended to the lift out of diamond anvil cells laser-heated samples and other high-pressure samples. But the range of applications is much more than that. In this presentation, I will show different applications of FIB in the high-pressure field. This encompasses the recovery of high-pressure samples, the patterning and micro machining of diamond-anvils, the micro machining of gaskets and high-pressure cell loadings as well as the development of 3D imaging.
Chemistry of metal-silicate reactions in Earth's deep interior

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The present core-mantle-crust structure of the Earth was set by chemical reactions that have taken place since our planet's formation more than 4.5 billion years ago, and continue today. Understanding these chemical reactions requires experimental studies of silicates and metals at the extreme pressure, temperature conditions (>100 GPa, 5000 K) that exist in deep planetary interiors. Advances in electron microscopy, especially FIB sectioning, now permit microanalysis of experimental samples recovered from such conditions. This talk will describe metal-silicate reactions simulating those that occurred deep inside the Earth during its formation and differentiation to silicate mantle and metallic core. The trace element distribution between metal and silicate can be tied to the present day composition of Earth's mantle to provide insight into the conditions of Earth's core formation. Moreover, the observed alloying of silicon and oxygen into the metal is supporting evidence that these two elements make up much of the light element component coexisting with Fe in the core, consistent with geophysical constraints.
Melting experiments in a diamond-anvil cell combined with ex-situ textual and chemical characterizations by FIB/SEM/TEM

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Samples for high-pressure and -temperature experiments in a diamond-anvil cell (DAC) are very small, typically several tens to hundred microns in diameter, and thus synchrotron X-rays are useful for sample characterization in-situ at high pressure. Complementary to such X-ray studies, ex-situ characterization of DAC samples is also very important for three-dimensional textural observations and chemical analyses with high spatial resolution and high precision.

Our group has been working on melting experiments in a laser-heated DAC for both mantle and core materials (e.g., Tateno et al., 2014 JGR; Ozawa et al., 2013 GRL). Quenched molten samples always have specific melting textures, showing quenched liquid, liquidus phase, and subsolidus part. After making a cross section of quenched molten area in a focused ion beam (FIB), chemical compositions of liquid and coexisting solid are obtained by microprobe analyses. We sometimes recognize that the texture of such molten sample becomes more complex with increasing the duration of laser-heating (e.g., due to Soret diffusion for silicate samples). However, very short heating duration like ~1 sec above melting temperature should be long enough for chemical equilibrium between coexisting liquid and solid, considering the fact that the size of a solid phase is very small, typically less than 100 nm in a DAC (Nomura et al., 2011 Nature). I will introduce our recent results of a series of melting experiments on silicates and iron alloys, together with those of time-series experiments.
Constraints on terrestrial accretion and core differentiation from partitioning experiments in diamond anvil cells.

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The distinctive pattern of siderophile elements abundance in the silicate portion of the Earth is a direct consequence of metal separation during core formation. Accordingly, partitioning experiments have been largely used to construct models of Earth's accretion and core differentiation.

The thermodynamic expressions used to constrain the metal-silicate partitioning behavior of siderophile elements were mainly established starting from large volume press experiments that do not allow covering the full range of potential pressure (P) and temperature (T) conditions. Conversely, experimentation in diamond anvil cell (DAC) allows achieving required P-T, but at the price of reduced sample volumes that for long time prevented quantitative determination of metal-silicate partitioning. Only recently, experimental protocols have been developed to effectively link high P-T DAC experimentation with analytical techniques such as focused ion beam device (FIB), electron microprobe, transmission electron microscopes, and NanoSIMS.

Here I will present our advances in both experimental and analytical methods, specifically considering the partitioning of four siderophile elements (Ni, Co, Cr, and V) that have been extensively studied at lower P-T conditions. Results obtained for Ni and Co, highly sensitive to pressure, will be used to estimate the final depth of metal-silicate equilibration. Results obtained for Cr and V, more sensitive to redox conditions, can be use to address core differentiation scenarios and the nature of the accreting materials. The ensemble of these experimental results and literature work, allows discussing the metal-silicate partitioning behaviors of oxygen and silicon and hence to place constrain of light element budget of the Earth's core.
Nanometer-scaled Secondary Ion Mass Spectrometry (NanoSIMS) is the unique analysis facility that has the capability of analyzing isotopes and/or trace elements with a lateral resolution up to 50nm. The Beijing NanoSIMS lab was installed in March, 2011, and the instrument has 7 ion detectors, each equipped with an electron multiplier (EM, for a low counting rate of <10^6 cps) and a Faraday cup (FC, for a high counting rate >10^6 cps). A Cs+ source is applied for analysis of non-metallic elements (e.g. H, C, N, O, Si, S, P), whereas the O- source for metallic elements (e.g. Na, Fe, Mg, Al). However, the O- primary beam size is usually 4 times as large as the Cs+ beam size.

With the NanoSIMS 50L, efforts have been made to prove analytical precision and/or lateral resolution, to meet a wide range of applications. Analysis of water contents were measured in two analysis model, one to obtain the water contents with H isotopic rates, and the other for water and volatile elements (e.g., S, Cl, P). The results were calibrated with a set of standards. Background of H was reduced to <10 ppm, by improving vacuum of the analysis chamber, using high primary beam current and blanking the margins of the analysis area [1]. REE and other trace elements were analyzed for coexisting ringwoodite and olivine in the shock-induced melt veins in meteorites. Sulfur isotopes were analyzed with a precision of 0.2‰ for 10–10 μm, 1‰ for 2–2 μm [2]. Zircon U-Pb and Pb-Pb dating was achieved a precision of 2-3% with a lateral resolution of <5μm (U-Pb) or <3 μm (Pb-Pb) [3].

In order to increase spatial resolution of analysis of metallic elements, we tried to use Cs+ instead of O- primary beam, by counting M16O- ions. To further improve the lateral resolution, samples were analyzed in the image mode, and the interesting areas were selected to calculate the concentrations of elements. A lateral resolution better than 1 μm has been achieved for line scanning profiles, which can be used for measurement of zoned minerals.
Quality of the surface is important for NanoSIMS mapping. FIB was used to prepare very high quality surface of sample. NanoSIMS mapping of FIB slices demonstrated significant improvement of the quality of the ion images, because of reducing topographic effects of the sample surface. Another key factor is the standards. We proposed to synthesize very homogeneous crystals via sintering nanocrystals, and it has been proved successful by the synthesis of calcite crystals [4]. For specific analyses, suitable standards need to be prepared ahead.

References:
Integrated Approach to Investigate the Chemical Compositions and Interior Processes of Planetary Cores

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Terrestrial planet formation starts with small dust grains and ends with differentiated bodies like the Earth with a metallic core. The central question to be address is the chemical composition of the core which links to the temperature and physical state of the core. High-pressure experiments provide crucial data necessary to understand the core formation processes and the chemical composition of the planetary cores. In this talk, I will describe experiments that simulate percolative core formation process, core-mantle differentiation, and inner core crystallization. Using FIB/SEM crossbeam technology, we visualize the core formation process by monitoring the migration of liquid metal in silicate matrix in three dimensions (3D). The new imaging technique provides a powerful tool to precisely determine the critical parameters needed for theoretical modeling and paves the way for researchers to explore planetary core formation processes through experimental simulation combined with visualization. I further examine light element partitioning between solid and liquid iron in both multi-anvil apparatus and the laser-heated diamond-anvil cell. I have established protocols to obtain high-quality partitioning data in the laser-heating diamond-anvil cell combined with FIB/SEM crossbeam technology. The partitioning data obtained at extreme pressures provide additional criteria to explain the observed density and velocity jumps at the inner core boundary.
**Nanomineralogy of Shocked Meteorites: Discovery of New High-Pressure Minerals**

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Nanomineralogy is the study of Earth and planetary materials at nanoscales, focused on characterizing nanofeatures (such as inclusions, exsolution, zonation, coatings, pores) in minerals and rocks, and revealing nanominerals and nanoparticles. With advanced high-resolution analytical scanning electron microscope (FE-SEM with EDS and EBSD), we are now capable to characterize solid materials down to nanoscales easier and faster. Nanofeatures are being identified in many common minerals, providing insights into genesis and physical properties. New minerals and new materials with important geological significance are being discovered at micron to nanoscales.

During our ongoing nanomineralogy investigation of shocked meteorites since 2009, four new high-pressure minerals have been discovered. They are bridgmanite (MgSiO₃-perovskite) from the Tenham L6 chondrite [1], ahrensite (Fe₂SiO₄-spinel) and tissintite ((Ca,Na,□)AlSi₂O₆-clinopyroxene) from the Tissint martian shergottite [2], and liebermannite (KAlSi₃O₈-hollandite) from the Zagami martian shergottite [3]. The findings not only provide new insights into shock conditions and impact processes on small bodies in the early solar system or on Mars, but natural high-pressure minerals found in meteorites also help investigations of phase transformation mechanisms in the deep Earth. Presented here are our discovery stories of the new minerals, demonstrating how nanomineralogy works and plays a unique role in Earth and planetary sciences research.

Pressure Selected Reactivity and Kinetics Deduced from High-Pressure Photochemistry of Ethylene Glycol

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The photon-induced reactivity of liquid ethylene glycol (EG) was investigated in a diamond anvil cell at pressures up to ~ 4 GPa and ambient temperature. The near-UV radiation at \( \lambda = 350 \) nm was employed to photodissociate EG via the two-photon absorption processes. The reaction evolution was monitored as a function of time and the reaction products were characterized by using in situ FTIR spectroscopy. At low initial loading pressures, the IR spectra show two distinctive sets of profile evaluations indicating sequential photo-induced chemical reactions, which are designated as primary and secondary photochemical processes respectively. By careful examination of the characteristic IR bands and possible reaction pathways, over ten species as the primary and secondary reaction products were unambiguously identified. Significantly, we found that one of the photodissociation product CO\(_2\) forms specific clathrate hydrate structures or clusters that are both time and pressure dependent, indicating interesting and unique sequestration behavior of CO\(_2\) at high pressures. Quantitative analysis on selective reaction products allows detailed reaction kinetics involving competitive reaction channels to be probed. In particular, the type and quantity of reaction products as well as the kinetics were found highly pressure dependent. Moreover, the pressure variation of the system along the reaction progression allows the interpretation of possible reaction mechanisms involving different carbon species under high pressures.
The isotopic behaviors of elements under high pressures
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There has been increasing interest recently in the use of metal stable isotopic composition variations for fingerprinting the material from which Earth accreted and for tracing various planetary processes. For instance, the difference in silicon isotopic composition between the meteoritic materials and the Earth has been largely attributed to Core-Mantel separation and segregation of isotopically lightly Si into the Core. First-principle calculations predict isotopic fractionation can occur for many elements between two co-existing minerals even under high-temperature and high-pressure conditions. The isotopic fractionation usually decreases with temperature. However increasing pressure can potentially increase such fractionations especially in cases where phase transition occurs. Conducting high-pressure experiments to study the isotopic behaviors between two co-existing phases, especially between the metal and the silicates has become an active research area of isotope geochemistry, and provide bases for the correct interpretation of the isotopic difference between the meteoritic materials and the Earth. Such types of experiments are also important for understanding the isotopic composition of the deep mantle and the core, as much of the Earth is under pressure.
Application of FIB fabrication and transmission x-ray microscopy in extreme condition

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Exploring properties of matters beyond megabar pressure only within nano scale is being made possible by micro-nano fabrication of new generation diamond anvil cell and modern synchrotron nano probe technology. Preliminary works have been carried out in using FIB to efficiently and precisely fabricate micro anvils of various configurations. Excimer laser micro machining system was used as a supplementary tool for fast anvil fabrication. Transmission x-ray microscopy (TXM), as an in situ direct nano resolution characterization tool, has superior advantages over SEM and TEM in terms of non destruction and void of vacuum, which is more realistic in extreme condition. With fine sample preparation by FIB, formation of iron melt network at lower mantle conditions was studied using 3D TXM techniques. FIB and 3D TXM was also applied in revealing the unique properties of metallic glass in extreme condition.
New insights into the composition of Earth’s deep lower mantle: combining in-situ multigrain analysis with ex-situ composition measurements

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Models of the Earth’s deep interior have been built upon the basic assumption that the lower mantle down to the top of the D" layer mainly consists of perovskite (pv) with nominally 10 mol% Fe. However, seismic observations suggest compositional heterogeneity in the bottom 1000 km of the lower mantle, implying variations in the mineralogical constitution of this region. Our recent study using laser-heated diamond anvil cell (DAC) technology coupled with synchrotron x-ray diffraction (XRD) has demonstrated the disproportionation reaction of (Mg,Fe)SiO\(_3\) perovskite (pv) to a nearly Fe-free pv and an Fe-rich H-phase with a previously unknown hexagonal structure at 95-101 GPa and 2200-2400 K. This finding further complicates the geochemistry and geophysics of the bottom half of the lower mantle. It has been long challenging for structure identification and accurate unit-cell calculations in mineral assemblages when multiple low symmetry phases coexist. Applying the multigrain method to megabar pressure, the crystal chemistry and unit-cell parameters are investigated in-situ at high pressure for each individual phase in lower mantle mineral assemblages. The composition of each phase in the quenched sample is determined by ex-situ FIB/SEM/TEM. The crystal chemistry and phase relations of minerals at high P-T are used to understand the composition and dynamics of the lower mantle.