

Detection of low isotopic ratio of iron in anthropogenic aerosols and evaluation of its contribution to the ocean

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Productivity of phytoplankton affects global carbon cycle, and may also affect the climate. Iron (Fe) is an essential element for phytoplankton, but its solubility is low and much of it is removed as Fe (III) hydroxide. Therefore, it has been reported that phytoplankton growth in the High Nutrient-Low Chlorophyll (HNLC) regions is limited by Fe concentration (Martin and Fitzwater, 1988). Aerosols are important sources of Fe species to the surface seawater. They are classified into anthropogenic and natural ones. Particle sizes of anthropogenic aerosols are generally smaller than those of natural ones because of their different formation processes (Whitby, 1977). Previous studies have shown that high soluble Fe species were included in anthropogenic aerosols (e.g., Takahashi et al., 2013). In terms of Fe isotope composition, Mead et al. (2013) compared Fe isotopic compositions between coarse aerosols ($> 2.5 \mu\text{m}$) and fine ones ($< 2.5 \mu\text{m}$) and suggested that the Fe isotopic composition of finer aerosols (anthropogenic source; $\delta^{56}\text{Fe} = -0.10 \text{‰}$) is lighter than that of coarse aerosols (natural source; $\delta^{56}\text{Fe} = 0.08 \text{‰}$). However, it is possible that the separation of the aerosols at the particle size of $2.5 \mu\text{m}$ cannot fully separate the two sources. The purpose of this study, therefore, was to detect anthropogenic aerosols and measure their Fe iron isotopic compositions. Size-fractionated aerosol samples were collected at Higashi-Hiroshima City using a cascade impactor (particle sizes: $> 10.2 \mu\text{m}$, $4.2 \sim 10.2 \mu\text{m}$, $2.1 \sim 4.2 \mu\text{m}$, $1.3 \sim 2.1 \mu\text{m}$, $0.69 \sim 1.3 \mu\text{m}$, $0.39 \sim 0.69 \mu\text{m}$, $< 0.39 \mu\text{m}$), which could specify the isotopic compositions of anthropogenic Fe. Iron isotopic compositions of bulk aerosols and soluble aerosols for simulated rain water were measured using multi-collector inductivity-coupled plasma mass spectrometry (MC-ICP-MS; Neptune Plus, Thermo Scientific). The chemical species were also identified by employing Fe K-edge X-ray absorption fine structure (XAFS) spectroscopy and their solubility for seawater was evaluated by leaching experiments. As a result, Fe isotopic compositions ($\delta^{56}\text{Fe}$) of larger particles were around $+0.25 \text{‰}$, whereas smaller particles showed lower isotopic composition ($-0.5 \sim -2 \text{‰}$). In addition, smaller particles of soluble component for simulated rain water showed much lower $\delta^{56}\text{Fe}$ values ($\delta^{56}\text{Fe} = -3.9 \text{‰}$) than bulk particles, suggesting that anthropogenic Fe has much lower isotopic compositions. The value was the lowest among other environmental samples reported so far. This means that the large isotopic fractionation of anthropogenic aerosols occurs when Fe species evaporate. $\delta^{56}\text{Fe}$ value of the remaining materials after the water-extraction experiment was calculated using the values of bulk Fe and soluble Fe, and it was revealed to be similar to that of earth's crust ($+0.25 \text{‰}$). This means that the anthropogenic Fe in aerosol is completely soluble and has very low $\delta^{56}\text{Fe}$. It has been suggested that Fe in aerosol contributed significantly to the supply of Fe in surface seawater. When considering Fe isotopic budget for surface seawater using the value measured in this study as a $\delta^{56}\text{Fe}$ of anthropogenic aerosol (-3.9‰), it is suggested that aerosols is main source of Fe dissolved in the surface seawater.

Keywords: iron isotopic composition, aerosol, anthropogenic iron

The evaluation for ion trajectory and transmittance of Laser Ionization Mass nanoScope (LIMAS)

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In analyses of interstellar materials in meteorites, target material sizes are generally smaller than 100 nm. Therefore, analytical method with high sensitivity and a high mass resolution is required for sub-microscale in-situ analysis.

We have developed a tunnel ionization time of flight sputtered neutral mass spectrometer: LIMAS. This apparatus mainly consists of a focused ion beam system (Ga-FIB), a femtosecond (fs) laser system and a MULTi-TURN time-of-flight Mass spectrometer II (MULTUM II) (Ebata et al., 2012).

The fs laser is used for tunnel ionization of neutral particles that are sputtered by the Ga-FIB beam. Because the energy density of the fs laser is more than 2×10^{15} W/cm², all of elements can be ionized.

Based on the ion optics of MULTUM II, time of flight of the ion can be infinitely extended to get high mass resolution.

In this study, we operated voltages of einzel lenses and deflectors in an ion injection optics based on the result of an ion optics simulation using SIMION. A parameter setting of MULTUM II was based on (Okumura., 2005). As a result, we evaluated mass resolving power and the transmittance of fs laser induced ions in the MULTUM II.

Sample surface was kept on ground state, and the acceleration voltage was fixed at -4 kV. The voltages of the ion injection optics and MULTUM II were floated on -4 kV. Then, post-ionized positive ions were injected into MULTUM II. The ion injection optics consists of three stage injection and acceleration lens, two einzel lenses, and two sets of two direction deflectors. The ~30% of ions were injected into MULTUM II from the result of the ion simulation. We operated parameters in the ion injection optics for an ion was focused on a cycle starting focal point in MULTUM II. Focal point in ion injection optics of ion trajectory moves to sample position side to become a large aperture angle by the high electrode voltage of injection lenses. The focal point in MULTUM II was determined by the aperture angle and voltage of the einzel lenses.

The above eight parameters were changed and adjusted based on the result of the ion simulation. Toroidal fields in MULTUM II were optimized by operating electrical potential valance among the fields.

After the optimize of the electrode voltages, we obtained the mass resolving power of more than 27,000 (²⁴Mg⁺, number of cycle: 100 cycles in MULTUM II) without laser (SIMS mode), and of more than 40000 (²⁴Mg⁺, number of cycle: 100 cycles) with laser (SNMS mode). The ion transmittance in MULTUM II was evaluated. Relationships of the ion transmittance of MULTUM II with the number of cycles are as follows. Assuming that the ion intensity of linear mode (from sample surface to the detector) is 100%, the ion transmittances at 20 cycles are 28% and 5% for SIMS and SNMS modes, respectively. The transmittances of 100 cycles are 26% and 2% for SIMS and SNMS modes, respectively. The decreasing of the intensity can be explained by two factors. One is that the half of the injected ions cannot meet a condition of the ion trajectory of MULTUM II. Another is ion collision with residual gas molecules in MULTUM II.

Keywords: TOF-MS, SNMS, fs-laser

A current status of high precision in situ isotopic analysis by SIMS in JAMSTEC and perspectives for future researches

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Secondary Ion Mass Spectrometry (SIMS) has a unique capability of isotopic and elemental measurements for micrometer-scale distributions in region-of-interests in variety of samples. With this unique capability, researches with SIMS brought out new evidence for understanding of processes occurred under extreme environment (e.g., Earth's earliest crust formation, reactions in Earth's deep interior, and high temperature processes in the solar nebula) and processes caused by biological/biochemical activities (e.g., biomineralization, metabolic functions of microorganisms).

While SIMS is a destructive technique, required amount of sample with SIMS analyses is very small (e.g., for oxygen two-isotope analysis, less than 1ng with a pit of ~10 micrometer in size and ~1 micrometer in depth) [e.g. 1,2]. SIMS analysis with a smaller beam and improvement of efficiency of analysis are highly required for multilateral analyses of the same sample.

A large geometry and ultra-high sensitivity magnetic sector SIMS with multiple detectors (CAMECA IMS 1280-HR) was installed in the Kochi Institute for Core Sample Research, JAMSTEC in early 2014. The Kochi's latest generation IMS 1280-HR has a capability to perform in-situ stable isotope analyses with sub-permil (down to +/-0.2 permil, 2SD) precision and accuracy for samples of a few to tens micrometer in size [1,3].

Here, we will present preliminary results of oxygen two-isotope (¹⁸O/¹⁶O) measurements in selected minerals using two Faraday cup detectors in multi-detection, and the Pb three-isotope (²⁰⁶Pb/²⁰⁷Pb/²⁰⁸Pb) measurements in several standard materials using an axial electron multiplier detector with mono-collection. The achieved spot-to-spot reproducibility for ¹⁸O/¹⁶O is ~+/-0.3 permil (2 SD) with a ~10 micrometer spot for silicates and carbonates. The achieved precision and spatial resolution are promising to explore seasonal variations of precipitation recorded in speleothems [e.g., 4]. The spot-to-spot reproducibility for Pb three-isotopes is ~+/-7 permil with a ~20 micrometer spot for USGS BCR-2G standard glass ([Pb]=11ppm). Developed Pb isotopic measurements can be applied to researches for glass inclusions entrapped in minerals, which elucidate heterogeneity of the Earth's mantle [e.g., 5]. In the future work, we will use multiple electron multipliers to detect three Pb isotope signals simultaneously. This may provide better precision with a smaller spatial scale (~10 micrometer).

In addition to the development of high precision and high spatial resolution analysis with SIMS, we are planning to build a coordinated analytical system which provides information of microstructure and elemental/isotopic distributions for smaller-scale samples, such as a piece of asteroid which will be returned by the JAXA Hayabusa-2 mission in 2020 and samples of the ultra-deep drilling by Chikyu.

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Keywords: high precision in situ isotopic analysis, ion microprobe, SIMS, oxygen isotope, lead isotope

MTT44-04

Room:102B

Time:May 26 16:30-16:45

How to build a habitable planet for geochemists in Japan ?

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In this talk, I would like to present the methods to build a habitable planet for geochemists in Japan.

Keywords: The Geochemical Society of Japan, JpGU, Sampling method, Education

Is it representative of the Earth? -Necessity of ultrahigh-speed massive analysis in petrology-

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Earth and planetary sciences target at very large-scale subjects, such as the evolution of the Earth and the Solar system, but we usually treat very small samples taken from the Earth and the outer space. This means that we have to read various phenomena of the spatial scale order-of-magnitude larger than the samples we can have. In petrology, we usually use rock samples smaller than palm size. In addition, it's difficult to take rock samples from the whole globe like those of the ocean and atmosphere, because we have to take rocks from underground. In other words, petrologists is forced to understand large-scale phenomena using data from a limited number of rocks taken from limited areas. Therefore, we always have to question ourselves "are those samples representative of things and phenomena we want to know about?"

I have been interested in the behavior of platinum-group elements in the mantle, which would provide us with a key to understand the early-Earth differentiation and subsequent chemical evolution of the Earth's interior. Platinum-group elements in mantle peridotites are concentrated in base-metal sulfides (BMS) and platinum-group minerals (PGM). So it is very important to reveal the stability and genesis of BMS and PGM in order to understand the behavior of platinum-group elements in the mantle. Because BMS and PGM are very small both in size and amount, it has been quite difficult to describe the occurrence of them in peridotites. Recent developments in small-scale analyses, such as FE-SEM, laser-abrasion ICP-MS and synchrotron micro XRF, enable us to analyze BMS and PGM in submicrometer scale, and we are getting to know the occurrence and genesis of BMS and PGM in peridotites. However, we can still analyze only limited number of BMS and PGM in small portions of a sample because of their smallness in size and amount, and therefore we don't know whether the BMS and PGM we observe are representative of the sample they are included in, not to mention of the Earth's mantle. Even if we get able to analyze much smaller-size minerals, it is uncertain whether we can know better about BMS and PGM in the mantle. What we want to know is the behavior of platinum-group elements in the mantle, not genesis of them in a particular sample.

Then, what should we do? It's not to advance the methods for small-scale analyses with much higher precision, but to develop methods for analyzing a large number of samples in limited time. In other words, we need "ultrahigh-speed" analysis of rock samples. We don't need to care so much about precision and accuracy, because, at least in the case of platinum-group elements, concentration data even with +/- 100% precision would tell us much about geochemistry of platinum-group elements. The way petrologists and geochemists must go is not only to higher precision and accuracy, but also to ultrahigh speed.

Keywords: small-scale analysis, wide-area analysis, massive analysis, mantle, heterogeneity

Studies of the Earth's Interior and Geochemistry

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In this presentation, I would like to discuss the following points, in terms of the relationship between studies of the Earth's interior and geochemistry, referring to several examples from the combined studies. First, geochemistry concerns both geoscience and chemistry. How we balance the two does matter for both geochemists and the others. Second, how we relate mechanisms and processes of an elemental scale to global scale-phenomena requires some concrete methods which lie often outside geochemistry. An approach bridging the two scales may play an important role. Third, since the Earth (and the planetary) system is highly complex, there is no doubt that combining information available from all geoscience fields (including geochemistry) is crucial. As an example, 'Geofluid Map' in the crust and mantle is discussed.

We are always on the frontier!

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Oxygen isotope anomaly in the solar system was found from a meteorite by Clayton et al. (1973). The origin is still unknown and it is principally unsolved although we can infer it precisely. More interesting puzzle for the oxygen isotope anomaly than the origin may be the anomalous distribution among minerals and within a mineral in a Ca-Al-rich inclusion (CAI). CAIs are the oldest rock in the solar system, and are largely mm to cm in size. The CAIs formed in the solar nebula by crystallization from liquid droplet or from surrounding hot gas. However, nobody has been succeeded to describe how to establish heterogeneous oxygen isotope anomaly in a CAI according to known chemical reactions so far because the oxygen isotopic distribution is apparently inconsistent with phase relation and crystal growth in the chemical system of CAIs. This is mysterious because the chemical system of CAIs seems to be much simple comparing with terrestrial rocks. In this talk, I show an attempt to clarify this mystery predicts that oxygen isotope anomaly distributes globally but changes the degree systematically on all solar system objects including outer planets. The global change of oxygen isotope anomaly in the solar system should involve isotope anomalies of hydrogen and nitrogen. The attempt also predicts that isotope anomalies of these three elements are universally observed in exoplanetary systems, which degrees may be an indicator for habitability. These predictions can be proved by development of planetary explorations and astronomical observations, which are parts of cosmochemistry, even if the origin of the oxygen isotope anomaly in the solar system is principally an unsolved issue.

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Keywords: Geochemistry, Frontiers

My identity as a geochemist in mineral physics

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In the long-standing progress of earth sciences, the interplay between seismology and high-pressure mineral physics greatly contributed to understanding of deep earth. It is my understanding that scientists in these fields establish the communities and share the observational data, large facilities and so on. In contrast, it seems to me that many of geochemists, including myself in a sense, construct their own laboratories equipping state-of-the-art device. The difference in research style is noteworthy and may give a clue to the breakthrough of traditional geochemistry.

One of my research interests is to investigate the structure and properties of hydrous materials which potentially exists in deep earth. To achieve these research projects in Japan, I joined to a research consortium and we have constructed a new high-pressure beamline at the spallation neutron source, J-PARC for deep-earth mineralogy. We have been studying structures of hydrous materials and ices; recent progress will be introduced in my talk.

Recently, our attention is focused into chemical evolution of organic materials during planetary shock bombardment process generating high pressure and high temperature simultaneously. We try to understand temperature-induced reaction and pressure-induced reaction independently. Our recent study on pressure-induced reactions on organic compounds and insights into evolution of organic materials will be introduced.

Keywords: high pressure, neutron diffraction, organic compounds

Molecular Geochemistry as a Future Topic in Geochemistry

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Professor V. M. Goldschmidt is a father of geochemistry. He wrote in 1954 that *geochemistry is the study of the distribution and amounts*. Based on this concept, he discussed (i) substitution of trace elements into major element within a certain crystal, (ii) reaction of metal ions with the ligands in water in terms of ion potential ($= z/r$; z : charge; r : ionic radius), and (iii) classification of all the elements in the periodic table in terms of chemical bonding nature such as ionic, covalent, and metallic bonding. Using X-ray emission spectroscopy, which was the state-of-the art method at that time, he determined abundances of trace elements in various geochemical samples.

However, his discussion on the distribution of these elements *on the basis of the properties of their atoms and ions* could not be proved by any methods, since it was difficult at that time to clarify the chemical species (bonding nature and structure) of trace elements. At present, on the other hand, we can determine the neighboring atom and interatomic distance of trace elements in various samples by advanced speciation methods such as by X-ray absorption fine structure (XAFS) spectroscopy. As shown in our recent studies, abundances and isotopic compositions of various elements in natural samples strongly depend on the chemical state of various elements in nature. This fact shows that we can predict behaviors and isotopic fractionation of various elements based on physic-chemical properties. This field can be called as "Molecular Geochemistry". This field includes (i) identification of organic polymolecules in nature which can be used for the paleoenvironment reconstruction, (ii) isotopomers of various molecules, and (iii) fundamental understanding of isotopic fractionation such as mass-independent fractionation. Thus, I propose "Molecular Geochemistry" as an important future topic of geochemistry, which cannot be conducted by researchers in other fields in earth and planetary sciences and must be conducted by Prof. Goldschmidt if he could use the methods to reveal the atomic- and molecular-level information in geochemical samples.

Keywords: Molecular Geochemistry, Goldschmidt