

## 論文内容の要旨

論文題目 : **Development of in-situ determination of Cu isotope ratios and its applications to geochemical samples**

(銅同位体比局所分析法の開発と地球化学試料への応用)

氏名 : 池端 慶

### Introduction

Copper (atomic number 29) belongs to main-transition elements (d-block elements) and is a period 4 element of group 11 on the periodic table. Copper is reddish colored and takes a bright metallic luster. It is malleable, ductile, and a good conductor of electricity and heat. It is the second highest to silver in electrical conductance and is the third highest in thermal conductivity among all chemical elements at room temperature.

Copper is a trace element which occurs at tens of ppm level abundances in most terrestrial and extra-terrestrial materials. The exceptions are ore minerals where Cu occurs as a native element metal (native copper, Cu), sulfide minerals (e.g., chalcopyrite,  $\text{CuFeS}_2$  and chalcocite,  $\text{Cu}_2\text{S}$ ), oxide minerals (e.g., cuprite,  $\text{Cu}_2\text{O}$ ) and hydroxy-carbonate minerals [e.g., malachite,  $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ ]. These minerals are observed under various geological or tectonic environments.

Copper has two stable isotopes  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ . To detect the natural variation in  $^{65}\text{Cu}/^{63}\text{Cu}$  ratio of the geochemical samples, thermal ionization mass spectrometer (TIMS) has been widely used. The measured  $^{65}\text{Cu}/^{63}\text{Cu}$  ratio varied significantly by as much as 12 ‰. Because of time-dependent mass fractionation effect, resulting precision of the TIMS analyses was approximately  $\pm 1-1.5$  ‰, so it is difficult to discuss detailed Cu isotope variation using Cu isotope data with such a large precision. Recent advances in multiple collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) have made it possible to measure Cu isotopic ratios in natural and synthetic materials with high precision and accuracy ( $< \text{c.a. } 0.2$  ‰), and a number of previous studies using MC-ICP-MS have demonstrated that Cu isotopic ratios of selected copper-bearing materials scatter up to 17 ‰. Several recent investigations by using solution MC-ICP-MS have showed that mafic volcanic rocks and primary igneous Cu-rich minerals from high temperature sea-floor hydrothermal in

mid-ocean ridge and from magmatic ore in continental setting display a relatively restricted range from -1.3 to +1.2 ‰ (Range of Terrestrial Igneous Cu). In contrast, secondary Cu-rich minerals that are formed during low-temperature oxidation, alteration and weathering of primary Cu-rich minerals yield a wide range of Cu isotopic ratios from -8 ‰ to +9 ‰, presumably due to mass dependent stable isotope fractionations that occurred at low temperatures. Previous studies on Cu isotope ratio variation in nature were concentrated in view of mineralogical points. They lack global point of view. Until now, few studies have been carried out on Cu isotopes in samples from island arc and back arc setting, where subduction and associated magmatism created a dynamic, rapidly changing geological environment. Therefore, it is very important to examine high-temperature Cu isotope variation of materials from island arc setting for a full understanding of homogeneity or inhomogeneity of Cu isotopic composition, the characterization of isotopic reservoirs of Cu, Cu cycling in the Earth.

As for recent analytical methods of Cu isotopes, bulk analyses of rock or mineral samples have been adopted: the samples have to be digested and the obtained solutions are analyzed by MC-ICP-MS, after complete chemical separation of Cu. In such a conventional analysis, it is difficult to reveal a special variation in Cu isotope ratios in a sub-mm scale. To overcome this, new technique to measure isotopic ratios in much smaller scale than sub-mm must be applied.

Laser ablation ICP-MS (LA-ICP-MS) provides one of the most powerful techniques for isotope analyses of solid samples with an extremely small area. Laser ablation technique does not require a complicated sample preparation procedure, so the risk of contamination or sample loss can be minimized. Until now, only a handful of studies have applied LA-ICP-MS with intention of developing methods for in-situ Cu isotope ratio analysis. Reported Cu isotopic ratio showed significant level of mass bias effect (0.7-4.8 ‰) relative to the ratio data measured by the conventional solution nebulization technique. The main reason of the poor precision and accuracy of their laser ablation experiments is thermal-induced elemental and isotope fractionation that may occur during laser ablation utilizing nanosecond-pulsed laser ablation systems. Recently, femtosecond laser ablation systems with short pulse widths have become available. The use of femtosecond ablation drastically reduces thermal effects and redeposition of ablated particles around pit crater, and thereby minimizes isotope fractionation and matrix effects for chemical analysis of solid samples. Therefore, femtosecond laser ablation showed improvements in precision and accuracy compared to nanosecond laser ablation.

In this study, in order to measure Cu isotope composition in minute natural samples as small as tens of  $\mu\text{m}$ , I have developed a new method for in situ measurement of Cu isotopic compositions of pure Cu metal and Cu-rich minerals including native copper, cuprite, chalcocite, chalcopyrite and malachite using a femtosecond laser ablation system with a laser spot diameter of 15  $\mu\text{m}$ , combined with MC-ICP-MS. To evaluate the precision and accuracy of my laser ablation technique, Cu isotopic compositions of the same sample materials were also measured by conventional solution MC-ICP-MS using the same MC-ICP-MS system. Moreover, I applied this method to the measurements of Cu isotopic ratios in variety of ore-forming mineral samples of Kuroko deposits, Besshi-type deposits and in ultramafic rocks from island arc setting in order to investigate variability of Cu isotopic compositions in the island arc, back-arc and mid-ocean ridge environments. In addition, I determined bulk Cu isotopic compositions of volcanic rock and Cu-rich sublimate samples from island arc setting by utilizing conventional solution nebulization MC-ICP-MS after sample dissolution and chemical purification. I also measured Cu isotopic compositions of mid-oceanic ridge basalts (MORB) for comparison with those of island arc samples. All these data are compiled with previous Cu isotope data and discussed in terms of Cu isotope significance related to global mantle processes.

#### **Development of in-situ determination of Cu isotope ratios by NIR femtosecond LA-MC-ICP-MS**

Mass spectrometer used in this study is a Nu Plasma 500 MC-ICP-MS (Nu Instruments, Wrexham, UK). The

mass dispersion of the ion beam is varied using a pair of quadrupole lenses that act as a zoom lens that focuses the ion beams into a fixed collector array with 12 Faraday cups and three electron multiplier ion counters.

For solution samples, sample was introduced into the ICP through nebulization using a MicroMist 100 (Glass Expansion, Melbourne, Australia). At the start of each analytical session, torch position and lens tunings were adjusted to maximize the sensitivity and stability. Two approaches have been adopted to correct for instrumental mass bias and drift. One is standard-sample-standard bracketing method, where samples are measured interspersed with standards. The other is Zn-doping method with the exponential mass fractionation law.

For *in situ* Cu isotope analyses, the MC-ICP-MS is coupled to a Cyber Probe 1 Ti:sapphire femtosecond (227 fs) laser ablation system (Cyber Laser Inc. Japan), operating in the near-infrared wavelength range (780 nm). A single spot analysis with an ablation pit diameter of 15  $\mu\text{m}$  was adopted for all samples and standards in this study. The laser was operated at constant pulse energy of 5  $\mu\text{J}$ , with a repetition rate ranging from 5 to 10 Hz, depending on Cu concentrations of the analyzed samples. The laser ablation was conducted under a helium atmosphere in an ablation chamber. Argon gas was mixed into the sample-out line from the ablation chamber. The laser induced sample aerosols and He-Ar gas mixture was then passed to the plasma source. The sample cell is mounted on a stage that can be moved in the x, y and z direction by computer control and several samples can be loaded simultaneously. The place of the ablating can be viewed continuously with reflected light using an on-line CCD video camera and monitor. For each sample, copper isotope analyses of 5 or 6 spots were made with 10s integration times for each spot and washout time between spots was ca. 25 s, resulting in a total analysis time of ca. 3 min. An on-peak baseline was measured for 30 s on the carrier gas before the start of ablation and subtracted from each analysis. Time resolved analysis (TRA) was utilized for the acquisition of each individual analysis, and a standard-sample-standard bracketing technique was applied to correct the instrumental mass fractionation and drift.

The long-term analytical reproducibility of Cu isotopic ratio measurements of pure copper metal sample over a 6-months period using laser ablation analysis was 0.05 ‰ (2SD), which is comparable to that obtained by conventional solution MC-ICP-MS analysis (0.05 ‰, 2SD). The copper isotopic compositions measured relative to NIST-SRM976 Cu standard (pure Cu metal) both on laser and solution MC-ICP-MS techniques are in excellent agreement for pure Cu metal and native copper samples. Copper isotope ratio of cuprite samples could be determined using NIST-SRM976 Cu standard, while matrix-matched standards are required for reliable *in situ* Cu isotope analysis of chalcocite, chalcopyrite and malachite samples. Repeated measurements of Cu isotope ratios for all samples provide an analytical precision of better than 0.14 ‰ (2SD). The femtosecond LA-MC-ICP-MS method provides a rapid and effective approach to determine the Cu isotopic composition of pure copper metal and typical copper ore minerals at analytical scales down to 15  $\mu\text{m}$ , with comparable precision and accuracy to that attainable with the conventional solution nebulization techniques, without requiring time-consuming chemical separation procedures.

#### **Determinations of Cu isotope ratios in selected geochemical samples using a developed LA-MC-ICP-MS method and a conventional MC-ICP-MS method**

The developed femtosecond LA-MC-ICP-MS method were applied to the measurements of Cu isotopic ratios in variety of ore-forming minerals (native copper, chalcopyrite, and malachite) of Kuroko-type deposits, Besshi-type deposits and in ultramafic rocks (Horoman peridotite) from island arc setting in order to evaluate the variability of Cu isotopic compositions in the island arc (back arc) and mid-ocean ridge environments. In addition, I determined bulk Cu isotopic compositions of volcanic rock and sublimate samples from Izu-Ogasawara island arc setting and MORB by utilizing conventional solution nebulization MC-ICP-MS after sample dissolution and chemical purification.

The Cu isotopic compositions, expressed as  $\delta^{65}\text{Cu}$   $\{\delta^{65}\text{Cu} = [({}^{65}\text{Cu}/{}^{63}\text{Cu})_{\text{sample}}/({}^{65}\text{Cu}/{}^{63}\text{Cu})_{\text{standard}} - 1] \times 10^3\}$ , of

primary (high temperature) Cu-rich minerals and volcanic rocks formed on back arc and island arc environments are relatively homogeneous in the range of  $\delta^{65}\text{Cu} = -0.18$  to  $+0.49$  ‰, which are comparable to the reported Cu isotopic range of the "Terrestrial Igneous Cu" ( $\delta^{65}\text{Cu} = -1.3$  to  $+1.2$ ‰). These results, together with Cu isotope values of MORB and Cu-rich minerals formed on mid-ocean ridge environments (Besshi-type deposits) suggest that bulk (upper) mantle Cu isotope ratios displayed a relatively restricted range when compared to the overall variation range (up to 17 ‰) in nature. Moreover, these data also show that high temperature magmatic processes cause negligible Cu isotope fractionation.

In contrast, Cu isotopic ratios of secondary (low temperature) Cu-rich minerals vary from  $-0.62$  to  $+2.93$  ‰. The low temperature secondary processes are responsible for the most cases of Cu isotope variation, which indicate that Cu isotope geochemistry may be a useful tool for deciphering details of natural alteration and redox processes.