Lithium and boron isotopic ratio analyses using laser ablation-multiple Faraday collector-ICPMS

*Qing Chang[1], J.-I. Kimura[1], T. Ishikawa[2], T. Tsujimori[3]

1. Dept. Solid Earth Geochem., JAMSTEC, 2. Kochi Institute of Core Sample Research, JAMSTEC, 3. Center for Northeast Asian Studies, Tohoku Univ.

We report the origin of isotope fractionation induced by laser parameters, and instruments optimization for accurate *in situ* measurement of lithium (d7Li) and boron (d11B) isotope ratios in glasses and minerals using laser ablation multiple Faraday collector ICP-MS. Laser ablation parameters were examined using 266 nm femtosecond (266 fsLA) and 193 nm nanosecond excimer (193 exLA) laser ablation systems for crater diameters of 30–200 mm. We found that higher laser repetition rates and larger crater diameters have led to enhanced fractionation of lighter isotopes, as much as -8 permil for both d7Li and d11B. Fractionation was primarily affected by the ICP aerosol loading and secondly by the thermal fractionation at the LA site. The former was accounted for by mass loading effects, which lowered the plasma temperature and led to insufficient aerosol vaporisation. The latter was related to the molten layer on the crater walls, which resulted in coarser and heavier d7Li and d11B aerosols that did not reach the ICP. Both processes can result in Rayleigh fractionation during aerosol formation and vaporisation. Controlled ablation using a constant crater size, repetition rate, and high laser fluence of 193ExLA enabled reproducible ablation for the standard NIST SRM 61x glasses and unknown basalt glasses. Based on the principles of isotopic fractionation deduced from our experiments, we propose a novel ablation volume correction (AVC) protocol for accurate isotopic analyses of various samples with different matrices. Both the repeatability and the laboratory bias of the d7Li and d11B measurements using the new AVC protocol were better than 1 permil for samples containing a few tens to a few tens of thousands ppm Li and B. We also report significant local heterogeneity of up to several permil found in some basalt glasses, but not in NIST SRM 612 and 610.

Keywords: LA-MFC-ICPMS, isotope fractionation, Li isotopic ratio, B isotopic ratio, glass and mineral

©2017. Japan Geoscience Union. All Right Reserved.

Setting up of oxygen extraction system for stable isotope analysis of silicate minerals.

*Kubota Miho[1], Madhusoodhan Satish-Kumar[1]

1. Niigata University

The mass spectrometers at Niigata University (Finnigan MAT-251 and Thermo MAT-253) are capable of measuring stable isotope composition of carbon dioxide for ultra-small volume (<0.1 micro moles) and with high precision (<0.1 ‰). In this study, we developed a system for high precision analysis of oxygen isotope composition of small volume silicate minerals. The new sample preparation line was installed that comprises of three main parts. 1) the reaction chamber; 2) the gas purification line, and 3) O_2-CO_2 converter.

The reaction chamber separate oxygen from silicate minerals by reacting with the fluorine released from CoF_3 at 700ºC. After purification of the released oxygen with liquid nitrogen, the gas is passed through KBr trap to remove the excess fluorine. Pure oxygen gas is then allowed to react with graphite at 750ºC, to form carbon dioxide, which is used to measure oxygen isotopes using mass spectrometer.

A technique has been developed in which CoF_3 is used as a reagent for quantitative liberation of oxygen from oxides and silicates. By doing several trial experiments, the background in the reaction line was reduced by preheating of KBr trap, the converter and respective filters. For the converter, it was found that good reproducibility can be obtained at 750 ºC and 30 minutes of reaction time. Analysis and measurement of NBS-28 quartz standard reference material were performed, but in this study it was unable to get good reproducibility. The possible reasons and remedies are discussed in detail. The possible candidates that contaminate oxygen are water vapor that instantaneously react with CoF_3, reaction of fluorine gas with adsorbed water inside the vacuum line or fractionation of oxygen during transportation inside the line. Further improvements in preparation procedure are being carried out.

©2017. Japan Geoscience Union. All Right Reserved.

Climatic and Tectonic Evolution during about 27-13 Ma of the northeastern part of the Qinghai–Tibetan Plateau evidenced by geochemical and mineralogical records in the Xunhua Basin

*Zhao Liu[1]

1. China University of Geosciences

The Xunhua Basin which located at the northeastern part of the Qinghai–Tibetan Plateau provides a valuable opportunity to understand the climatic and tectonic evolution of Qinghai–Tibetan Plateau. Here we present a synthesis of clay mineralogy, bulk mineral composition and bulk-rock geochemistry of sediments during about 28-14 Ma in the Xunhua Basin. Climate changes during the episode were documented in the sediments and were expressed by the proportion of clay species (Smectite, illite, chlorite) and clay indices, the proportion of non-clay minerals (calcite, quartz, gypsum, orthoclase, and plagioclase), as well as chemical weathering indices, Rb/Sr and Ba/Sr ratios. The results suggest that a warm and seasonally dry and humid climate prevailed over the period ~27-25 Ma, followed by a relatively cold and dry climate in the period ~25-23 Ma. During the period ~23-17Ma, the climate is colder and drier than the previous period and a subsequently warm and humid climate in the period ~17-13 Ma. The dramatic reduction of chlorite proportion at 23 Ma suggested that the source materials changed because of the uplift of mountains around such as Laji mountain. The climate in Xunhua Basin could have been controlled by global climate and the climate cycles of the East Asian monsoon might add additional influence.

Keywords: paleoclimate, geochemistry, clay mineral

©2017. Japan Geoscience Union. All Right Reserved.

Major element composition of the Hadean crust: constraint from high-pressure melting experiments

*Nozomi Kondo[1], Tetsu Kogiso[1]

1. Graduate School of Human and Environmental Studies, Kyoto University

Processes of the mantle-crust differentiation and composition of the crust in the Hadean era (> 4.0 Ga) are essential to understand the early stage of the chemical mantle evolution due to the extraction and recycling of the crust. The existence of the granitic-andesitic crust has been vigorously debated from analyses of the Hadean zircon and early Archean pelitic gneiss (Hopkins et al. 2010; Kemp et al. 2010; Iizuka et al. 2015; Komiya et al. 2015; Reimink et al. 2016), but the processes to form the Hadean crust and its quantitative composition are still unclear. In this study, we aim to determine the major element composition of the Hadean crust and constrain the early stage of the mantle-crust differentiation in the Hadean era.

Previous studies have suggested that the Hadean mantle would have had high potential temperature (Korenaga 2013), and that the crust generated through melting of the mantle peridotite at high mantle potential temperature (MPT) has komatiitic composition (Takahashi & Scalfe 1985). Because the existence of liquid water has been implied from the oxygen isotope composition of the Hadean zircon (Mojzsis et al. 2001), and the hot Hadean mantle could have generated steep thermal gradient in the crust, the Hadean mafic-ultramafic crust could have experienced hydrous melting upon subduction, and generated granitic-andesitic melt.

We estimated style of the igneous activity in Hadean era and composition of the crust generated through melting of the primitive mantle peridotite, referring previous mantle convection models at high MPT (Korenaga 2009; Foley et al. 2014). The crust would have formed from the melt generated through near-solidus melting just under a thick (-200km) lithosphere before the onset of the plate-tectonics, and after the onset of the plate-tectonics, from the melt generated through large-scale melting under ridges. Then, the composition of the crust was estimated from high pressure melting experiments (Kondo et al. 2016) in the case before the onset of the plate-tectonics, and from calculations with pMELTS (Ghiorso et al. 2002) in the case after the onset of the plate-tectonics. The compositions of the melt were estimated to be komatiitic in both cases, though the FeO, TiO2, Na2O, and K2O contents are higher in the melt for the case of the pre-plate-tectonics. We refer this Fe, Ti, and alkali-rich komatiite composition as S(solidus)-komatiitic.

We assumed the pre-plate-tectonic regime involving intermittent and drip-like subduction (Foley et al. 2014), and hydrous melting of the S-komatiitic crust. Hydrous melting of komatiite has been scarcely investigated, and we performed high-pressure hydrous melting experiments of the S-komatiite. We synthesized starting powders of the S-komatiitic composition from oxide and carbonate powders. Then, we performed hydrous melting experiments at 1-3 GPa and 1000-1300 °C with the piston-cylinder high pressure apparatus. In these experiments, the oxygen fugacity was carefully controlled and assessed. The major element composition of the melt generated through the hydrous melting of the S-komatiite was revealed to be picritic and rich in Ti and alkali elements, reflecting the composition of the starting material. Thus, in the Hadean era before the plate-tectonics, the S-komatiitic crust was generated firstly from the melting of the primitive mantle peridotite, and then subduction-related hydrous melting of the S-komatiitic crust generated Ti- and alkali-rich picritic crust.

©2017. Japan Geoscience Union. All Right Reserved.

Keywords: Hadean, crust, major element composition, high-pressure melting experiment

©2017. Japan Geoscience Union. All Right Reserved.

Highly siderophile elements in Hawaiian xenoliths: Implications for the origin of low 187Os/188Os signatures in oceanic mantle

*Akira Ishikawa[1,2], Katsuhiko Suzuki[2], Tetsu Kogiso[3], Norikatsu Akizawa[3]

1. Department of Earth Science and Astronomy, The University of Tokyo, 2. Research and Development Center for Submarine Resources, Japan Agency for Marine-Earth Science and Technology, 3. Graduate Scool of Human and Environmental Studies, Kyoto University

Mantle xenoliths in ocean islands basalts (OIB) are generally regarded as fragments of shallow oceanic lithosphere accidentally brought by deeply-derived magmas en-route to the surface, and are genetically unrelated to the hot spot magmas which embed them and their mantle sources. However, it has been proposed that peridotite xenoliths from Salt Lake Crater in Oahu Island (Hawaii) and a high-temperature group of peridotite xenoliths in Malaita, Solomon Islands (Ontong Java Plateau) may represent the pieces of subcreted plume material which cause the primary volcanic activity on their regions (Bizimis et al., 2009 EPSL; Ishikawa et al., 2011 EPSL). This idea is largely based on characteristic contrast of the frequency distribution of whole-rock $^{187}Os/^{188}Os$ compositions between these xenolithic peridotites and Pacific uppermost mantle deduced from abyssal peridotites and mantle tectonites in ophiolites.

In this study, we investigated whole-rock abundances of highly siderophile elements (HSE: Os, Ir, Ru, Pt, Pd and Re) together with other major-trace lithophile elements in peridotites from Salt Lake Crater in Oahu Island (Hawaii) with the aim of examining whether peridotite xenoliths having low $^{187}Os/^{188}Os$ compositions ($^{187}Os/^{188}Os < 0.120$) represent (1) ancient depleted mantle domain produced by shallow melting, subsequently recycled back into deep mantle by subduction processes, or (2) lowermost mantle domain associated with ancient Re-depletion, possibly due to chemical interaction with metallic outer core and/or segregation of metallic materials. Our results demonstrate that refertilisation and melt-rock interaction are predominant mechanisms creating the observed major-trace element variations in Salt Lake Crater peridotites. By contrast, their HSE patterns are characterised by strong depletions in the Re, Pd and Pt relative to Ir-group platinum group elements (IPGE: Os, Ir, Ru), suggesting that refertilisation processes involving silicate melts can have little overall effect on the HSE compositions. This support the idea that their Os isotope records are strongly influenced by past melt depletion processes, and such ancient depleted materials are commonly embedded in deeply-derived mantle plumes.

Keywords: Highly siderophile elements, Os isotopes, mantle xenoliths, peridotite, Hawaii

©2017. Japan Geoscience Union. All Right Reserved.