

Ultra-high-sensitive simultaneous determination of halogens and noble gases by an extension of Ar-Ar and I-Xe methods

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Noble gas isotope ratios in various geochemical components in the Earth are significantly different, making them useful tracers to constrain origin of volatiles in the mantle. The development of noble gas mass spectrometry during the last two decades has enabled us to detect less than 10000 noble gas atoms (e.g., [1]).

An extension of Ar-Ar and I-Xe dating methods allows us to simultaneously determine trace amounts of noble gases, halogens, K, Ca, Ba, and U by use of ultra-high-sensitive noble gas mass spectrometry on neutron-irradiated samples. This method has several advantages: (i) detection limits for halogens are three or four orders of magnitude lower than those of other conventional analytical methods, (ii) several components of different origin can be distinguished based on their relations with specific noble gas isotopes such as mantle-derived ³He and by using various noble gas extraction methods such as laser microprobe [2], and (iii) in-situ production of radiogenic noble gas isotopes (such as ⁴He and ⁴⁰Ar) after the entrapment of the noble gas component of interest in the sample can be corrected by the simultaneously determined their parent elements, such as U and K, when the age of the entrapment is known or can be assumed.

We have developed a new noble gas mass spectrometric system for this method based on an Ar-Ar and I-Xe dating system [3]. Accuracy and precision of our method were examined by analyzing GSJ and USGS reference materials, their original rocks, and scapolite standards [4] and by comparing the halogen data with those obtained with ion chromatography and ICP-MS followed by pyrohydrolysis extraction [5].

By using this method, we analyzed halogens and noble gases in exhumed mantle wedge peridotites and eclogites from the Sanbagawa-metamorphic belt, southwest Japan and those in mantle-derived xenoliths from Kamchatka and N. Philippines, in all of which relicts of slab-derived water are contained as hydrous mineral/fluid inclusions. The striking similarities of the observed noble gas and halogen compositions with marine pore fluids [6,7] challenge a popular concept, in which the water flux into the mantle wedge is controlled only by hydrous minerals in altered oceanic crust and sediment (e.g., [8]).

On the other hand, halogen ratios of olivines in lavas from the northern Izu-Ogasawara arc [9] indicate insignificant contribution to the mantle wedge of pore fluid-derived halogens. This implies a relatively small amount of the pore water subduction fluids would be released from the Izu slab at a sub-arc depth resulting in further subduction to great depths in the mantle, possibly resulting in the seawater-like heavy noble gas composition of the convecting mantle [10].

Based on the relation with ¹²⁹Xe produced from decay of short-lived nuclide ¹²⁹I during stepwise heating noble-gas extraction of the Allende and Shallowater meteorites, intrinsic I and U to the meteorites were distinguished from those of terrestrial contamination origin.

These results demonstrate that simultaneous determinations of noble gases, halogens, K, Ca, Ba, and U in mantle-derived rocks and meteorites provide important information about their origins.

[1] Sumino et al. (2001) *J. Mass Spectrom. Soc. Jpn.* 49, 61-68. [2] Sumino et al. (2008) *J. Volcanol. Geotherm. Res.* 175, 189-207. [3] Ebisawa et al. (2004) *J. Mass Spectrom. Soc. Jpn.* 52, 219-229. [4] Kendrick (2012) *Chem. Geol.* 292-293, 116-126. [5] Muramatsu & Wedepohl (1998) *Chem. Geol.* 147, 201-216. [6] Sumino et al. (2010) *Earth Planet. Sci. Lett.* 294, 163-172. [7] Kobayashi et al. (2013) *Mineral. Mag.* 77, 1484. [8] Schmidt & Poli (1998) *Earth Planet. Sci. Lett.* 163, 361-379. [9] Sumino et al. (2013) *Mineral. Mag.* 77, 2285. [10] Holland & Ballentine (2006) *Nature* 441, 186-191.

Keywords: noble gas, halogen, mass spectrometry, Ar-Ar dating, I-Xe dating

Unspiked K-Ar dating for lavas from Zao volcano

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Zao volcano is located in the central part on the volcanic front of the NE Japan arc. Previous study revealed that the onset of the volcanic activity is ca. 0.8 Ma, the main edifice-building stage is ca. 0.3-0.1 Ma, and the newest stage is from 0.03 Ma to the present. On this volcano, about 50 K-Ar age data are reported, but not all units are covered and some data contradict the stratigraphy probably because of low-K and/or excess Ar contamination. We report new unspiked K-Ar age data for the lavas collected also from unexplored units, in order to construct the detailed history of the volcano.

Keywords: Zao volcano, K-Ar dating

Diffusion experiment by stepwise heating and muscovite

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It is generally recognized that diffusion experiment on micas in vacuum during stepwise heating for $^{40}\text{Ar}/^{39}\text{Ar}$ dating was unsuitable for diffusion studies because of the destruction of crystal structure from dehydration. However, we showed that estimates of closure temperature from single grain biotites during laser heating experiment gives reasonable values. The problem in case of muscovite is that it seems to have structural transition or significant destruction between 600 and 700°C. The recent study using hydrothermal environment reported the activation energy E of 63 kcal/mole and an estimation of closure temperature exceeding 400°C. The high E and closure temperature T_c are derived on the steep slope in Arrhenius plot. Without change in crystal structure, muscovite does not give high E and T_c . This is contradictory for samples with high E and T_c . It is necessary to separate diffusion phenomena from structural change, and even a hydrothermal experiment at high temperatures in a laboratory may not be suitable for such studies. Muscovite is known to have relatively high T_c in field. To make a practical estimate for T_c , it is necessary to consider both laboratory and field setting.

Keywords: diffusion experiment, argon, closure temperature, stepwise heating, muscovite

Luminescence dating and analysis of environmental change of fine grained sediments from Lake Yogo, Japan

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We applied optically stimulated luminescence (OSL), infrared stimulated luminescence (IRSL), post-IR IRSL (pIRIR) and ¹⁴C dating to the sediment core YG11-3 (294cm) from Lake Yogo, Japan. The fine grained quartz and polymineral sample are used for equivalent dose (D_e) estimation. As a result of several basic tests, the preheat temperature of 200 °C for 10 s and a cut heat of 160 °C were suitable to all OSL measurements. The accepted aliquots are about 90 % per measurement discs and the range of D_e s are 0.3 ~3.5 (Gy). The bulk ¹⁴C ages are ca. 300 years older than those of plant residue. After subtracting this age difference from bulk ¹⁴C ages, the corrected ages agree with the OSL ages except the ages of sediments from some depths. Two excepted OSL ages are older than the corrected bulk ¹⁴C ages (YG11-3-245, YG11-3-343) and these layers include a lot of plant residue enough to analyze the plant residue ¹⁴C ages. It seems that these sediments from two layers have been transported quickly in muddy stream based on a temporary environmental event. Additionally, the result of the IRSL_{50/225} and pIRIR₂₂₅ age confirms the existence of this temporary event. By comparing the OSL ages with ¹⁴C, IRSL and pIRIR ages, the quartz from the small catchment area can be applied to reconstruct the age model of sediment core in Japan.

Keywords: OSL dating, pIRIR dating, lake sediments

U-Pb dating of Eoarchaeon zircon using a NanoSIMS -implication for the measurement of volatile in the inclusions

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Volatiles, such as hydrogen or sulfur, trapped in the Eoarchaeon igneous rocks, are one of the most important tracers of the evolution of the interior of the early Earth. Apatite or glass inclusions found in the zircon crystal, are expected to preserve such volatiles. However, because of their scarceness, high-sensitive, high-resolution analytical methods are required for quantify them and reveal their isotopic compositions. Furthermore, discriminating between pristine compositions and later alteration is problematic. We are trying to approach these issues carrying out analyses by NanoSIMS50.

Euhedral to subhedral zircons were separated from a tonalite which was from the Eoarchaeon Nuvvuagittuq supracrustal belt, Superior Craton, Canada. The reported U-Pb age of this tonalite is 3661 ± 4 Ma by using LA-MC-ICP-MS [1]. The size distribution of zircons was from approximately 50 micrometers to 200 micrometers. Some of them have inclusions of apatite and glass whose size were 10 to 30 micrometers in diameter. Dating measurements were done avoiding such inclusions.

We performed ^{238}U - ^{206}Pb and ^{207}Pb - ^{206}Pb dating in the same analytical spot of zircon crystals. A 5 nA O^- primary beam, with spot size of approximately 10 micrometers in diameter, was used for ionizing the sample surface, and secondary positive ions were collected in a multicollector. The detector system was modified to measure $^{30}\text{Si}^+$, $^{90}\text{Zr}_2^{16}\text{O}^+$, $^{204}\text{Pb}^+$, $^{206}\text{Pb}^+$, $^{238}\text{U}^{16}\text{O}^+$, and $^{238}\text{U}^{16}\text{O}_2^+$ ions simultaneously in ^{238}U - ^{206}Pb dating session. In ^{207}Pb - ^{206}Pb dating session, $^{204}\text{Pb}^+$, $^{206}\text{Pb}^+$, and $^{207}\text{Pb}^+$ ions were collected in the same detector by changing the magnetic field. Detailed analytical procedure and standard calibration is described in Takahata et al.(2008) [2].

Measured $^{206}\text{Pb}/^{238}\text{U}$ ratios range from 0.4932 to 0.7993, and the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios range from 0.3052 to 0.3443. After the correction of common Pb, those values were plotted on Tera-Wasserburg Concordia diagram, giving a corrected age of 3633 ± 35 Ma, consistent with the previous value obtained by [1]. On the other hand, some samples showed a discordant age. Since such crystals are thought to have suffered metamorphism with subsequent loss of Pb, volatiles in the inclusions might have lost their initial information as well. Now we are proceeding to measure the volatile compositions of inclusions based on the results of U-Pb dating.

[1] David et al., GSA Bulletin, 121, 150-163, 2008.

[2] Takahata et al., Gondwana Res., 14, 587-596, 2008.

Keywords: U-Pb dating, NanoSIMS, zircon, inclusion, Archaean

Geochronological-geochemical characterization of Proterozoic age, western part of the Napier Complex, East Antarctic

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The Napier Complex in East Antarctica has attracted considerable interest from a viewpoint of long Archaean crustal history from 3800 Ma to 2500 Ma (e.g., Harley & Black 1997) and >1000 °C ultrahigh-temperature (UHT) metamorphism in a regional scale (e.g., Sheraton et al., 1987; Harley & Hensen 1990). The timing of ultrahigh-temperature metamorphism is in argument either >2550 Ma or <2480 Ma (Kelly and Harley, 2005). However, some previous works reported relatively younger ages, such as 2380 Ma, ~2200 Ma, and ~1820 Ma (e.g., Grew et al., 2001; Owada et al., 2001; Suzuki et al., 2001, 2006; Carson et al., 2002; Hokada and Motoyoshi, 2006). In addition, Horie et al. (2012) reported similar ages in felsic orthogneiss from Fyfe Hills and quartzite from Mt. Cronus via zircon U-Pb dating. In this study, we try to characterize the "younger ages" in order to interpret thermal history after the UHT metamorphism in the Napier Complex.

A quartzo-feldspathic gneiss, YH05021606A, collected from Fyfe Hills by Y.H. during the field work at the 2004-2005 Japanese Antarctic Research Expedition was analyzed by using a high-resolution ion microprobe (SHRIMP II) at the National Institute of Polar Research, Japan. The zircon U-Pb ages of the YH05021606A sample are already reported in Horie et al. (2012). The sample shows multiple age peaks centered at ca. 3025, 2943, 2883, 2818, 2759, 2674, 2518, and 2437 Ma, and evidence of the "younger ages" has never been reported. In this study, primary ion beam was focused up to 10 μm in order to observe detailed zircon structure. The U-Pb analysis of zircon yielded similar age population to the previous work and revealed the "younger ages" of ca. 2273, 2195, 2106, and 1980 Ma. Distribution of the "younger ages" is consistent with those of a felsic orthogneiss, YH05021603A, in Fyfe Hills and those of a quartzo-feldspathic gneiss, YH05021701A, and a quartzite, YH05021701H, in Mt. Cronus (Horie et al., 2012). The "younger ages" in this sample could be found in overgrowth rim and single grain, which indicates that both of Fyfe Hills and Mt. Cronus had been affected by any geological events after the UHT metamorphism. Previous workers suggested that the ca. 2200 Ma age that they obtained for beryllium syn-metamorphic pegmatites reflects post-emplacement deformation and metamorphism (Grew et al., 2001), and a ca. 1930-1800 Ma U-Pb upper intercept age for zircons were affected by aqueous fluid from Paleozoic pegmatite (Carson et al., 2002). Horie et al. (2012) only suggests that these 2380-820Ma ages represent local fluid infiltration or a local deformation events. We will discuss about character of the "younger ages" zircon with trace element signature.

Keywords: East Antarctica, Napier Complex, zircon, U-Pb dating, rare earth element, metamorphism

Sr and Nd isotope systematics of metacarbonate rocks as proxies for reconstructing extinct oceans: Mozambique Ocean

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Geochemistry of sedimentary rocks is widely used for understanding the depositional environment and tectonic setting, including source rock composition and paleo-ocean signature. In particular, chemically deposited carbonate rocks are directly precipitated from saturated seawater are supposed to hold key information of extinct paleo-oceans. An important geochemical tool that can lead to the identification of contemporaneous seawater is isotopic composition of strontium and neodymium in carbonate rocks, because these elements have distinct residence and mixing time in seawater and also characterized by surrounding continents.

In the Sør Rondane Mountains (SRMs), East Antarctica, metasedimentary rocks including metacarbonate rocks are widely distributed. These rocks were supposed to have formed in the paleo-ocean called as "Mozambique Ocean". SRMs are divided into two terranes, the SW and NE terranes, by the Main Tectonic Boundary (MTB). In the SW terrane, metaigneous rock that were formed at ca. 1000 Ma and metasedimentary rocks occur as main lithological units, which underwent metamorphic evolution along a anticlockwise *P-T* path, whereas the NE terrane is dominated by metasedimentary rocks, with a characteristic clockwise of *P-T* path. Additionally, metapelitic rocks in the SW terrane have similar detrital age population with the nearby metaigneous rocks, in contrast to those in the NE terrane show older detrital ages (~ca. 3300Ma)(Osanai *et al.*, 2013). If it is possible to reveal the relationship between ocean and continents during depositional timing of carbonate rocks in both terranes, we will be able to put forward a model to explain the difference in depositional setting between SW and NE terranes. To achieve this, analyzed detailed study of Sr and Nd isotopic composition of metacarbonate and metamorphosed silicate rocks, such as pelitic, felsic, mafic and ultramafic rocks, from several important outcrops throughout SRMs were carried out. Based on these data, we discuss about the relationship with continent and depositional basin of carbonate sediments before the final amalgamation of Gondwana.

After geochemical screening for post-depositional alteration, using oxygen isotopes, trace elements and REE + Y patterns, strontium isotope chemostratigraphy was applied to the metacarbonate rocks from SRMs and depositional ages of 880-850 Ma and 820-790 Ma (late-Tonian and early-Cryogenian age) were estimated (Otsuji *et al.*, 2013). Metacarbonate rocks in the Bratnøpene and Tanngarden regions in the SW terrane are showing typical seawater-rock mixing relationship in a ϵSr vs. ϵNd cross-plot indicating the deposition of metacarbonate rocks nearby meta-tonalitic and orthogneiss dominated continental arc. By contrast, the Perlebandet region exhibits an extremely different depositional setting of a seamount based on Nd model and depositional age and REE and ϵNd compositions. Moreover, the Balchen metacarbonate rocks show a signature of depositional setting surrounding a continent, based on the comparison of metacarbonate rocks with continental and oceanic derived rock units. A comparison of isotopic characteristics of Balchen carbonate rocks with the basement rocks from neighboring Gondwana regions suggested the presence of an ancient continent that is different from Kalahari and Dharwar Craton.

Thus, the Sr and Nd isotopic compositions of carbonate rocks deposited in the Mozambique Ocean have preserved important information about depositional setting of sedimentary rocks and relationship with surrounding basement and continents. In summary, geochemical proxies such as Nd and Sr isotopes of metacarbonate rocks can yield key information not only of paleo-oceans but also about the surrounding rocks during depositional timing, which can lead to a better understanding of oceanic closure during the formation of supercontinents.

Reference cited: Osanai *et al.*, 2013. PR, 234, 8-29. Otsuji *et al.*, 2013. PR, 234, 257-278.

Keywords: Sr and Nd isotope ratios, metacarbonate rocks, the Sor Rondane Mountains, Mozambique Ocean, Gondwana

Geochemistry of Archaean Banded Iron Formations in the Chitradurga Schist Belt, Dharwar Craton, Southern India

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Banded iron formations (BIF) are marine chemical sediment rocks precipitated mostly in Archaean and early Paleoproterozoic between 2.7Ga and 2.3Ga. This time interval record profound changes in the redox state of the oceans and atmosphere, such as the Great Oxidation Event (GOE). We present here the geochemical data obtained from 3.0 Ga banded iron formation (BIF) in the Chitradurga Schist Belt, Dharwar Craton, Southern India. This region exposes the Archaean strata predominated by supracrustal greenstone belts, stratigraphically overlying the Peninsular gneiss. Chitradurga schist belt comprises of three important BIF layers distributed in the Bababudan and Chitradurga groups. We present here the salient geochemical characteristics and strontium and neodymium isotope results of the BIFs and discuss the depositional environment.

BIF contain very low content of Al₂O₃ (<1wt.% except 1 sample) indicating less detrital components. The PAAS-normalized REY patterns shows positive La and Eu anomaly, low concentration of rare earth element, depletion of light rare earth elements (LREEs) relative to heavy rare earth elements (HREEs). These features differ with other Archaean BIFs in terms of lack of positive Y anomaly. The large positive Eu anomalies in Archean BIF of Chitradurga schist belt attribute to high-T hydrothermal fluid fluxes (>250 °C), while the negative Ce anomaly reflects the lack of significant oxidizing agents.

Sr isotopic composition of BIF shows large variations suggesting post depositional alterations, whereas Nd isotope ratios gave consistent information. Most of the samples show $\epsilon\text{Nd}(3000\text{Ma})$ in the range of +2 to +4 and T_{DM} model age in accordance with sedimentation age. The $\epsilon\text{Nd}(3000\text{Ma})$ of depleted mantle is about +4, which suggests that most of the Chitradurga BIFs were deposited in an environment strongly affected by input from a depleted mantle. However samples with different REY pattern show higher $\epsilon\text{Nd}(3000\text{Ma})$ between +6 and +14 and their T_{DM} model age are not equal to the sedimentation age. The geochemical results thus suggest that the BIFs in the Chitradurga schist belt were deposited near possible ridges affected by hydrothermal activities.

Keywords: Banded Iron Formations, Dharwar Craton, Archaean, Nd isotope