

Ar-Ar及びI-Xe年代測定法の拡張による極微量ハロゲン・希ガス多元素同時分析 Ultrahigh-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 ultrahigh-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.

キーワード: 希ガス, ハロゲン, 質量分析, Ar-Ar年代測定法, I-Xe年代測定法

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

蔵王火山溶岩の感度法による K-Ar 年代測定 Unspiked K-Ar dating for lavas from Zao volcano

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蔵王火山は東北日本の火山フロントの中央部に位置する複成火山である。先行研究では、約 80 万年前に活動を開始し、主となる山体は約 30-10 万年前に形成され、その後、約 3 万年前から現在までの最新活動期が続くと考えられている。本火山は初めて K-Ar 法における質量分別補正の必要性が示された火山であり、約 50 試料の年代値が報告されているが、未調査地域も残っており、一部カリウム含有量が低い試料や過剰アルゴンの混入が疑われる試料等について層序や古地磁気データと矛盾する場合もあった。本研究では、蔵王火山の活動史の全体像を明らかにするために、これまで未調査だった地域を含めて調査・試料採取を行ない、感度法による K-Ar 年代測定を実施したので、その結果を報告する。

キーワード: 蔵王火山, K-Ar 年代測定
Keywords: Zao volcano, K-Ar dating

段階加熱による拡散実験と白雲母 Diffusion experiment by stepwise heating and muscovite

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一般に結晶水を含む鉱物のアルゴンの拡散パラメーターを決定するとき真空中での段階加熱実験は加熱中に結晶格子の破壊が起きるため正確な値が得られず不相当であるとされてきた。以前報告したレーザー段階加熱による単結晶黒雲母の結果では冷却速度を考慮すると実際の値と変わらない範囲に収まることがわかっている。一方、真空中での白雲母の拡散実験の結果は従来のデータとの不一致が大きく実用的な適用が難しいと考えられた。白雲母のレーザー加熱による実験での大きな問題は脱水反応もしくは構造相転移による脱ガスが 600°C 以上で急激に進行し、拡散現象では解釈できなくなる要素が大きい。真空中の実験の場合、拡散パラメーターを見積もる Arrhenius 実験では脱水の影響が顕著でない 600°C 以下でのデータを用いたが、拡散するガス量が少なく誤差が大きい問題があった。ほとんどの場合、活性化温度は 30-40 kcal/mole の領域であり、その値から得られる閉止温度は 300°C を超える値は少ない結果となった。むしろ 400°C 以上の高い温度は温度領域を 600-700°C にして急激な拡散を起こす状態でのデータから得られた。近年、熱水環境下での実験で活性化エネルギーは 63 kcal/mole、冷却速度、拡散半径に依存するが閉止温度は、400°C と見積もられている。(Harrison et al., 2009)。このデータは 600-700°C での値を使用し、構造的な変化が起きていないという保証はない。熱水環境下で仮に結晶格子が安定的に存在したとしても同じ温度領域で構造相転移がおきるとすれば拡散パラメーターは独立に分離できない。単に数学的側面からは Arrhenius plot で大きな活性化エネルギー E もしくは周波数因子 D_0/a^2 を得るには急な傾きすなわち急激な脱ガスが必要となる。これは実は拡散においてゆっくりとした振る舞い (E, D_0/a^2 が大きい) をすることは矛盾する領域で拡散現象を見ていることになる。一方、野外においては白雲母が高い閉止温度を示している証拠もみついている。すなわち単に実験室において条件をみただけでなく、野外での条件に基づく考察を平行して行う必要があり、白雲母の閉止温度の意味を再考する必要がある。

キーワード: 拡散実験, アルゴン, 閉止温度, 段階加熱, 白雲母
Keywords: diffusion experiment, argon, closure temperature, stepwise heating, muscovite

滋賀県余呉湖細粒堆積物のルミネッセンス年代測定と環境変動解析
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 basically test, 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 these 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.

キーワード: OSL 年代測定, pIRIR 年代測定, 湖沼堆積物
Keywords: OSL dating, pIRIR dating, lake sediments

NanoSIMS を用いた太古代ジルコンの U-Pb 年代測定 -包有物中揮発性元素の測定を目指して U-Pb dating of Eoarchaeon zircon using a NanoSIMS -implication for the measurement of volatile in the inclusions

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太古代火成岩中の水素や硫黄などの揮発性成分の同位体比値を明らかにすることは、初期地球の内部進化を解釈する重要な手掛かりの内の一つである。火成岩中に産するジルコン中のアパタイトやガラスなどの包有物はそのような揮発性成分を保持していると期待されるが、これらはしばしばマイクロスケールで存在するため、高空間分解能な分析手法が求められる。同時に、そうした包有物が初生的な情報を残しているかを評価することも重要である。本研究では NanoSIMS50 を用いてこれらの問題へのアプローチを行っている。

測定は、カナダ、Nuvvuagittuq supracrustal belt のトーナル岩から分離されたジルコンを対象に行った。過去の研究で報告されているこのトーナル岩の年代は、LA-MC-ICP-MS を用いた U-Pb 年代測定法で 3661 ± 4 Ma である [1]。測定では、自形から半自形で結晶の長軸方向の長さが 50 から 200 μm 程度のジルコンを対象とした。いくつかのジルコンには直径 10 μm 以下のアパタイトやガラスの包有物がみられ、年代測定はこれら包有物を避けて行われた。

²³⁸U-²⁰⁶Pb 及び、²⁰⁷Pb-²⁰⁶Pb の 2 種類の年代測定を同スポットに対して行った。測定手法は Takahata et al.(2008) に準じた [2]。1 次イオンビームとして 5nA の酸素イオンを用いた。²³⁸U-²⁰⁶Pb の年代測定では、³⁰Si⁺, ⁹⁰Zr¹⁶O⁺, ²⁰⁴Pb⁺, ²⁰⁶Pb⁺, ²³⁸U¹⁶O⁺, ²³⁸U¹⁶O₂⁺ を多重検出器で同時に測定し、²⁰⁷Pb-²⁰⁴Pb の年代測定では ²⁰⁴Pb⁺, ²⁰⁶Pb⁺, ²⁰⁷Pb⁺ を一つの検出器で磁場を変化させながら測定した。

測定の結果、²⁰⁶Pb/²³⁸U 比は 0.4932 から 0.7993 とバリエーションをとり、²⁰⁷Pb/²⁰⁶Pb 比は 0.3052 から 0.3443 の値をとることが分かった。得られたそれぞれの値を Tera-Wasserburg コンコーディア図にプロットすると、過去の研究と良く一致する 3638 ± 19 Ma の年代が得られた。一方で、一部の試料において 2 つの年代値の不一致 (ディスコード) が見られた。こうした試料では鉛を失うような変成作用を経験しているため、包有物中の揮発性元素の始原性は失われている可能性が高いと考えられる。U-Pb 年代測定の結果をもとに、ジルコン中包有物の揮発性元素の分析を進めている。

[1] David et al., GSA Bulletin, 121, 150-163, 2009.

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

キーワード: ウラン鉛年代測定, ナノシムス, ジルコン, 包有物, 太古代

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

東南極ナピア岩体西部における原生代の年代的・地球化学的特徴 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.

キーワード: 東南極, ナピア岩体, ジルコン, U-Pb 年代測定, 希土類元素, 変成作用

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

変成炭酸塩岩中のストロンチウム、ネオジウム同位体を用いた古海洋の復元 —東西ゴンドワナ間のモザンビーク海— 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 Sor 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 Bratnipene and Tangarden 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

南インドダールワークラトン中の縞状鉄鉱層を用いた地球化学的研究 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.

キーワード: 縞状鉄鉱層, ダールワークラトン, 太古台, Nd 同位体

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