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SGL42-01

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## Why is the IntCal13 special?

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Please see Japanese abstract (the presentation will be in Japanese).

Keywords: IntCal13, Radiocarbon dating, Radiocarbon calibration, Varved sediment, Lake Suigetsu, Marine reservoir effect

## An evaluation of the effect on $^{14}\text{C}$ dating (AMS) by alkaline treatment of the ABA method on charcoal sample

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Charcoal treatment by means of the Acid-Base-Acid (ABA) method (or Acid-Alkali-Acid; AAA method) has been widely used for radiocarbon ( $^{14}\text{C}$ ) dating in the Earth Science and Archaeological field. Although the ABA method is a basic charcoal pretreatment method for  $^{14}\text{C}$  dating, the evaluation of processing conditions of the ABA method based on any chemical indicator does exist few until today. This study aims to clarify the error of  $^{14}\text{C}$  dating caused by the alkaline pretreatment which is not studied hitherto. The author performed 3 types of experiments for the purpose. The first experiment was performed for confirmation of the reproducibility of ges. The second experiment was performed for confirmation of optimal treatment time of an alkaline solution. The third experiment was performed for confirmation of the optimal concentration of alkaline solution for the ABA pretreatment.

The first experiment:  $X^2$  test of the results shows  $T=0.45$ ( $df=3$ ;5% risk rate  $T >12.59$ )for the treated samples which means high convergent validity, while  $T=10.74$ ( $df=4$ ;5% risk rate  $T >9.49$ )for the untreated samples which means large scattering and significant variability.

The second experiment: even after the visual judgment of the completion of alkaline extraction, 3-DF detected humic acid in the retrieved NaOH solution, and Atsumi et. al. (2009) showed that radiocarbon ( $^{14}\text{C}$ ) dating was influenced the existence of humic acid. These results suggest that visual observation is inadequate for the judgment of the completion of alkaline extraction, and that 3-DF is more effective for monitoring the presence of dissolved organic contamination.

The third experiment: three charcoal samples from a single archaeological context were split into 8 aliquots respectively, and treated with 8 different concentrations of NaOH solutions ranging from 0.001 to 2.0 mol/l. Dating results and  $X^2$  tests showed minimum convergence at 1.2 mol/l. This is supported by 3-dimensional fluorescent (3-DF) analysis, which clearly shows different leaching characteristics between 2.0-1.0 and 0.5-0.001 mol/l. 0.5-0.001 mol/l NaOH solutions were too weak in humic leaching capacity at low excitation ranges, which is thought to be the phenomenon that generates the scattering of dates. We recommend using from 1.0 to 1.5 mol/l NaOH for radiocarbon pretreatment.

These results show that the  $^{14}\text{C}$  age is affected by difference of the residual of humic acid caused by the difference of chemical conditions of the pretreatment .

Keywords:  $^{14}\text{C}$  dating, ABA pretreatment, 3-D fluorescent spectroscopy, Humic acid, Charcoal sample

## Dating of sea-floor hydrothermal barite collected at the Okinawa Trough by ESR and radioactive disequilibrium

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The temporal change of submarine hydrothermal activities has been an important issue in the aspect of the evolution of hydrothermal systems which is related with ore formation (Urabe, 1995) and biological systems sustained by the chemical species arising from hydrothermal activities (Macdonald et al., 1980). Dating methods using disequilibrium between radioisotopes such as U-Th method (e.g. You and Bickle, 1998), <sup>226</sup>Ra-<sup>210</sup>Pb and <sup>228</sup>Ra-<sup>228</sup>Th method (e.g. Noguchi et al., 2011) have been employed for such studies.

Okumura et al., (2010) made the first practical application of ESR (electron spin resonance) dating technique to a sample of submarine hydrothermal barite to obtain preliminary ages, while Kasuya et al. (1991) first pointed out that barite can be used for ESR dating. Toyoda et al. (2011) determined the optimum ESR condition while Sato et al. (2011) confirmed that the signal is thermally stable enough for an age range of several thousand years. Takamasa et al. (2013) obtained U-Th and ESR ages which are roughly consistent with each other.

The samples were taken by research cruises operated by JAMSTEC. Barite (BaSO<sub>4</sub>) was extracted from hydrothermal sulfide chimney samples taken from two sites at the Okinawa Trough. Blocks of sulfide deposits were cut into pieces, and about 2.0g was crushed. The samples were soaked in 12M hydrochloric acid, left for approximately 24 hours. Then, 13M nitric acid was added. Finally, after rinsing in distilled water, the sample was filtered and dried. Impurities were removed by handpicking. An X-ray diffraction study was made to confirm that the grains are pure barite. After gamma-ray irradiation at Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency, they were measured at room temperature with an ESR spectrometer (JES-PX2300) with a microwave power of 1mW, and the magnetic field modulation amplitude of 0.1mT. The bulk Ra concentration was measured by the low background pure Ge gamma ray spectrometer. Assuming that Ra is populated only in barite, the dose rate was calculated with the alpha effectiveness of 0.043 (Toyoda et al., 2012), where the decay of Ra (a half life of 1600 years) was also taken into account.

The obtained ages range from 4.1 to 16000 years, being consistent with detection of <sup>228</sup>Ra in younger samples and radioactive equilibrium/disequilibrium between radium and daughter nuclei. The variation of the ages within each sample is mostly within the statistical error range. The relative order of the ages is consistent with the result of <sup>226</sup>Ra-<sup>210</sup>Pb method, where the difference in absolute ages would be explained by several hydrothermal events that form the chimney. It was found that Yoron Hole field is the youngest, then, Daiyon-Yonaguni Knoll field, Hatoma Knoll field, being nearly equal to Iheya North Knoll field, then Izena Hole field, which is consistent with the direct observation from the submersible.

Keywords: barite, hydrothermal activities, electron spin resonance, dating

## Thermoluminescence property of calcite

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In earth science, the date of past event is very important. To determine accurate age, we have to select suitable dating method for an analyzed sample.

Thermoluminescence dating method calculates a date from equivalent dose estimated by emitted luminescence when mineral is heated. Thermoluminescence dating has been often applied to carbonate minerals because it emits strong luminescence and wider age range applicable than C14 dating method is an advantage of thermoluminescence dating.

However, thermoluminescence dating of calcite is sometimes problematic; e.g., sensitivity change of calcite occurred through repeated heating of samples, possible anomalous fading, difference in characteristics of luminescence response against different kinds of radiation (e.g., gamma-ray, beta-ray, alpha-ray, and x-ray), and so on.

In this study, calcite from Philippine, Mongol, and synthetic calcite are analysed to understand luminescence characteristics of calcite. Mgnesite is also analyzed to see the effect of chemistry. Luminescence was detected by Photon Multiplier (R649, HMA-MATSU) with filter of 600-650nm. Chemical composition, especially impurity concentration was measured by LA-ICP-MS.

First, we evaluate X-ray induced thermoluminescence property of each sample.

Second, we measured luminescence caused by alpha-ray, beta-ray and gamma-ray and compare it to the luminescence induced by the x-ray. .

Finally, the relationship between luminescence characteristics (namely a-x-value, b-x-value and c-x-value) and impurity concentration is examined.

As a result;

1. Most calcites have thermoluminescence peak at 80 and 230 degrees Celsius.
2. In thermoluminescence peak of calcite at 80 degrees Celsius, fading is detected, while at 230 degrees peak is stable.
3. Results show negative or positive relationship between luminescence efficiency factors (a-x-value, b-x-value and c-x-value) and Mg, Mn, Fe and Sr concentrations.
4. The concentration of Fe has a correlation with a luminescence emitting efficiency.

Fe plays an important role for thermoluminescence of calcite. Thermoluminescence property of calcite may be subject to multiple chemical factors (ex; Mg, Mn and Sr), therefore, further analyses on calcites with the variety of impurity is necessary to evaluate a relation between multiple impurity concentration and thermoluminescence properties quantitatively.

Keywords: thermoluminescence, calcite, dating

## Zircon observation by atomic force microscope: Fission track or alpha recoil track?

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Fission track (FT) method is a dating technique based on the observation of damage (tracks) by spontaneous fission of <sup>238</sup>U left in a mineral. The number of tracks is counted under an optical microscope after etching (chemical expansion of a track). However, as FT density per unit area rises, it becomes difficult to count the number of tracks. This is due to the fact that FTs overlap one another and are unable to be readily distinguished. The atomic force microscope has a potential to observe FT with high track density after a short time etching. However, when etching time is too short, the number of counted tracks were increased probably due to difficulties in recognizing the FT among structures other than FT (e.g., alpha recoil tracks). In the observation of young zircons collected from modern volcanic product, the surface structures found in old zircons do not exist, and a hole with the depth of ~10nm can be found on the smooth surface. These countable holes may lead us to the alpha recoil track dating.

Keywords: zircon, fission track, alpha recoil track, atomic force microscope

## Excess argon in phengite from the Sanbagawa eclogites: Constraints on argon behavior during subduction zone metamorphism

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K-Ar system dating of phengitic mica is a powerful tool to determine cooling ages of HP/UHP metamorphic rocks. However, discordant ages in a same metamorphic unit have been often reported, particularly from rocks in Alpine-Himalayan type collisional metamorphic belts. For example, UHP-metamorphosed continental crust materials of the Dola Maira massif (western Alps, Italy) show the discrepancy due to the existence of excess argon in metamorphic minerals that has been inherited from the precursor rocks with polyphase metamorphic records. Over the last two decades, we have addressed an excess-argon free hypothesis in oceanic petrogenesis of Pacific-type convergent margins. According to the hypothesis, metamorphosed oceanic materials in Pacific-type HP metamorphic belts with only a monophase metamorphic records do not contain significant amount of excess <sup>40</sup>Ar; in other words, the K-Ar system in syn-metamorphic phengitic mica is significantly reset during fluid-induced metamorphic recrystallization at a Pacific-type convergent margin. Well-documented geological examples are of schists from Sanbagawa, Suo and Renge metamorphic belts in SW Japan, and from Otago metamorphic belt in New Zealand. Ar-Ar phengite analyses of HP-UHP metamorphosed oceanic lithologies of the Lago di Cignana (western Alps, Italy) also show negligible excess <sup>40</sup>Ar in eclogite-facies syn-metamorphic phengitic mica.

In the year 2000, as a preparation to guide participants for the IEC Conference in Japan, we have determined K-Ar ages of phengite and paragonite from the eclogite-facies Sanbagawa metamorphic rocks in Shikoku; the twenty-two results were obtained from four localities including Seba (84-89 Ma), Gongen (123-136 Ma) and Western Iratsu (78-80 Ma), and Kotsu/Bizan (82-88 Ma). Excepting for the quartz-rich kyanite eclogite from Gongen (GO), phengite and/or paragonite yields similar cooling-age ranges of metasedimentary rocks of the Sanbagawa metamorphic rocks in central Shikoku. Phengite K-Ar ages of GO eclogites are significantly older than syn-metamorphic zircon U-Pb ages at the same unit. These old ages are interpreted as the presence of excess <sup>40</sup>Ar in phengitic mica. The bulk-rock compositions of GO eclogites suggest a sedimentary protolith such as greywacke. When, where and how has the excess argon been trapped in phengite crystals? Considering the geological fact that the GO eclogites are closely associated with the Higashi-Akaishi (HA) meta-peridotite body, the false age obtained from phengite were likely attributed to an interaction between the meta-sediment (GO eclogite) and the meta-peridotite (HA peridotite) at eclogite-facies depth. We postulate that the fluids exchange between deep-subducted sediments and mantle material enhanced a hydration of peridotite and mantle-derived noble gas (including extreme <sup>40</sup>Ar) was diffused from mantle material to the sediments. During the exhumation of them, the rigid HA peridotite might have prevented a ductile deformation of GO eclogite and consequently mantle-derived argon gained from HA peridotite in GO eclogite might have been inherited by the limited-argon-depletion due to less deformation. This is not only very rare example of false K-Ar age of metamorphosed oceanic materials but also remarkable observation to explain argon behavior during sediments/peridotite interaction at a deep portion of subduction zone environment.

Keywords: Sanbagawa belt, eclogite, phengite, excess argon

## Deciphering early Earth's differentiation using short-lived isotope systematics

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<sup>1</sup>Tsuyoshi IIZUKA

Knowledge of the timescale and nature of early Earth's differentiation is central to understanding the evolution of the young Earth. Here I discuss short-lived isotope systematics of terrestrial samples that extended our knowledge of early Earth's differentiation. Recent high-precision W isotopic studies revealed positive  $^{182}\text{W}$  anomalies of up to 0.15 epsilon unit in ca. 3.8 Ga Itsaq rocks from West Greenland and 2.8 Ga Kostomuksha komatiites from Russia. I explored the geologic significance of the  $^{182}\text{W}$  anomalies by combining with trace element and other isotopic data. In this context, the W isotopic data are interpreted to reflect early silicate differentiation events on Earth. Under the assumption that the bulk silicate Earth has a 5% higher Sm/Nd than the chondrite average, the  $^{182}\text{W}$ - $^{142}\text{Nd}$ - $^{143}\text{Nd}$  chronometry constrains the age of the source mantle differentiation for the Itsaq samples to 4.53-4.49 Ga. The age may reflect the timing of silicate differentiation during a sequence of magma ocean solidification.

Keywords: Hadean, early differentiation, extinct radionuclides, non-chondritic Earth

## Formation age of Fengtien Nephrite, Taiwan: Dating low-temperature thin (<20 $\mu\text{m}$ ) zircon rims by NanoSIMS

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Nephrite in the Fengtien area is associated with serpentinites within the subduction-accretionary complex in eastern part of the Central Mountain Range, Taiwan. In addition to nephrite, there are also other metasomatic rocks, such as diopsidefels and epidotite, present between serpentinites and their country rocks (metapelites and metapsammites). Among these metasomatic rocks, diopsidefels is the most common one observed, while nephrite and epidotite are less frequently present in association with diopsidefels. When all these rocks are present at one outcrop, the common lithologic sequence is serpentinite-nephrite-diopsidefels-epidotite- metasedimentary rocks. Nephrite, diopsidefels and epidotite were interpreted resulting from fluid-rock (serpentinite+country rocks) interactions during subduction metamorphism. Field occurrence and petrographic observations clearly showed that while nephrite and diopsidefels are mainly metasomatic products after serpentinite, epidotite is after metapsammite. The formation temperature has been estimated to be 300 - 400 °C based on regional geology and thermodynamic calculations by previous studies. Timing of these metasomatic processes, however, has not been constrained, although the hosting subduction-accretionary complex was thought to be of late Cretaceous in age due to paleo-Pacific subduction beneath the Eurasia continent and to be correlated with the Sambagawa belt in Japan. Zircons were separated from one epidotite sample in this study. Most of these detrital zircons were shown to have a thin zircon rim, which is less than 15 - 20  $\mu\text{m}$  in thickness. These zircon rims were considered to be newly formed during metasomatic interactions between serpentinite and country rocks, which also led to nephrite/diopsidefels/epidotite formation. The CAMECA NanoSIMS NS50 at AORI, the University of Tokyo was employed to date these low-temperature thin zircon rims with a  $\sim 5$  nA O<sup>-</sup> primary beam confined to a  $\sim 15$   $\mu\text{m}$  diameter. Sample surface was pre-ablated for 5 minutes to remove the surface Au coating and any possible surface contaminants. Data acquisition time was 500 seconds. The resulting  $^{238}\text{U}/^{206}\text{Pb}$ - $^{204}\text{Pb}/^{206}\text{Pb}$  inverse isochron gave a young age of  $3.3 \pm 1.7$  Ma (MSWD = 2.1, n = 5). The date clearly showed that the Fengtien nephrite would have formed during the (initial) exhumation of the subduction-accretionary complex, which should be of late Cenozoic in age related to subduction of the South China Sea plate beneath the Luzon arc. The present study gave a good example that NanoSIMS is able to date zircon rims with a thickness about 15  $\mu\text{m}$  formed under low temperature conditions only a few million years ago. The instrument has a great potential in future studies dating various low-temperature hydrothermal, metasomatic or metamorphic zircon overgrowths.

Keywords: NanoSIMS, zircon, U-Pb dating, Nephrite, Central Mountain Range, Taiwan



## Significance of external morphology and zircon chemistry for precise U-Pb zircon dating

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Improvement of U-Pb zircon dating by microbeam analysis has been provided opportunity of discussion about more detailed geological events. Recent analytical precision of less than 2% at Paleogene zircon allows us to investigate shorter period events such as crystallization differentiation in magma chamber. However, the highly precise U-Pb age data yield an importance of confirming their accuracy and assaying disturbance of U-Pb system and incorporation of exotic components. In this study, we introduce data processing method of the highly precise ages based on zircon morphology, trace element abundances as well as statistics.

The precise U-Pb zircon dating by using a sensitive high-resolution ion microprobe (SHRIMP II) at National Institute of Polar Research, Japan, was applied to igneous rocks of the Tertiary Ishizuchi Cauldron in the Setouchi volcanic belt of Miocene age in northwestern Shikoku. A primary ion beam of about 10 nA was used to sputter an analytical spot of about 40  $\mu\text{m}$  diameter. A retardation lens system was utilized as a means to increase signal-to-noise ratio, and a secondary ion optics including slits of source and collector was adjusted to maximum transmission of the secondary ion under suitable mass resolution avoiding isobaric interferences on Pb isotopes. The surfaces of grain mounts were carefully washed with diluted HCl and ultra pure water to remove Pb contamination. A correction for common Pb was made on the basis of the measured <sup>204</sup>Pb and the model for common Pb composition.

Weighted mean ages were calculated from <sup>206</sup>Pb/<sup>238</sup>U ratios corrected by <sup>207</sup>Pb. In order to ensure the accuracy of U-Pb age, age known zircon, OD-3, was analyzed together with unknown sample. Concentrations of Hf and rare earth element (REE) in zircons were also measured at the same analytical spot of U-Pb dating by SHRIMP.

Zircon grains from the Bansyodani-biotite-rhyolite were divided to two types based on the external morphology: sharply euhedral type and relatively rounded edge of prism and pyramid type. <sup>206</sup>Pb/<sup>238</sup>U data of whole zircon grains were widely scattered beyond analytical uncertainty and show a weighted mean of  $14.78 \pm 0.18$  Ma (mean square weighted deviation, MSWD: 3.4). On the other hand, the euhedral zircons yielded the weighted mean of  $14.21 \pm 0.19$  Ma (MSWD: 1.0), whereas the relatively rounded zircons were older than the euhedral zircons, which suggests the incorporation of exotic components.

Zircon chemistry supported the classification by the morphology and the U-Pb dating. An average of Hf contents of the euhedral zircons were 9523 ppm ranging from 8883 to 10496 ppm and those of the relatively rounded zircons were 8475 ppm ranging from 7616 to 8803 ppm. Hf contents of the euhedral zircons were higher than those of relatively rounded zircons. C1 chondrite-normalized REE patterns of the euhedral zircons were characterized by a large fractionation between light REE and heavy REE, large positive Ce anomalies and large negative Eu anomalies. In contrast, those of the relatively rounded zircons were enrichment of light REE, weaker anomalies of Ce and Eu. Difference of the zircon chemistry between the euhedral zircons and the relatively rounded zircons reflects source melt composition. Therefore, the external morphology, Hf content, and REE abundance are useful criteria for the data processing of the highly precise U-Pb age data.

## LA-ICP-MS U-Pb dating of Oki Dozen volcano using non-polished zircons

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LA-ICP-MS U-Pb dating using zircon is now widely used with great success. The normal dating process includes polishing zircons. This process is good in terms of avoiding surface contamination of common Pb and/or Pb loss and is essential for SHRIMP, in which only small fraction (drilling depth of 1-2  $\mu\text{m}$ ) is used for dating. Compared to SHRIMP, LA-ICP-MS ablates a much larger volume (drilling depth of  $>10 \mu\text{m}$ ) of zircon. This means that it is easy to date zircons from the surface to the inner core of the crystal and examine the existence of inherited cores and potentially investigate the timespan of crystallization. Here we dated non-polished zircons for some reference samples (Fish Canyon Tuff and OD-3) and samples from Oki Dozen volcano. Zircons were ablated for 30 seconds using 213 nm Nd-YAG laser with 10 Hz repetition rate and 4-5  $\text{J}/\text{cm}^2$  energy density. Final drilling depth for 5  $\text{J}/\text{cm}^2$  was 27  $\mu\text{m}$  and the  $^{206}\text{Pb}/^{238}\text{U}$  ratio from 9-18  $\mu\text{m}$  depth were used to determine ages. It was found that non-polished zircons yield reliable ages because of agreement with reference ages. The Oki Dozen samples yielded 6-7 Ma ages, in agreement with or slightly older than K-Ar ages of 5.4-7.4 Ma.

Keywords: U-Pb dating, zircon, LA-ICP-MS, Oki Dozen volcano

## Crustal noble gases anomaly associated with fault movement and aftershock the 3.11 Northeast Japan Earthquake

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Noble gases have unique characteristics that they are rarely combined with other chemicals as their very stable nature. Because its main reservoir is atmosphere, their isotopic composition is well defined and believed to be uniform all over the world insensitive to disturbance from anthropogenic and/or natural emission of geologically trapped noble gases in the earth interior. Based on our preliminary friction experiment, however, detectable amount of noble gases seem to be emitted accompanied with a fault motion (Sato et al., 2009). After the extreme Northeast Japan Earthquake occurred on March 11, 2011, extraordinary increase of seismic activity as numerous aftershocks e.g. over 4000 felt earthquakes in four months, which may be a source of non-atmospheric component preserved in the earth interior. In terms of anthropogenic component, (Nuclear Power Plant) is a potential source, which is frequently monitored by radioactive species of noble gases.

We widely collected atmosphere samples all over Japan from Hokkaido, Honsyu, Chugoku and Kyusyu Is. The atmospheres have been sampled into vacuumed containers, Isotube®, at each sampling site to evaluate time-series changes. The elemental and isotopic compositions of the samples were analyzed mainly by quadrupole residual gas analyzers (RGA-200, SRS Co.) and partly confirmed by sector-type mass spectrometers (GVI-5400, GV instruments). In the duplicated analyses of the selected a few samples, the measured elemental and isotopic compositions were consistent within analytical uncertainties.

The relative elemental abundances were changed at least in heavier noble gases. Argon was enriched to pre-3.11 Earthquake atmospheres associating with a high <sup>40</sup>Ar/<sup>36</sup>Ar ratio. It might be contributed by emission of crustal Ar at aftershock earthquakes, deformation and fault movements. In addition, a frictional melting was occurred in a >M5 earthquake as reported by Kanamori et al. (1998). Further, radioactive Ar isotopes (<sup>42</sup>Ar and <sup>39</sup>Ar) were slightly abundant than those in "pre" 3.11 Earthquake atmospheres. These radioactive Ar isotopes were regarded to be detected limitedly in neutron irradiated geological samples especially in Ar - Ar dating. These altered atmospheric Argon isotopic composition in Eastern Japan area were observed until typhoon season.

Keywords: noble gas, 3.11 Northeast Japan Earthquake, aftershock earthquake, nuclear power plant disaster, Ar Isotope

## 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 <sup>3</sup>He 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 <sup>4</sup>He and <sup>40</sup>Ar) 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 <sup>129</sup>Xe produced from decay of short-lived nuclide <sup>129</sup>I 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 <sup>14</sup>C 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 <sup>14</sup>C ages are ca. 300 years older than those of plant residue. After subtracting this age difference from bulk <sup>14</sup>C ages, the corrected ages agree with the OSL ages except the ages of sediments from some depths. Two exceptional OSL ages are older than the corrected bulk <sup>14</sup>C ages (YG11-3-245, YG11-3-343) and these layers include a lot of plant residue enough to analyze the plant residue <sup>14</sup>C 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<sub>50/225</sub> and pIRIR<sub>225</sub> age confirms the existence of this temporary event. By comparing the OSL ages with <sup>14</sup>C, 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  $3661 \pm 4$  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  $^{238}\text{U}$ - $^{206}\text{Pb}$  and  $^{207}\text{Pb}$ - $^{206}\text{Pb}$  dating in the same analytical spot of zircon crystals. A 5 nA  $\text{O}^-$  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  $^{238}\text{U}$ - $^{206}\text{Pb}$  dating session. In  $^{207}\text{Pb}$ - $^{206}\text{Pb}$  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  $3633 \pm 35$  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  $\epsilon\text{Sr}$  vs.  $\epsilon\text{Nd}$  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  $\epsilon\text{Nd}$  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 Al<sub>2</sub>O<sub>3</sub> (<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