

## Present status for in-situ noble gas analysis by Sputtered Neutral Mass Spectrometry with tunneling ionization

BAJO, Ken-ichi<sup>1\*</sup>

<sup>1</sup>Hokkaido University

LIMAS (Laser Ionization MAss nanoSCOpe) was installed in 2011. In-situ analysis for trace elements in nanometer-scale is a concept of this apparatus. I have conducted mechanism of solar wind (SW) implantation into extra-terrestrial materials such as Itokawa particles. Because depth profile of SW-He have not been determined by using conventional noble gas mass spectrometer (NG-MS) in a quantitative way, a depth profiling of the SW noble gas contributes to the great progress for understanding implantation and removing processes of the SW noble gases. The processes imply the space-weathering history of the materials on its asteroid surface.

LIMAS is mainly composed Ga focused ion beam (FIB) for primary ion, femtosecond (fs) laser for tunnel ionization of sputtered particles, and time-of-flight mass spectrometer. Depth profiling procedure is as follows. The FIB system is carried out high spatial resolution with large primary current. The smallest beam size was 8 nm at 3 pA, and the largest size was 600 nm at 30 nA. The fs laser can ionize the all element even He because of high energy density. The energy density is  $8E15 \text{ W/cm}^2$  because the pulse energy and width was 6.3 W and 30 fs, respectively, and the laser pulse was focused on a volume of  $50 \times 50 \mu\text{m}^2$ . This laser pulse induces tunneling ionization (Delone and Krainov, 1998). Helium depth profile method in a few micrometer has been developed with LIMAS and atomic force microscope for crater depth measurement.

LIMAS can detect tens ppma He from sub-micrometer area on solid surface. In presence useful yield of He is 0.02% which should be up to 1% by optimize laser focusing and irradiation position. The yield of 0.02% corresponds to 4000 He atoms for single He ion count. The back ground of He is much less than that of the NG-MS because LIMAS is used by dynamic operation under the ultra-high vacuum.

LIMAS can measure locally concentrated noble gas because the sputter rate of the pulsed FIB is low, which indicates that this measurement is almost non-destructive isotope analysis. This feature can play a role for analysis of tiny and precious samples such as the Itokawa particles. U,Th-He and K-Ar dating for single grain can be applied by the in-situ noble gas analysis. The in-situ dating may obtain a new insight of thermal history of igneous rocks by comparing conventional in-situ dating method such as U-Pb age.

Keywords: noble gas, in-situ analysis, Sputtered Neutral Mass Spectrometry

## New preparation apparatus for noble gas isotope analyses to measure submarine hydrothermal fluids and renewed GVI-5400

SATO, Keiko<sup>1\*</sup> ; KUMAGAI, Hidenori<sup>1</sup> ; IWATA, Naoyoshi<sup>2</sup> ; SUZUKI, Katsuhiko<sup>1</sup> ; TAKANO, Susumu<sup>3</sup>

<sup>1</sup>R&D CSR, JAMSTEC, <sup>2</sup>Faculty of Science, Yamagata University, <sup>3</sup>Hiruzen Institute for Geology and Chronology

Hydrothermal activity is an essential phenomenon to drive geochemical differentiation on the Earth's surface, which should form polymetallic massive sulfide ores. Noble gas isotopes are regarded to be a powerful tracer even for the geochemical study on hydrothermal activity; however, there are abundant interference volatiles, e.g. halogens and hydrogen sulfide. Here, we designed a new preparation system to remove such volatiles using non-traditional gettering materials. This new preparation system consists of following components: the water preparations system, composite gettering system (halogen getter, sulfide getter and Ti-Zr getter), cryogenic pump, Saes-getter pump and charcoal trap to analyze the all noble gases. The new preparation system has compact volume, which needs small amount of seawater sample of 2-5 cc in volume. It is almost 1/20 compared to the typical requirement for He isotope measurement.

To design new noble gas measurement system in JAMSTEC, another critical problem is to be solved. One of widely used noble gas mass spectrometers, GVI-5400, is now not listed in commercial production models. Thus, all successor models of VG-5400 series have entirely finished their production support since several years ago. However, the VG-5400 series and its successor models still show satisfactory sensitivity and precision to determine noble gas isotope ratios. If we decide to use them much longer, we should maintain their control units, such as power supply, emission control or source control and so on, which requires replacement of essential electrical parts, including vacuum tube (!), regularly. At present, some of these parts are not supplied anymore and we are forced to choose between not replacing them with the new/second-hand electrical parts while they still worked, or renew their electrical circuits with currently manufactured electrical parts. By chance we had started the project to re-use old model of power supply unit. The first trial was applied to the very original VG5400 that was moved from Univ. Tokyo to Yamagata Univ. As the second case, we renewed the power supply and the emission control unit equipped for the JAMSTEC-2 noble gas mass spectrometer (GVI-5400He).

Here we report the better performance of new version of the renewed power supply unit, noiselessness and better stability, with the new noble gas preparation system.

Keywords: noble gas, getter pump, hydrothermal activity, mass spectrometer, extraction system

## High sensitive noble gas mass spectrometer equipped with a Giese-type ion source

SUMINO, Hirochika<sup>1\*</sup> ; NAGAO, Keisuke<sup>1</sup>

<sup>1</sup>GCRC, Grad. Sch. Sci., Univ. Tokyo

Although noble gas isotopes are powerful tracers in geosciences, their extremely low abundances in mineral and rock samples make their analysis quite difficult. For example, concentration of <sup>3</sup>He, which is a good indicator of mantle-derived component because of its primordial origin, is as high as 0.01 parts-per-trillion in volcanic rocks and mantle-derived materials. Such scarce noble gas isotopes are detected with a special mass spectrometer operated in static mode. We have made it possible to detect 10<sup>3</sup> to 10<sup>4</sup> atoms of noble gas isotopes by modifying a commercial sector-type single focusing noble gas mass spectrometer (VG5400), which is equipped with a double collector system to detect <sup>3</sup>He and <sup>4</sup>He simultaneously with a secondary electron multiplier and Faraday cup, respectively [1]. Here we report an attempt of further improvement of sensitivity of the mass spectrometer by installation of a new ion source (Giese-type source).

The Giese-type electron ionization (EI) ion source is equipped with two electrostatic quadrupole lenses [2]. This source has been reported to have up to two orders of magnitude higher sensitivity than conventional Nier-type EI source because of the absence of a beam defining slit to collimate the ion beam and thus high transmission [3]. We designed a Giese-type source to have an adequate resolution to separate <sup>3</sup>He<sup>+</sup> from HD<sup>+</sup> and H<sub>3</sub><sup>+</sup>, to have the source housing volume as small as possible, and to be bankable at up to 300 °C to reduce outgas from the source materials. The ion and electron optics were based on a calculation by Lu and Carr [4] and refined using SIMION-3D software [5]. Prior to the installation on the mass spectrometer, the ion beam profile emitted from the source was monitored by a microchannel plate and phosphor screen to optimize the configuration of the quadrupole lens.

A sufficient mass resolution over 500 essential for <sup>3</sup>He/<sup>4</sup>He analysis has been achieved with an improved sensitivity approximately three times higher than the previous condition. The amount of helium required to obtain a precision with <sup>3</sup>He/<sup>4</sup>He ratio is two orders of magnitude smaller than that with the condition installed by the manufacture. However, total ion transmission is estimated to be about 30%, suggesting further refinement of the source condition is required to obtain the maximum sensitivity.

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Keywords: Noble gas, Mass spectrometer, Quadrupole lens, Ion source

## Ar-Ar dating by fluid inclusions in hydrothermal quartz, compared with its field and microscopic observations

SAITO, Takuya<sup>1\*</sup> ; QIU, Huaning<sup>2</sup> ; SHIBUYA, Takazo<sup>3</sup> ; MARUYAMA, Shigenori<sup>4</sup>

<sup>1</sup>Department of Earth and Planetary Science, Tokyo Institute of Technology, <sup>2</sup>Chinese Academy of Sciences, Guangzhou Institute of Geochemistry, <sup>3</sup>Precambrian Ecosystem Laboratory, Japan Agency for Marine-Earth Science and Technology, <sup>4</sup>Earth-Life Science Institute, Tokyo Institute of Technology

The chemical evolution history of the ocean must have been one of the most critical factors to unravel the evolution of life on the Earth. However, this topic has not fully understood yet. Recently, de Ronde et al. (1997) and some studies try to estimate seawater composition during Archean and Proterozoic using fluid inclusions trapped in hydrothermal quartz correlated with pillowed basalt, which is expected to erupt in sub-seawater condition. Lowe and Byerly (2003) claims that the hydrothermal minerals used by de Ronde et al. (1997) were formed at far younger age (Quaternary) than expected age of eruption of the matrix lavas (3.2 Ga), based on the only field and microscopic observations. This problem must be solved by dating of the fluid inclusions trapped in hydrothermal quartz and comparing the age of pillowed basalt as a matrix in addition to field and microscopic observations. We carried out Ar-Ar dating of the fluid inclusions with stepwise crushing techniques at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.

Analyzed samples in this study are from 2.2 - 2.4 Ga Ongeluk Formation, Transvaal Supergroup, South Africa. Above Ongeluk Formation, two younger volcanic layers exist, one is mafic intrusions of the Malopo Farms complex formed at  $2044 \pm 24$  Ma, the other is porphyritic andesite of the Hartley Formation formed at  $1928 \pm 4$  Ma.

The analyzed samples are hydrothermal quartz with growth zoning texture, filling the primary shaped drainage cavities and interstitial spaces of lava flows of the Ongeluk Formation without quartz vein crosscut pillow of lava, suggesting the quartz had precipitated soon after eruption of the lava. We analyzed four of the most primary-rich samples (GU84, GU91, GU103a and GU103b), in terms of microscopic observations. However, secondary fluid inclusions are not excluded completely, in other words, argon gas extracted the quartz samples including some secondary fluid inclusions origin in the analysis.

Three samples, GU 84, GU103a and GU103b, yielded Ar-Ar isochron ages of  $2688 \pm 584$  Ma,  $1952 \pm 279$  Ma and  $1967 \pm 64$  Ma Ar-Ar isochron ages, respectively. GU91 was also dated in the same manner as well, but failed to obtain a tight line of isochron with a diffused age ( $611 \pm 517$  Ma).

Comparing the age of the Ongeluk lava and younger two volcanisms with the results, the age from GU84 has a wide range of error, but is consistent with Ongeluk lava, GU103a has also a wide range of error, but is consistent with all three volcanisms, and GU103b has the narrowest range of error and is consistent with Malopo Farms complex and Hartley Formation, especially match with Hartley. Based on field and microscopic observations, it is unlikely to precipitate quartz with filling cavities 100-200 Myr after eruption of Ongeluk lava. Two probable mechanisms to explain the results, one is that fluid inclusions were re-equilibrated at younger volcanisms in terms of the argon with preserving primary textures. The other is that secondary fluid inclusion formed by younger volcanism driving hydrothermal circulations and that extracted argon gas in the analysis is mainly composed of the secondary inclusions. The secondary fluid inclusions have argon ratio suggesting younger age than primary fundamentally, suggesting that GU84 obtaining the oldest argon age is the most primary rich samples. Assuming that obtained younger ages than Ongeluk lava are resulted in argon gas from secondary fluid inclusions, the consistency with Ar-Ar age of GU84, the most primary-rich sample, and Ongeluk lava support that our field and microscopic observations are robust and that the primary fluid inclusions formed soon after Ongeluk lava eruption.

Keywords: fluid inclusion, Ar-Ar dating, quartz, seawater

## Possibility of K-Ar age mapping on the moon using cosmogenic $^{39}\text{Ar}$

TAKESHIMA, Yuko<sup>1</sup> ; HYODO, Hironobu<sup>2\*</sup> ; ITAYA, Tetsumaru<sup>2</sup>

<sup>1</sup>NEC Aerospace systems, <sup>2</sup>RINS, Okayama Univ. of Sci.

Rapid and wide range of age survey on the moon surface requires in situ measurement.  $^{39}\text{Ar}$  of cosmogenic origin from  $^{39}\text{K}$  in meteorite has been noticed since the early stage of noble gas research, and became a cue to the  $^{40}\text{Ar}/^{39}\text{Ar}$  method. If the production rate of  $^{39}\text{Ar}$  is considered uniform, the production and decay of  $^{39}\text{Ar}$  reaches to equilibrium after a long time, since  $^{39}\text{Ar}$  has a half life of 293 years. This half life is long enough to detect  $^{39}\text{Ar}$  in meteorites and moon rocks, and short enough to reach equilibrium of the isotope. Thus, such rocks or minerals possess a certain amount of  $^{39}\text{Ar}$  proportional to their potassium content. Using meteorites or rocks on moon surface under the same exposure condition,  $^{40}\text{Ar}/^{39}\text{Ar}$  age can be determined. For a start, a precise date of one of those samples in a laboratory and  $^{40}\text{Ar}/^{39}\text{Ar}$  ratio measurement of the same sample in the field are required to obtain J-value in the field.  $^{40}\text{Ar}/^{39}\text{Ar}$  ratios measurement of the rest of unknowns in the field allow us to calculate ages. Interfering isotopes from calcium will not affect much as long as Ca/K ratio is low. Samples in a depth or a shadow from exposure are not suitable for the measurement since the neutron density attenuates with depth. However, no need for atmospheric contamination, mass measurement and  $^{36}\text{Ar}$  measurement may provide us more mobility and rapid measurement.

Keywords:  $^{39}\text{Ar}$ , Cosmogenic, age distribution,  $^{40}\text{Ar}/^{39}\text{Ar}$  age, moon surface