(Form14-2)

International exchange on chemical pretreatment and measurement techniques for isotope analysis of geological and archaeological samples

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1. Purpose of this project

Through this international technical exchange (ITE), geochemistry and archaeology researchers from Nagoya University (NU) and the Korea Institute of Geoscience and Mineral Resources (KIGAM) share techniques for chemically preparing and measuring samples using mass spectrometers. The goal is to enhance the researchers' technical capabilities, including those of early-career scholars, through personnel exchanges, thereby improving the accuracy of isotope analysis in geological and archaeological samples. While FY2024 focused on improving analytical techniques for geological samples, such as sediments and rocks, FY2025 applies these techniques to archaeological and geological samples as part of a research initiative on the Transdisciplinary Network linking Space-Earth Environment Science, History, and Archaeology. This project focuses on analyzing isotopes of lithium (Li), strontium (Sr), and neodymium (Nd) in various geological and archaeological samples.

2. Methods

The project members are Dr. Seung-Gu Lee, KIGAM, Korea; Dr. Narges Daneshvar, Institute for Space–Earth Environmental Research (ISEE), NU; Mr. Kazuma Wakayama and Mr. Takashi Tsuchiya, Graduate School of Environmental Studies (GSES), NU; Prof. Seiji Kadowaki, Nagoya University Museum (NUM); Prof. Masayo Minami, ISEE, NU; and Dr. Asahara, GSES of NU.

In this project, the chemical pretreatment of the samples was carried out in the cleanroom chemistry laboratories of GSES of NU and KIGAM. The following mass spectrometers were also used in the project:
(a) thermal ionization mass spectrometer (TIMS), GVI IsoProbe-T, with 9 Faraday cups (NU),
(b) multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), ThermoFisher Scientific Neptune Plus, with 9 Faraday cups (KIGAM), and
(c) inductively coupled plasma mass spectrometers (ICP-MS), Perkin Elmer NexION350 (KIGAM) and Agilent 7700x (NU).

3. Periods of stay in ISEE / International stay

(i) Stay in KIGAM, Korea, from 22/2/2026 to 27/2/2026. Asahara, Y., Wakayama, K.
(ii) Stay in ISEE, NU, Japan, from 16/3/2026 to 21/3/2026. Lee, S.-G.

4. Achievements obtained from the program

4-1 Sr and Nd isotope ratio measurement for archaeological samples by TIMS (Apr. 2025~Mar. 2026)

Tsuchiya, Kadowaki, and Asahara focused on the relationship between the archaeological types of the Jomon pottery excavated from the Tenjinyama site in the Chita Peninsula, Aichi Prefecture, and their chemical and Sr isotopic compositions. Daneshvar, Minami, and Asahara examined the provenance and chemical and Sr-Nd isotopic characteristics of Haji pottery excavated from the Irino Castle ruins in Shikoku Island of Southwest Japan. The results of Sr isotope analysis of Jomon pottery from the Tenjinyama site suggest that the source materials likely came from the Chita Peninsula region surrounding the excavation site. Additionally, the chemical and isotopic analyses revealed that changes in source material coincided with shifts in pottery styles. Meanwhile, the chemical and Sr isotopic compositions of the Haji pottery from the Irino Castle ruins indicate that the source materials originated from the neighboring southern Shikoku region. A comparison with geochemical maps in the context of provenance analyses of archaeological samples also revealed certain issues with the geochemical maps. Specifically, the maps show depletion of zirconium (Zr) and heavy rare earth elements (HREE). Likely, the sediment sample preparation method used to create the

geochemical map is slightly flawed: heavy minerals, such as zircon, were significantly fractionated from other minerals during sample preparation. However, since these heavy minerals contain virtually no Sr or Nd, they do not affect Sr and Nd isotope ratios, and therefore, the isotope ratios are effective tracers for provenance analysis of archaeological sample sources.

Young researchers Tsuchiya and Daneshvar discussed the above results with Dr. Lee at the Annual Meeting of the Geochemical Society of Japan (Tohoku University, Sendai) in Sept. 2025 and during Dr. Lee's stay in Nagoya in Mar. 2026. Based on this discussion, Tsuchiya and Daneshvar have each finished the first drafts of their respective papers as lead authors and plan to submit them to international journals during the first half of FY2026.

4-2 Li isotope ratio measurement by MC-ICP-MS (Oct. 2025~Mar. 2026)

Lee, Wakayama, and Asahara performed Li isotope ratio ($^{7}Li/^{6}Li$) measurements on volcanic rock samples by MC-ICP-MS at KIGAM (Fig. 1). To reduce the impurities of titanium (Ti) and Zr in the chemically isolated Li fraction, which posed a challenge during the MC-ICP-MS measurements of Li isotopes in the FY2024 ITE project, we reconfigured the separation conditions of the ion-exchange resin column used in the chemical pretreatment. This significantly reduced the matrix elements in the Li fraction through two rounds of the column separation. Using this improved method, Li was isolated from the GSJ geochemical reference samples and the Quaternary volcanic rock samples in the Northeast (NE) Japan Arc, and the Li isotope ratios were measured using KIGAM's MC-ICP-MS in dynamic mode. After confirming that the Li isotope values of the reference rock samples were consistent with previous study results and were found to be sufficiently accurate, the Li isotope ratios were measured for several volcanic samples from the NE Japan Arc. In FY2026, we plan to systematically conduct the isotopic analyses of Quaternary volcanoes in the NE Japan Arc using the methods established through the ITE project from FY2024 through to FY2025 by NU and KIGAM.

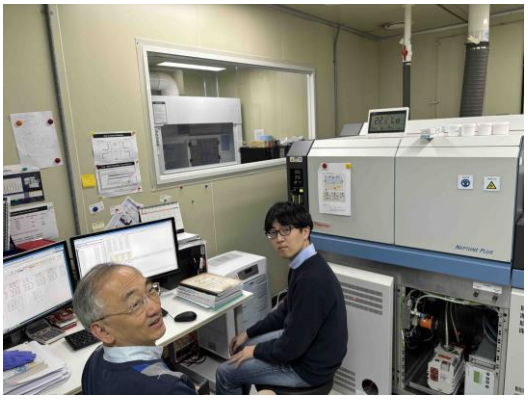

Fig. 1 Li isotope ratio measurement on volcanic rock samples by MC-ICP-MS at KIGAM (Feb. 2026).

4-3 Cross-validation of Nd isotope measurement between MC-ICP-MS and TIMS (Dec. 2025~Mar. 2026)

In MC-ICP-MS, unexpected isotopic fractionation, which cannot be corrected, can occur due to changes in the condition of the solution sample introduction system or the plasma ion source, or due to the introduction of matrix elements (impurity elements) in the chemically separated sample solution. Dr. Lee, Daneshvar, and Asahara reanalyzed samples for which the Nd isotope ratio data obtained using KIGAM's MC-ICP-MS were considered anomalous for Nd isotope ratios, using the TIMS at NU. Since the cause of this anomaly could be trace amounts of matrix elements such as Ce and Sm present in the Nd fraction after chemical separation, we measured the Nd isotope reference material, JNdi-1, as well as JNdi-1 samples doped with trace amounts of Ce and Sm. As a result, normal isotope values were obtained from all samples, including the isotope reference material.

In TIMS, even if the Nd fraction contains trace amounts of impurities, the Nd and impurity elements on the filament will evaporate and ionize sequentially as the filament heats up. Experiments using geological and archaeological samples have confirmed that abnormal isotopic fractionation is less likely to occur or is less pronounced compared to MC-ICP-MS, where all elements ionize simultaneously. These results suggest that chemical pretreatment tailored to the sample is as important as instrument calibration in isotope analysis of various samples.

5. List of publications

1) Daneshvar, N., Azizi, H., Stern, R.J. (2025) Late Jurassic-Early Cretaceous sediment-hosted Zn-Pb mineralization in western Iran: a world-class example of passive margin mineralization. *International Geology Review* **68**, 162-186.
2) Daneshvar, N., Azizi, H., Minami, M., Asahara, Y., Tsuboi, M. (2025) Assessment of lithium potential for future exploration in the Ghahavand Plain of Western Iran. *Scientific Reports* **15**, 34798.