

SGC053-P01

Room:Convention Hall

Time:May 26 10:30-13:00

## Fully automated open column separation system - "Columnspider I" for efficient preparation of isotope analysis

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Sr, Nd, Pb and Hf isotope ratios are fundamental in our research on the evolution of the Earth's interior and surface. Until recent it was difficult to process rocks with very low concentrations or to target individual minerals in a tiny sample. At IFREE, JAMSTEC we have developed improved analytical methods for high precision analysis of very low concentration and small sized samples. This has expanded the scope of application of isotope analysis on broader variety of rock samples. The number of important samples we want to process has greatly increased. Therefore we must significantly improve the efficiency of the sample analysis and particularly the sample preparation.

Thermal Ionization Mass Spectrometer that includes some level of automation is used for measuring the samples without much labor and with decent speed. However the sample preparation process requires lengthy and labor-heavy pre-treatment compared to the actual measurements. Despite there are other simpler methods for direct sample measurement (laser ablation) the conventional method of separating the target elements using open column chromatography is still valuable and preferred in many cases.

In general, the rock sample preparation for isotope analysis is roughly divided into three steps: 1.Decomposition of the sample; 2.Extraction of the target element; 3.Dilution (MC-ICP-MS) or Loading on filaments (TIMS); All these three stages require cumbersome and lengthy manual labor. The most time-consuming and monotonous processes are found in the case of 2.Extraction of the target element. The possibility for human error is also very high here. Many of the sub-processes are easy to automate and it's relatively easy to simulate human manipulations.

This put the beginning of the project for a pipette robot that JAMSTEC and HOYUTEC CO.LTD. successfully co-developed. The fully automated open column separation system "Columnspider I" can be set up with 10 samples for simultaneous separation and extraction of target elements. By using this equipment we are able to save labor and valuable time and dramatically improve the performance for the preparation of the samples. In the context of the whole process of isotope analysis we expect it to play major role in achieving accurate analysis of increased number of samples. In this presentation I will introduce the features of "Columnspider I" in detail.

Keywords: Fully automated separation system, Open column, Sr,Nd,Pb,Hf isotope, Preparation, Column separation, Pipette robot

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## Determination of Ce isotopic ratio using a three-step separation procedure and thermal ionization mass spectrometry

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The rare earth elements (REE) have two long-lived decay systems, the  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  and  $^{138}\text{La}$ - $^{138}\text{Ce}$ . The combination of those isotope ratios provides information on ages, initial ratios, and enables estimation of the time-integrated REE evolution of complex geological reservoirs in the mantle or crust. However, the variation of Ce isotopic ratio ( $^{138}\text{Ce}/^{142}\text{Ce}$ ) due to secular radiogenic decay to  $^{138}\text{Ce}$  is smaller than those of Nd isotopic ratio because of the low abundance of  $^{138}\text{La}$  and its long half-life. Therefore, highly precise determination of Ce isotopic ratios is necessary to obtain reliable data for application of geochemical studies.

For precise determination of Ce isotopic ratio, it is necessary to separate Ce from the matrix and isobaric interfering elements. A three-step chemical separation procedure was developed for Ce separation in this study, which was proved to be able to sufficiently remove the isobaric interfering elements with low procedural blank. Ce was first separated as a REE fraction via cation exchange column with HCl. Then Ce alone was isolated from other REEs by selective extraction technique with chelating resin (Tazoe et al., 2007). In this step, Ce was separated easily from other REEs by oxidation from  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$  using  $\text{KBrO}_3$  in nitric acid. Ce was further purified using a third cation exchange column with HIBA as the eluent, which was modified from Makishima and Nakamura (1991).

The Ce isotopic ratios were measured by multicollector static measurement using TIMS (TRITON TI, Thermo Fisher Scientific Co., Germany) equipped with nine Faraday cups at IFREE, JAMSTEC. The Ce ion beams were measured as oxide species ( $\text{CeO}^+$ ) to obtain stable and large ion beams. During the Ce isotope measurement, Ce oxide ion beams were obtained at the intensity of  $3 \sim 10 \times 10^{-11}$  A for  $^{142}\text{Ce}^{16}\text{O}$  using a double Re-filament technique. The mass-dependent fractionation of Ce isotope ratio were normalized to  $^{136}\text{Ce}/^{142}\text{Ce}=0.01688$  and  $^{140}\text{Ce}/^{142}\text{Ce}=7.947$  using the power law. The  $^{18}\text{O}/^{16}\text{O}$  ratios were obtained in situ measurement. The data acquisition time for 450 ratios was about 1.2 hours. The analytical reproducibility and precision in the measurement of JMC 304, which is Ce isotope reference material (Tanaka and Masuda, 1982), were obtained  $\pm 0.008\%$  (2S.D.,  $n=46$ ) and  $< \pm 0.003\%$ , respectively.

The Ce isotope measurements of the Ames Laboratory Ce metal reference material (Willbold, 2007) were performed with an analytical reproducibility of  $\pm 0.007\%$  (2S.D.,  $n=36$ ) with normalization to JMC 304 in order to eliminate any inter-laboratory biases. The Ce isotope ratio for BCR-1, the USGS geochemical reference samples, was  $0.0225646 \pm 0.0000004$  (2  $\sigma_m$ ,  $n = 7$ ) and consistent with previously reported data (Makishima and Nakamura, 1991). We also performed the measurement of Ce isotope ratios in seven geological reference materials (JB-1a, JB-3, JA-1, JA-2, JR-1, JG-1a, and JMn-1) and the results were consistent with reported data but with improved analytical precision.

### Reference

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Keywords: Ce isotope ratio, TIMS, JMC304, BCR-1, chemical separation

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## Two primary magmas derived from Samoan mantle plume: less-degassed tholeiitic and EM2-type alkalic magmas

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Alkali basalts from Tutuila Island, American Samoa are interpreted as products of binary mixing of magmas derived from isotopically distinct source components (Farley et al., 1992): PHEM (primitive helium mantle,  $\frac{{}^3\text{He}}{{}^4\text{He}} > 24 R_{\text{A}}$ -type and EM2-type. Our new data show that the isotopic ratios in these lavas correlate with trace element ratios, clinopyroxene compositions, and phenocryst assemblage. PHEM-type basalts have lower Nb/Zr, LREE/HREE, and  $\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}$  and higher  $\frac{{}^{143}\text{Nd}}{{}^{144}\text{Nd}}$  and  $\frac{{}^{176}\text{Hf}}{{}^{177}\text{Hf}}$  ratios than EM2-type basalts. PHEM-type basalts include augite and orthopyroxene, while EM2-type basalts contain diopside together with olivine and/or plagioclase. The presence or absence of orthopyroxene and the difference in Ca-Ti-Na contents in clinopyroxenes suggest that the PHEM- and EM2-type end-member magmas are of tholeiitic and alkalic compositions, respectively. The reaction rims around the orthopyroxene phenocrysts indicates that PHEM-type tholeiitic end-member magmas mixed with EM2-type alkaline magmas before they were erupted. These results suggest that formation of tholeiitic basalts associated with the Samoan mantle plume can be detected by phenocryst assemblage and mineral compositions. Lack of systematic correlation between isotopic ratios and stratigraphy suggests that the end-member magmas were generated in the same period. The coexistence of tholeiites and alkaline magmas places important constraints for melting conditions and source materials for the Tutuila basalts.

Keywords: OIB, Samoa, primary magma

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## Magmatic processes of mafic dykes in Ryoke belt at Awaji and Shodo Islands, southwest Japan

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The synplutonic mafic dykes are widely exposed at Awaji and Shodo Islands in southwest Japan, which intrude into the Ryoke plutonic rocks of granitoids and/or gabbroic rocks (Yoshikura and Atsuta, 2000). Mode of occurrences of mafic dykes in the Awaji Island is characterized by the alignment of melanocratic lenticular enclaves with several centimeters in length. On the other hand, the mafic dykes in the Shodo Island occur as continued shape of mafic swarm intrusions.

Constituent minerals of mafic enclaves in Awaji Island or dyke in Shodo Island are plagioclase, hornblende and biotite. The chemical composition of plagioclase in the mafic rocks from the Awaji Island is  $An_{25-95}$ . On the other hand, chemical compositions of plagioclase in the mafic rocks from Shodo Island is  $An_{27-67}$  in matrix parts, and  $An_{62-92}$  in the phenocrysts parts.

The  $SiO_2$  wt.% contents of the mafic rocks from Awaji Island, and those from Shodo Island are 46-59, and 50-63, respectively. On the N-type MORB normalized spiderdiagram, the mafic rocks in both sites are shown similar by the LIL elements enriched and HFS elements depleted pattern. Moreover, on the variation diagrams, the Ti and V contents are shown by negative trends with respect to the variation of  $SiO_2$  contents. The K and Na contents are shown same or more value than granitic rocks. But most of the composition of granitic rocks are plotted on the extension line of enclaves.

These results suggest that the mafic dykes in Awaji Island and Shodo Island were formed by the processing of chemical mixing between mafic magma and felsic magma or alkaline fluid. The result that the  $SiO_2$  contents do not show significant correlation with respect to the variation of Fe/Mg ratio, and the presence of quartz and biotite in the mafic rocks of the lowest  $SiO_2$  contents (49 wt.%) may further support the evidence of chemical mixing between mafic and felsic magmas.

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Keywords: Ryoke belt, mafic rock, dyke, geochemistry, magma process

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## Improvement of web application of KML generator for visualizing geochemical data of rocks and sediments in Google Earth

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At present, cross-disciplinary researches are popular for constructing a new structure model on the Earth's interior. To promote these researches, visual presentation of different kinds of geochemical/geophysical data at once will be a great help to integrate and understand the research results from different fields. The layer system of the various virtual globes, e.g., Google Earth, easily provides the overlaying image of different types of geographic data on the same area. To plot the geographic data in Google Earth, the data should be written by Keyhole Markup Language (KML). For compiling various research results from different geoscience fields in Google Earth, we have developed several applications generating KML from original analytical/observational datasets. Our project launched in 2007 and we have already developed successful applications, called KML generator, for visualizing seismic tomographic model, geomagnetic field model, and geochemical data of rock and sediment samples in Google Earth. One of the KML generators converts geochemical and isotopic datasets in several online database systems into KML and allows users to visualize those data easily in Google Earth. The generator accepts data files produced by the database systems PetDB, SedDB, GEOROC, and GANSEKI and template data files that users themselves make. The data are plotted three-dimensionally as a bar graph on the surface of the virtual Earth at the sampling site for the rock and sediment samples. The major element compositions of samples can also be displayed as a stacked bar graph. A web application for the generator has already been available since 2008, so anyone can set the parameters for visualization over the Internet. Here we have improved User Interface (UI) of the web application to set the parameters of the generator intuitively. The sampling sites of the samples existing the uploaded data file will be plotted in map on the web UI of the generator, and the data range of selected composition or isotope ratio will also be graphically illustrated. For visualizing of one type of the composition or isotope ratio, histogram will be illustrated, and for ratio between two types of them, two-dimensional scattergram having x-axis for one type and y-axis for other type, will be constructed. These graphical images will help user to set the parameters, e.g., the data range to be plotted and the color of the graphs, for visualizing the data in Google Earth. Moreover, the visual image of the geochemical data in Google Earth can be confirmed on the web browser by using Google Earth API before the downloading the KMZ file.

Keywords: geochemical data, isotopic data, visualization, Google Earth, KML, web application