Korea-Japan Joint Conference

on the Geochemical and Cosmochemical Application of Microanalysis

12-16 June, 2023

Venue

KBSI Ochang Center 162 Yeongudanji–ro, Ochang, Cheongwon–gu, Cheongju, Chungbuk 28119

CAMECI

Field Excursion

Quarternary volcano in Jeju Island



CUT PLANET 2024 Research Infrastructure



PETROLOGICAL SOCIETY OF KOREA

Schedule

Schedule (12 June, Monday)

10:00 – 11:00 Lab tour (SHRIMP & IMS1300)

11:00 – 12:00 Lab tour (Laser ablation MC-ICPMS) & Poster presentation Femtosecond laser ablation MC-ICPMS U-Th and U-Pb dating of Quaternary zircons from Jeju Island, Korea

Youn-Joong JEONG*, Min-Ji JUNG, Ung-San AHN, Albert Chang-sik CHEONG

12:00 – 13:00 *Lunch*

13:00 – 13:40 Registration

Session 1 (chairpersons: Keewook YI & Changkun PARK)

13:40 - 14:20 (invited)

Hf-W dating of zircon from mesosiderite with sintered standard

Yuta KOYAMA, Yuji SANO*, Naoto TAKAHATA, Mizuho KOIKE, Makiko K. HABA, Sakata SHUHEI, Hideharu KUWAHARA, Tetsuo IRIFUNE

14:20 - 15:00 (invited)

Nano-scale analysis of noble gas implanted in solids

Hisayoshi YURIMOTO*

15:00 – 15:20 *Coffee break*

15:20 - 16:00 (invited)

Microanalyses in isotope geochemistry and cosmochemistry: A few examples applied at UC Davis Qing-Zhu YIN*

16:00 - 16:40 (invited)

REE isotopic variations found in extraterrestrial materials caused by cosmicray irradiation in space

16:40 - 17:20 (invited)

Development on non-destructive muonic X-ray analysis: Application to Earth and Planetary Science Kentaro TERADA*

18:00 Welcome Reception

Sessio	on 2 (chairperson: Yuri AMELIN)							
09:30 -	10:00							
Н	ligh-precision Pb-Pb chronology of Fe-Ti oxides by new HCl decomposition							
m	nethod Kengo ITO*, Magdalena HUYSKENS, Yuri AMELIN, Qing-Zhu YIN, Sota NIKI, Takafumi HIRATA, Tsuyoshi IIZUKA							
10:00 -	10:30							
Ir	-situ Sr isotope analysis of barite by LA-HR-MC-ICPMS							
10.30 -	10.50 Coffee break							
10.50	11.20							
10.50 -	11.20 Iltrafact geochemicta" Elemental and icotopic analyses of individual							
0	ana and isotopic analyses of individual							
11.00	anoparticles using ICP-MS Masaki NAKAZATO*, Kanoko KURIHARA, Takatumi HIRATA 11 FO							
11:20 -								
G	eoimaging: revolution in U-Pb geochronology							
	Sota NIKI*, Yusuke SAWAKI, Tsuyoshi KOMIYA, Takafumi HIRATA							
12:00 -	13:00 Lunch							
Sessio	on 3 (chairperson: Hiroshi HIDAKA)							
13.00 -	13.30							
M	/hat do Korean zircons tell us?							
13.30 -	14.00 (invited)							
10.00 M	letasomatic evolution of migmatites within the Veongdeok pluton							
ا•ا د	outbeastern Korea: Insights from mineral equilibria modeling and zircon							
St ic	sotopo data							
14.00	Hyeong Soo KIM [*] , Shinae LEE, Min-Ji JUNG, Albert Chang-sik CHEONG							
14:00 -	14.50 \mathbf{r}							
11	1-Situ oxygen isotope measurement of magnetite by SIMS							
14.30 -	14.50 Coffee break							
1 1 .50								
Sessi	ON 4 (chairperson: Qing-Zhu YIN)							
14:50 -	15:20							
Р	b-isotopic dating of meteorites and asteroidal materials: pushing the limits							
ir	n sample size Yuri AMELIN*							
15:20 -	15:50 (invited)							
С	hemical age dating of lunar zirconolite using electron microprobe							
	Changkun PARK*, Hwayoung KIM							
15:50 -	16:20 (invited)							
М	ficroanalysis and micromineralogy of Asian dust Gi Young JEONG*							
16:20 -	16:30 Group photo							
16:30 -	17:00 <i>Guide to field excursion</i> Keewook YI*							
17:00 -	17:30 Guide to the submission of papers to the special issue of the Journal of							
	Analytical Science and Technology Albert Chang-sik CHEONG*, Yuri AMELIN, Hiroshi HIDAKA							
18:00 D	inner							
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Schedule (13 June, Tuesday)

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Schedule (14–16 June, Wednesday–Friday)

Field Excursion (guided by Prof. Young Kwan SOHN)

Quarternary volcano in Jeju Island

Geological Splendors of Jeju Island

Korea Institute of Geoscience and Mineral Resources (KIGAM) Jeju Research Institute (JRI)

Abstracts

Hf-W dating of zircon from mesosiderite with sintered standard

Yuta Koyama¹, Yuji Sano^{1,2*}, Naoto Takahata¹, Mizuho Koike³, Makiko K. Haba⁴, Sakata Shuhei⁵, Hideharu Kuwahara⁶, Tetsuo Irifune⁶
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Introduction. Mesosiderite is a group of stony-iron meteorites, consisting of about equal parts of metallic nickel-iron and basaltic silicates. Their silicates are similar to Eucrite in mineralogy, chemistry and oxygen isotopes [1]. The earlier stratified parent body was possibly destroyed by a catastrophic impact and reaccreted with a core, mantle, crust materials mixture [2]. To study the history of mesosiderite parent body, we have investigated the Hf-W ages of mesosiderite zircons. The accurate Hf-W dating of zircons in a mesosiderite was firstly reported by ion microprobe in [3], however, there were no suitable standard zircons with adequate amount of tungsten, because of its incompatibility in zircon crystal. To overcome this difficulty, we have created new standard zircon with known amounts of hafnium and tungsten by a high-pressure experiment. We applied the standard to Hf-W dating of zircons in three mesosiderites using ion microprobe instrument.

Experiment. High purity zircon powder as well as hafnium and tungsten oxide were prepared at first. They were well crushed and mixed by a high energy ball mill (Emax, Retsch Co., Ltd) and sintered by a high-pressure method with multi-anvil apparatus (ORANGE-3000, Geodynamics Research Center, Ehime University). The W/Zr and Hf/Zr ratios of synthesized zircon was measured with a LA-ICPMS to verify homogeneity and abundance ratios. Seventeen zircon grains in total were extracted from three mesosiderites (Asuka 882023, NWA 1242 and Vaca Muerta) and embedded on epoxy resin disk. They are all anhedral and grain size varies

from 40 to 60 μ m. There is no growth bands and heterogeneous bright pattern by a cathode luminescence observation. All analyses of Hf-W dating are conducted using an ion microprobe (NanoSIMS 50, Atmosphere and Ocean Research Institute, University of Tokyo). A 2 nA O⁻ primary beam (5 μ m diamter) was used to raster a 30 μ m square on the zircon surface. Secondary ions of Hf and W isotopes were detected by a multi-ion counting system.

Results and Discussion. We obtained a relative sensitivity factor of Hf/W by two synthesized zircons whose Hf/W ratio were homogeneous at 20 μ m scale. Hf/W ratios of meteorite zircon samples were measured with the relative sensitivity factor. Absolute ages of each zircon grains were calculated with their ¹⁸²Hf/¹⁸⁰Hf values and the anchor age of 4568.3 Ma for CAIs [4]. These zircon ages in Asuka 882023, NWA 1242, and Vaca Muerta were 4536.9^{+2.4}-4.1 Ma, 4538.8^{+2.1}-3.2 Ma, and 4530.2^{+4.8}-11.0 Ma (1 σ), respectively. They are important, namely, different from Pb-Pb ages of mesosiderite zircon in literature (4559 Ma and 4525 Ma [5]), possibly representing the timing of metal-silicate mixing event on the mesosiderite parent body in addition to different closure temperature of U-Pb and Hf-W system.

- [1] Clayton and Mayeda, 1996. doi: 10.1016/0016-7037(96)00074-9.
- [2] Scott E et al., 2001. doi: 10.1111/j.1945-5100.2001.tb01927.x.
- [3] Koike M et al., 2017. doi: 10.1002/2016GL071609.
- [4] Burkhardt C et al., 2008. doi: 10.1016/j.gca.2008.10.023.
- [5] Haba M et al., 2019. doi: 10.1038/s41561-019-0377-8.

Nano-scale analysis of noble gas implanted in solids

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Noble gases have been utilized as tracers for geo- and cosmo-chemistry to understand origin and evolution of natural samples. We need a special technique to measure noble gasses, called as noble gas mass spectrometry, because of extremely low abundances in solids and their chemically inert characteristics. The detection limits of state-of-the-art noble gas mass spectrometry are at ~1×10⁻¹² cm³ STP (~3×10⁷ atom) for He [1, 2], corresponding to concentrations of 6×10^{-7} , 6×10^{-4} and 6×10^{-1} cm³ STP g⁻¹ (5×10^{13} , 5×10^{16} and 5×10^{19} atom cm⁻³; 0.0005, 0.5 and 500 ppma) for olivine of 100, 10 and 1 µm in diameter, respectively. Focused laser ablation techniques have been introduced in the noble gas mass spectrometry for in-situ analyses. The spatial resolution becomes achieved to ~50 µm for both lateral and depth directions [3-5]. The detection limit of concentration with the laser ablation is calculated to be ~2×10⁻⁶ cm³ STP g⁻¹ (2×10¹⁴ atom cm⁻³, 2 ppba) using the detection limit of the noble gas mass spectrometry.

Secondary ion mass spectrometry (SIMS) is a powerful in-situ technique for trace element analysis in solids and has been applied to noble gas measurements. The detection limits have been at ~0.1 cm³ STP g⁻¹ (~10¹⁹ atom cm⁻³, 100 ppma) for He with a spatial resolution of ~20 µm for lateral and ~10 nm in depth [6]. This concentration of detection limit is calculated to be ~1×10⁻¹² cm³ STP (~4×10⁷ atom) for He under the measurement volume. The absolute detection limit of He by SIMS is similar to that of the noble gas mass spectrometry although the spatial resolution by SIMS is much smaller than that of the laser-ablation noble gas mass spectrometry. However, the detection limit of concentration is ~5 orders of magnitude worse than the case of the laser ablation noble gas mass spectrometry. Because He concentrations of natural samples are less than 10⁻² cm³ STP g⁻¹ (~10¹⁸ cm⁻³) [7, 8], the measurement abilities of SIMS are not sufficient for natural sample analyses. In order to realize µm-scale lateral resolution for noble gas analyses, ionization efficiency of noble gas should be more enhanced.

We have applied strong field ionization for noble gas on secondary neutral mass spectrometry (SNMS) [9]. The detection limits have been at ~0.06 cm³ STP g⁻¹ (~5×10¹⁸ cm⁻³, 50 ppma) for He with a spatial resolution of ~3 μ m for lateral and ~10 nm in depth [10].

Recently, the detection limits have been improved to $\sim 3 \times 10^{-3}$ cm³ STP g⁻¹ (3×10^{17} cm⁻³, 3 ppma) for He with the same spatial resolution. This concentration of detection limit is calculated to be $\sim 4 \times 10^{-14}$ cm³ STP ($\sim 1 \times 10^{6}$ atom) for He atom detection from the measurement volume. In this talk we discuss recent developments of our SNMS studies and show some applications to cosmochemical materials.

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- [3] Nakamura T et al., 1999. doi: 10.1016/S0016-7037(98)00275-0.
- [4] Okazaki R et al., 2001, doi: 10.1038/35090520.
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- [9] Ebata S et al., 2012. doi: 10.1002/sia.4857.
- [10] Bajo K et al., 2015. doi: doi:10.2343/geochemj.2.0385.

Microanalyses in isotope geochemistry and cosmochemistry: A few examples applied at UC Davis

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In this talk, I will be presenting on three aspects of work on going at the Yin Lab at UC Davis, which might be of interests to the attendees of this joint conference.

The first topic is on short-lived radioactivity, with a focus on whether ²⁶Al is homogenous or heterogenous in the early Solar Nebula. This is a highly controversial topic and was a subject of long-term debate in cosmochemistry community. And the issue is an important one, because it is going to affect our ability to precisely date early solar system events; it affects heat budget calculations for the early planetary differentiation; and it affects our view on the origin and sources of short-lived radionuclides and degree of mixing in the protoplanetary disk as compared with other stable isotopes nucleosynthetic anomalies. In collaboration with Dr. Yuri Amelin at ANU, we have published jointly a series of papers between 2008 - 2019 [1-7]. I will be giving a pre-pandemic overview and a post-pandemic update on this issue based on the new work soon to appear in print [8].

The second topic that I plan to discuss is a high precision chemical abrasion – isotope dilution – isotope ratio mass spectrometry (CA-ID-IRMS) U-Pb dating of zircons applied to problems such as testing Snowball Earth hypothesis [9], as well as L-chondrite parent body break up event occurred in asteroid belt as dated by the Ordovician limestones strata where the fossil meteorites were found [10].

The third and final topic that I plan to present is our recent effort to use CA-ID-IRMS technique to provide a benchmark U-Pb data of common accessary minerals to serve as standards for in-situ dating methods such as LA-ICP-MS and SIMS. The minerals we worked on include zircon, apatite, titanite, monazite, fluorite, scheelite, columbite-tantalite, and carbonate. I will focus this part of my talk on light rare earth carbonate-fluoride mineral called bastnaesite ((La, Ce)CO₃F). I will be showing the textbook example of this mineral's extraordinary ability to keep the U-Th-Pb system closed, where ²³²Th-²⁰⁸Pb isochron, ²³⁸U-

²⁰⁶Pb isochron, ²³⁵U-²⁰⁷Pb isochron, U-Pb concordia, Th-U concordia, model ages of ²⁰⁸Pb/²³²Th, ²⁰⁶Pb/²³⁸U, ²⁰⁷Pb/²³⁵U all agree within 0.1%. This unpublished work will likely become my contribution to the special volume of the joint conference.

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REE isotopic variations found in extraterrestrial materials caused by cosmic-ray irradiation in space

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The estimation of neutron fluence using isotopic variations in association with neutron capture can be applied for cosmochemistry. Two types of nuclear reactions, spallation and neutron-capture, mainly occur at the surficial parts of airless solar-planets that are exposed to cosmic-ray in space. The neutron-captured isotopic shifts of 149 Sm- 150 Sm by 149 Sm(n, γ) 150 Sm and 157 Gd- 158 Gd by 157 Gd(n, γ) 158 Gd are often observed in meteorites and lunar surface materials, and can be used for characterization of the extra-terrestrial materials.

In general, the neutron-capture cross sections for most nuclides vary as $E^{-1/2}$ in the thermal energy region (E < 1 eV), and have many sharp peaks, called as resonances, in the intermediate energy (epithermal) region (1 eV < E < 1 MeV). The cross section at the epithermal region including the resonances is quantitatively treated with resonance integral (RI) defined as the following:

$$RI = \int_{E_c}^{E_{max}} \sigma(E) \frac{dE}{E}$$

where E_c is a cut-off energy, typically used as 0.5 eV, and E_{max} is the highest energy in the region of neutron adsorption resonance, and $\sigma(E)$ is a neutron capture cross section as a function of energy.

$$\sigma_{\rm epi} = \frac{{\rm RI}}{\int_{{\rm E_c}}^{{\rm E}{\rm max} d{\rm E}}}$$
 is given as

Table 1. Selected nuclides having significantly large neutron capture cross sections and RI (unit in barns=10⁻²⁴ cm²) for thermal (σ_{th}) and/or epithermal (σ_{epi}) energy regions

	nuclide	σ_{th}	RI	σ_{epi}
	¹⁴⁹ Sm	4.01×10 ⁴	3.38×10 ³	4.77×10 ²
L	¹⁵⁵ Gd	6.09×10 ⁴	1.54×10 ³	2.57×10 ²
Ļ	¹⁵⁷ Gd	2.53×10⁵	7.59×10 ²	1.19×10 ²
	¹⁶⁷ Er	6.49×10 ²	2.98×10 ³	3.59×10 ²
	¹⁶⁸ Yb	2.30×10 ³	2.13×10 ⁴	3.56×10 ³
145 155 167 168	¹⁶⁹ Tm	1.05×10 ²	1.62×10 ³	1.95×10 ²

an average cross section of the energy range between E_c and E_{max} over the thermal energy from RI divided by the integral of dE/E. Epithermal neutron capture cross sections for individual isotopes in this study are calculated by the determination of E_{max} from the upper energy of individual resonance peaks. The used Emax values (eV) for the calculation of individual σ_{th} are 600 for ¹⁴⁹Sm, 200 for ¹⁵⁵Gd, 300 for ¹⁵⁷Gd, 2000 for ¹⁶⁷Er, 200 for ¹⁶⁸Yb, and 2000 for ¹⁶⁹Tm.

¹⁴⁹Sm, ¹⁵⁵Gd and ¹⁵⁷Gd react sensitively with thermal neutrons rather than epithermal neutrons, whereas ¹⁶⁷Er and ¹⁶⁸Yb react with thermal as well as epi-thermal neutrons. Systematic isotopic analyses of Sm, Gd, Er, and Yb collected from a single material are planned to obtain information on neutron fluences in a wide energy range from thermal to epithermal region. A comparison of the neutron-capture cross sections data listed in the table shows that ¹⁶⁷Er is hundreds times less sensitive to neutrons than ¹⁴⁹Sm and ^{155, 157}Gd. The detection limit of neutron fluence from the Er isotopic shift is simply calculated to be >10¹⁶ n cm⁻². This suggests that the Er isotopic approaches are effectively used for all meteorites and lunar surface materials that have been irradiated by the neutron fluences over 10¹⁶ n cm⁻² [1-2].

The Yb isotopic approach is somewhat more complicated for the quantitative discussion rather than those of Sm, Gd, and Er, because the neutron capture reaction of ¹⁶⁸Yb is not (n,γ) -type but $(n,\gamma\beta^+)$ -type. ¹⁶⁸Yb converts to ¹⁶⁹Tm by the neutron capture of 168 Yb(n, $\gamma\beta^+$) 169 Tm. In addition, 169 Tm has larger σ_{epi} than σ_{th} , and converts to 170 Yb by the neutron capture reaction of 169 Tm(n, $\gamma\beta^+$) 170 Yb. As a reference, the Yb isotopic compositions of the Oklo natural fission reactor materials, which are known to be irradiated with neutrons of $10^{20} \sim 10^{21}$ n cm⁻², show a small but significant deficit of ¹⁶⁸Yb by ¹⁶⁸Yb(n, $\gamma\beta^+$)¹⁶⁹Tm and enrichment of ¹⁷⁰Yb produced from ¹⁶⁹Tm($n,\gamma\beta^{-}$)¹⁷⁰Yb [3-4]. It is worthwhile to find the isotopic variations of ¹⁶⁸Yb and ¹⁷⁰Yb in extraterrestrial materials irradiated with neutrons of 10¹⁶~10¹⁸ n cm⁻². Since the isotopic abundances of both ¹⁶⁸Yb and ¹⁷⁰Yb are originally small, 0.13 % and 3.04 % to total, respectively, careful measurements should be required to detect their isotopic variations. I have utilized a modified TRITON Plus thermal ionization mass spectrometer equipped with multi- Faraday cups fitted with two 10¹³ Ohm amplifiers for the detection of ¹⁶⁸Yb and ¹⁷⁰Yb isotopes and seven 10¹¹ Ohm amplifiers for the detection of other five Yb isotopes and two isobaric interferences to perform high-accuracy and precise Yb isotopic analyses.

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Development on non-destructive muonic X-ray analysis: Application to Earth and Planetary Science

Kentaro Terada^{*}

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The muon is a lepton with a mass of 105.7 MeV/c², approximately 200 times heavier than the electron. In general, electron-induced characteristic X-ray analysis has been widely used to determine the chemical compositions of materials in Earth and Planetary Science. In recent years, analysis of characteristic X-rays from muonic atoms, in which a muon is captured, has attracted attention because both a muon beam and a muon-induced characteristic X-ray have high transmission abilities, of which energies are about 200 times higher (e.g., muonic carbon-K α is 75keV, whereas electron-induced carbon-K α is 0.3 keV). Therefore, muonic Xray analysis has great advantages in several ways; (1) non-destructive elemental analysis from light to heavy elements, (2) depth profile analysis, (3) isotopic measurement for heavy elements and (4) investigation of chemical condition (redox-state). Since 2010, we have been conducting non-destructive 3D X-ray analysis using a negative muon beam and applying carbonaceous chondrites [1-2], aiming at rare samples collected from a C-type asteroid, Ryugu.

Very recently, this muon non-destructive analysis method was successfully applied to a C-type Asteroid Ryugu sample [3] and/or various lunar meteorites [4]. Especially, it should be noted that we succeeded in quantifying the abundances of important major elements nondestructively of Ryugu, including C, N, and O, without exposing them to the Earth's atmosphere [3].

At the workshop, I will review the principle of muon non-destructive analysis, our recent results and further application to Earth and Planetary Science.

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High-precision Pb-Pb chronology of Fe-Ti oxides by new HCl decomposition method

Kengo Ito^{1*}, Magdalena Huyskens², Yuri Amelin³, Qing-Zhu Yin⁴, Sota Niki¹, Takafumi

Hirata¹, Tsuyoshi Iizuka¹ ¹The University of Tokyo ²Geological Survey of Norway ³Korea Basic Science Institute ⁴University of California at Davis * presenting author, k.ito@eps.s.u-tokyo.ac.jp

Introduction: Fe-Ti oxides are complex ternary systems in which FeO-Fe₂O₃-TiO₂ are in solid solutions. For Fe-Ti oxides, three solid solution series exist; (i) ulvöspinel (Fe₂TiO₄)-magnetite (Fe₃O₄) series, (ii) ilmenite (Fe₂TiO₃)-hematite (Fe₂O₃) series, (iii) ferropseudobrookite (Fe₁Ti₂O₅)- pseudobrookite (Fe₂TiO₅) series. The complexity and diversity of these chemical compositions are mainly due to the variation in the ratio of ferric to ferrous iron due to changes in oxygen fugacity. It has been pointed out that Fe-Ti oxides have potential as a U–Pb chronometer [1-2], but previous studies have been limited due to their low U concentrations (< 100 ppb) and complex relationships with coexisting minerals. Furthermore, no previous studies have low U and radiogenic Pb concentrations, the main challenge for high–precision Pb–Pb chronology of Fe-Ti oxides is to obtain Pb isotope compositions of Fe-Ti oxides that are free from non-radiogenic Pb derived from other minerals. In this study, we have developed a new method for extracting Pb from Fe-Ti oxides by partial dissolution in HNO₃ + HCl and applied it to ulvöspinel in the angrite meteorite, Northwest Africa (NWA) 4590. In addition, the possibility of in-situ U–Pb dating of Fe-Ti oxides was investigated using LA-ICP-MS.

Sample and Method: Northwest Africa (NWA) 4590 is a small, very fresh, fusion-crusted fragmented single stone of 213 g. Pb–Pb ages of pyroxenes and silico-phosphate in this meteorite were precisely determined to be 4558.07 ± 0.31 Ma and 4557.73 ± 0.26 Ma, respectively [3]. Given the rapid cooling rate of ~0.15 °C/year [4], it is expected that ulvöspinel has an identical Pb–Pb age to that of pyroxenes and silica- phosphate, thereby allowing for the assessment of the accuracy of our Fe-Ti oxide Pb–Pb dating.

We have carried out: high-precision Pb isotopes analysis using TIMS and in-situ trace elements analysis using LA-ICP-MS. First, we analyzed 8 ulvöspinel fractions (1–2 mg) from NWA

4590. Sample fractions were leached in 0.5 M HNO₃ with ultrasonic agitation (L-1), hot 6 M HNO₃ (L-2), and ulvöspinel was decomposed by hot 12 M HCl (L-3). Minerals that did not dissolve in the previous leaching steps were digested in a mixture of 25 M HF and 12 M HNO₃ (R). Pb isotopes were measured on a Thermo Scientific TRITON Plus TIMS at the University of California, Davis, USA. Next, to test the feasibility of in-situ U–Pb dating and to determine the value of Th/U in ulvöspinel, minerals were analyzed using LA-ICP-MS at the University of Tokyo. The isotopes (²⁷Al, ³¹P, ⁴⁴Ca, ⁴⁷Ti, ⁵⁷Fe, ⁹⁰Zr, ²⁰²Hg, ^{204,206,207,208}Pb, ²³²Th, and ²³⁸U) were registered.

Results & Discussion: Pb, Th, and U contents of ulvöspinel from LA-ICP-MS analysis were 0.302–0.458 [μ g/g], 0.000–0.001 [μ g/g], 0.189–0.291 [μ g/g] (n=4), respectively. The ²³²Th/²³⁸U value for ulvöspinel was 0.002 ± 0.001 (2 σ , n=4). Pb-isotopic composition of ulvöspinel was radiogenic (²⁰⁶Pb/²⁰⁴Pb between 175–1750), albeit not as radiogenic as in pyroxene (²⁰⁶Pb/²⁰⁴Pb between 2160 to over 100,000; Amelin, 2008). Model values of ²³²Th/²³⁸U calculated from TIMS ²⁰⁸Pb/²⁰⁶Pb ratios: ulvöspinel (7 data from L-3, 3 data from L-2) has ²³²Th/²³⁸U = 0.01–0.43, which was significantly lower than the bulk rock value (3.39 ± 0.17; Tissot et al., 2017) (Fig. 1). Th/U in Fe-Ti oxides is much lower than the value of the bulk rock because they selectively incorporate U and exclude Th [5]. Hence, the low Th/U in L-3 (and some L-2) indicates that radiogenic Pb from ulvöspinel was successfully extracted by the HCl decomposition method.

Pb isotope data from ulvöspinel yielded a precise Pb–Pb isochron age of 4558.09 ± 0.88 Ma (n=10, MSWD=1.4: Fig. 2); where the ²³⁸U/²³⁵U from the bulk rock value of 137.772 ± 0.025 for NWA 4590 [6] was taken for age calculation. The isochron passes through primordial Pb [7]. The Pb–Pb age of ulvöspinel agrees within error with the Pb–Pb ages of pyroxenes and silica-phosphate. In the in-situ analysis, the values of Pb isotopes and ²⁰⁶Pb/²³⁸U corrected by NIST SRM 612 glass were on the concordia line of the Tera-Wasserburg diagram.

Conclusion: This is the first report of Pb–Pb dating and in-situ U–Pb dating of extra-terrestrial Fe-Ti oxide. The efficient decomposition of Fe-Ti oxides can be performed by HCl. Ulvöspinel is a major U carrier with low Th/U in the angrite NWA 4590 and contains radiogenic Pb. The age of 4558.09 ± 0.88 Ma is consistent with the ages of pyroxenes and phosphate obtained in previous studies. Our method can be applied to other extra-terrestrial Fe-Ti oxides in eucrites and lunar samples.

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for leachates and residues of each fraction.



Fig. 2. Pb–Pb isochron plots for low Th/U fractions in NWA 4590.

In-situ Sr isotope analysis of barite by LA-HR-MC-ICPMS

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Sr isotopic ratios in the Earth's interior changed between the crust and mantle after the differentiation of the Earth. Liquid-phase concentrated Sr and Rb were distributed to the crust, while these elements were depleted in the mantle. Therefore, the isotopic evolution curves of Sr87 and Sr86 have changed in each of these regions, and it is important to elaborate the evolution curve for the mantle, which is the more Sr-depleted one, because it is one indicator that puts constraints on continental variations. Previous studies of Sr isotopic ratio measurements at the beginning of differentiation are currently being conducted by McCulloch et al. using thick ancient Barite. However, in these studies, denatured Barite was also included in the measurements, and the results do not reflect the values at that time. Therefore, in this study, we attempt a local analysis of Barite using laser ICP-MS. In the analysis, it is necessary to establish a method to remove interfering ions. Since we are measuring an unknown sample, it is necessary to take into account the presence of interfering ions as shown in the table, and the removal of each of these ions is difficult. Initially, a theoretical removal method based on the natural abundance ratio of interfering ions was considered as a removal method, but it was difficult to remove all of them because of the variety of possible types of interfering ions (Fig. 1) [1]. Therefore, a new removal method using peak separation was developed. Specifically, as shown in Fig. 2, this method utilizes the subtle difference in mass number between Sr, the target element, and BaAr²⁺, one of the interfering ions, to remove only those portions of the signal intensity that mainly reflect Sr. In this case, the detector position of the ICP-MS is adjusted so that only the Sr signal intensity is measured. For this purpose, a high-resolution measurement using Aridus was performed. One of the characteristics of high-resolution measurements is that the sensitivity of the signal intensity is reduced. One drawback of peak separation is that the detector cup position must be precisely aligned. After adjusting the detection position, we examined the effect of BaAr²⁺, one of the interfering ions, using a Sr solution and a Sr solution with Ba added. As a result, there was almost no correlation between the amount of Ba added and the signal intensity, suggesting that peak separation is indeed possible. However, other problems were observed, such as contamination of the isobaric Rb and instability of the signal

intensity. This was thought to be due to Rb contamination caused by the use of the same equipment as other researchers, as well as instrumental malfunction of Aridus. To eliminate this cause, the cone and torch were cleaned and re-measured.

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				引用:Wik <mark>ipedia(Ame2003 Atomic Mass Evaluationが引用元)</mark>									
		L4	L3	L2	L1	С	H1	H2	H3	H4			
Mass	89	88.5	88	87.5	87	86.5	86	85	84	83.5	83	82	
Sr			87.9056		86.9089		85.9093		83.9134				
Rb					86.9092			84.9118					
BaAr	88.9338	88.4341	87.9335	87.4340	86.9337		85.9337	84.9348					
Yb			87.9706		86.9694	86.4691	85.9682	84.9674	83.9669				
Hf	88.9716	88.4716	87.9707		86.9700								
Lu			87.9713	87.4704									
Er								84.9677	83.9662	83.4660	82.9651	81.9646	,
Kr							85.9106		83.9115		82.9141	81.9134	
Y	88.9058											Se:81.91	66

Fig. 1. variety of possible types of interfering ion



Fig. 2. Superposition of Sr and BaAr²⁺

Ultrafast geochemistry: Elemental and isotopic analyses of individual nanoparticles using ICP-MS

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Nanometer sized particles in matrix of carbonaceous chondrite hold cosmochemical information of *e.g.*, presolar materials, chemical reservoir in the solar nebula or secondary alterations occurred in a parent body of meteorite [1]. Therefore, elemental and isotopic analysis of these nanoparticles is essential to decode an evolution of the solar system. Since the matrix of chondrite consists of particles with various origins, a considerable number of particles must be analyzed to extract reliable information of each cosmochemical event, which requires an ultrafast analysis of individual nanoparticles. Recently, Morita *et al.* [2] reported an isotopic imaging technique of matrix grains with sizes of several micrometers using focused ion beamtime of flight-secondary ion mass spectrometry (FIB-TOF-SIMS). With this method, chemical compositions of major elements in particles were measured with a throughput of about a few particle/s. Yet, heavy elements (*i.e.*, elements heavier than Fe) were not measured with this method. Since heavy elements, such as refractory metal elements, can hold key information on chemical evolution in the early solar system, an analytical method sensitive to heavy elements needs to be established.

Hence, we developed an analytical technique for individual nanoparticles using inductively coupled plasma-mass spectrometry (ICP-MS). With this technique, more than 10 particles/s can be measured, and quantitative size analysis is possible for nanoparticles with sizes of 5 – 400 nm [3-4]. Moreover, by applying a time of flight-mass spectrometer (ICP-TOF-MS), multi-elemental analysis of individual nanoparticles can be achieved [5-6]. With the analytical technique developed here, elemental and isotopic analysis of superfine particles extracted from matrix of Allende meteorite was performed for both major phase-forming elements (Mg, Al, Si and Fe) and refractory siderophile elements (Os and Pt). In this presentation, possible cosmochemical process responsible for a formation of refractory metal particles will be discussed. Basic concepts and characteristics of particle analysis using ICP-MS will also be introduced.

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Geoimaging: revolution in U-Pb geochronology

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Mass spectrometry imaging techniques for both major- to trace-elements, and isotopic ratios have been extensively applied in diverse research fields such as environmental, geochemical, biological, and medical sciences. In geosciences, imaging data can serve as key information for observing internal structures of geological samples, and, especially in geochronology, imaging data is important to derive detailed chronological information for understanding formation processes of geological samples.

Among mass spectrometry imaging techniques, inductively coupled plasma mass spectrometry coupled to laser ablation sampling technique (LA-ICP-MS) is a primary option for elemental and isotopic mapping because of its high sensitivity for multiple elements [1]. The remaining major challenge associated with the current LA-ICP-MS imaging analysis is the spatial resolutions defined by the size of laser beam (e.g., $> 10 \mu$ m). The resulting spatial resolution achieved by the LA-ICP-MS is generally poorer than that obtained by electron microscopy or secondary ion mass spectrometry, and the spatial resolution of LA-ICP-MS imaging is often insufficient for distinguishing micron-scaled zonation inside mineral samples.

In this study, to deal with this challenge, a micron-resolution femtosecond laser ablation system equipped with the Galvanometric optics (femtosecond laser ablation; fsLA) is newly developed. The present fsLA system has a novel laser focusing optics utilising a short-focal-length objective lens, and the resulting ablation pit size can be minimised to 2 μ m. Despite lowering of the elemental sensitivity by decrease of sampling volumes with the improved spatial resolution, using an enhanced-sensitivity quadrupole-based ICP-MS with the ion transmission of ca. 0.1% [2-3], multiple elemental analysis for trace-elements being > 10 μ g g⁻¹ can be conducted on zircon samples. To demonstrate the analytical capability of the present system, imaging analyses was conducted on a zircon sample from Ashizuri (Fig. 1(a)) using both the conventional LA system (i.e., ablation pit size of 10–20 μ m) and the micron-

resolution fsLA system. The imaging data obtained by the conventional LA system is shown in Fig. 1(b), and the blurred elemental maps lack the spatial resolution to distinguish the internal zoning structure. Elemental maps obtained by the micron-resolution fsLA system are demonstrated in Fig. 1(c), and the improved spatial resolution by the present system setup is clearly represented compared to Fig. 1(b). In addition, elemental images of lanthanides, U and Th revealed the core–rim structure of the zircon crystal with multiple growth stages, and this is a critical advantage against imaging methods that cannot quantify trace-elemental concentration.

Owing to the recent instrumental development, high-quality imaging data can be readily available, and a new research field of Geoimaging is now opening. In the presentation, further efforts towards high-throughput analysis and isotope ratio imaging analysis are also introduced.

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Fig. 1. (a) Optical images of the analysed zircon sample collected from Ashizuri.(b) Elemental maps obtained by using the conventional fsLA system. (c) Elemental maps obtained by using the newly developed micron-resolution fsLA system.

What do Korean zircons tell us?

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The study of zircon (ZrSiO₄) has evolved into a distinct scientific discipline of "zirconology" that encompasses various sub-disciplines related to geochronology, sedimentology, petrology, volcanology, resource geology, and experimental mineralogy. Since the installation of a sensitive high-resolution ion microprobe (SHRIMP IIe/MC) at the Korea Basic Science Institute (KBSI) in 2008, Korean geologists have increasingly relied on zircon analysis to gain insights into the geological history and geochemical evolution of the Korean Peninsula. Currently, two large-geometry secondary ion mass spectrometers (KBSI SHRIMP and IMS1300-HR³) and several laser probe-connected ICPMS are providing *in situ* isotope and trace element data from zircon.

In this presentation, we provide a historical overview of zircon analysis in Korea and summarize significant achievements in geological and geochemical fields resulting from the study of Korean zircons. These include the geochronology of the Hwacheon granulite complex, accretionary and collisional tectonics in the Paleoproterozoic Gyeonggi and Yeongnam massifs, and Neoproterozoic metasedimentary successions and igneous suites associated with Rodinia supercontinent history. We also discuss detrital and inherited zircon geochronology and isotope geochemistry, which illustrate the juxtaposition of allochthonous terranes in central Korea, as well as the geochronological and geochemical systematics of magmatic responses to the interplay between collisional and accretionary orogenies during the Paleozoic-Mesozoic transition period and subsequent evolution of the Korean Cordillera. We also explore isotopic evidence of crustal self-cannibalization in the plutonic platform of the Gyeongsang Arc and beneath Mt. Baekdu (Baekdusan, also known as Changbaishan). To support our discussion, we present an atlas of electron microscope images of zircon crystals, and we emphasize the importance of zircon texture analysis for ensuring the validity of conclusions reached based on geochronological and geochemical data. Overall, the study of zircon in Korea has made significant contributions to our understanding of the geological and geochemical evolution of the Korean Peninsula and the broader East Asian region.

A list of research works derived from the KBSI SHRIMP is available at https://psd-

gskorea.notion.site/d9cbf83224674e749fe65db0ec9e9bfd?v=8c2d3e47f00d4671a18838c469 77b33b.

Metasomatic evolution of migmatites within the Yeongdeok pluton, southeastern Korea: Insights from mineral equilibria modeling and zircon isotope data

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The Yeongdeok adakite pluton in southeastern Korea serves as a key indicator of the interplay of collisional and accretionary orogenies, and consequent initiation of extensive arc magmatism during the Paleozoic–Mesozoic transition period [1]. The pluton contains abundant xenoliths of age-unknown metasedimentary sequences and Permian meta-igneous rocks. Its southern margin exhibits the occurrence of migmatites consisting of mafic amphibolites, gneissic diorite, and injected granitic melt. To unravel the metasomatic processes involved in the formation of these migmatites, this study employed mineral equilibria modeling utilizing pressure (P)–temperature (T)–bulk rock composition (X_{BC})–fluid composition (X_{CO2}) pseudosections, as well as zircon U–Pb and oxygen isotope data obtained at the Korea Basic Science Institute (KBSI).

The amphibolites can be divided into three types depending on mineral assemblages: (1) Amp (amphibole) + Cpx (clinopyroxene) + Pl (plagioclase) \pm Cal(calcite), (2) Amp + Pl + porphyroblastic Ep (epidote) \pm Cpx \pm Cal, (3) Amp + Pl \pm Bt (biotite) \pm Cal. The first type occurs as relict within type 2 amphibolites containing Ep porphyroblasts. Type 3 amphibolites contain mainly coarse to medium grained Amp and Pl with/without Bt and Cal. The gneissic diorite preserves Qtz(quartz)-feldspar-rich layer and mafic layers consisting of relict Cpx + Amp-bearing and magnetite-rich mineral assemblages.

 $P-T-X_{CO2}$ conditions for type 1 mineral assemblages are ~600°C at ~6 kbar with $Fe_2O_3\# [Fe_2O_3 / (Fe_2O_3 + FeO)] = 0.05$ and <0.1 of X_{CO2} . Then, epidote porphyroblast grew by decreasing P–T conditions down to 3.5 kbar and ~500°C belonging to Ab (albite)-Ep facies under $Fe_2O_3\# = 0.3$ and <0.1 of X_{CO2} . Whereas P–T– X_{CO2} conditions for the gneissic diorite containing magnetite + Amp-bearing mineral assemblages are ~3.0 kbar and ~550°C belonging to actinolite-Ca-rich Pl facies under $Fe_2O_3\# = 0.3$ and $X_{CO2} = 0.5$. These physicochemical variations indicate that the protoliths affected pervasive hydrothermal alteration under sub-

isothermal decompression, and mineral assemblages of the amphibolites strongly depends on variation of X_{CO2} in hydrothermal fluids combined with degree of Fe-oxidation.

Zircon grains were extracted from a mafic amphibolite (A1), two gneissic diorites (B1 and B2) and a pinkish granite (C1). SHRIMP U-Pb analysis of these samples yielded consistent results, showing a tight cluster around 250 Ma and older dates ranging from approximately 280 to 255 Ma. These ages correspond to the emplacement of the Yeongdeok pluton and the older, more mafic igneous rocks, respectively, as summarized in Cheong et al. [1]. Some zircon dates spanning from approximately 240 to 150 Ma indicate the occurrence of post-crystallization Pb loss events. These results make it evident that the migmatites formed through the modification of Permian mafic rocks due to the intrusion of the Yeongdeok pluton.

The analysis of zircon oxygen isotopes using the KBSI IMS1300 instrument yields substantial insights into fluid activity and magma source. The consistently observed relatively low $\delta^{18}O_{SMOW}$ values (<5‰) in zircons indicate a significant role of hydrothermal fluids in both magmatic and metasomatic systems. The range of $\delta^{18}O$ values within the magmatic zircon domains, combined with core-to-rim variations, suggests that the magma reservoirs experienced assimilation of hydrothermally altered rocks and replenishment by fresh magma. A distinct decrease in $\delta^{18}O$ observed in recrystallized zircon rims reflects intense subsolidus interaction with hydrothermal fluids. Our oxygen isotope data underscore the pivotal role of hydrothermal fluids in the formation of magma sources and post-magmatic modification processes, thereby contributing to the development of the Yeongdeok migmatites.

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In-situ oxygen isotope measurement of magnetite by SIMS

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Magnetite (Fe₃O₄), one of major Fe ore minerals, has been used as an important petrogenetic indicator as well as pathfinder mineral in mineral exploration [1]. Especially, oxygen isotope ratios of magnetite can be used to identify the origin and formation processes of iron-oxide deposits because they reflect isotopic equilibrium with magma and hydrothermal fluid. In spite of the development of in-situ analysis by secondary ion mass spectrometers (SIMS) and laser probe-connected ICPMS, however, most oxygen isotope ratios of magnetite have been analyzed by conventional isotope ratio mass spectrometer (IRMS). This is mainly due to crystal orientation effect of magnetite which causes the average precision of $\pm 2 - 3 \%$ from grain-to-grain of magnetite [2-3].

In this presentation, we report the in-situ oxygen isotope ratios of magnetite from Shinyemi skarn Fe deposit in South Korea, which were analyzed by a large-geometry secondary ion mass spectrometers (IMS1300-HR³) in KBSI, Ochang. The Cs⁺ primary beam at primary and secondary voltages of + 10kV and - 10kV, respectively. With the combination of SIMS analysis, laser fluorination-IRMS, EPMA and electron back-scattered diffraction (EBSD) mapping of magnetite were conducted to investigate the crystal orientation effectinduced mass instrumental fractionation during analysis of hydrothermal magnetite.

Inter grain variations of δ^{18} O values of magnetite range from 1 ‰ to 5 ‰ depending on samples whereas multiple analyses of δ^{18} O values on single grains show an average precision of ± 0.5‰. Even though previous study suggested a crystallographic effect on measuring the δ^{18} O values of magnetite by SIMS, no clear relationship between crystal orientation of magnetite grains and their δ^{18} O values was found. Also, variations of major elements (Fe, Si and Al) of magnetite grains have no distinct link between δ^{18} O values and major elemental compositions of magnetite. These results demonstrate that the difficulties for measuring δ^{18} O values of magnetite still remain considering the large δ^{18} O scatter up to 5 ‰ and unobvious relationship with crystallographic effect.

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Pb-isotopic dating of meteorites and asteroidal materials: pushing the limits in sample size

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In analysis of extraterrestrial materials, we are almost always limited by sample size. Small rocks delivered by sample return missions or recovered as rare meteorites are heterogeneous, and each component has to be split into many aliquots for different types of analyses, while preserving sufficient amount of material for future research. In Pb-isotopic dating, sample size restriction is exacerbated by low concentration of U and radiogenic Pb, typically in the low parts per billion range. Together with the need to measure Pb isotopic composition with the highest possible precision, sample size restriction forces us to continue searching for the methods that provide the best balance between precision and sensitivity. In other words, we seek to maximize the number of detected ions, and to avoid or minimize analytical artifacts that can spoil precision defined by counting statistics.

The number of detected ions for a given sample size depends on sensitivity of isotope analysis method, which is expressed by total ion yield (also called useful ion yield) – the ratio of the number of ions of the element of interest registered by the detection system of mass spectrometer to the number of atoms introduced at the onset of the analytical procedure. Yields of well-established sample dissolution and chemical separation procedures are close to 100%, and have little room for further improvement. Yields of the mass spectrometers for Pb isotope analysis are, however, much lower: about 5-10% for TIMS with the best known emission activators, and about 2-3% for MC-ICPMS with sample introduction systems configured for maximum sensitivity. These yield values have remained unchanged for about 15 years for MC-ICPMS, and about 25 years for TIMS. Development of more efficient ion emitters for TIMS, and increasing instrument transmission in MC-ICPMS could significantly (up to 3-5 times) reduce the uncertainty related to counting statistics.

Minimizing the content of non-radiogenic Pb in important for precision and accuracy of the Pb-isotopic dates. Step dissolution in acids, an inevitable procedure for removal of nonradiogenic Pb in meteorite dating, unfortunately also removes much radiogenic Pb and thereby reduces effective yield. Developing more efficient and more selective procedures for removal of non-radiogenic Pb, either by leaching or by other means (possibly selective evaporation?) would be highly desirable.

Analytical artifacts that increase uncertainty of Pb isotopic ratios beyond the values set by counting statistics are introduced both by sample preparation and by isotope analysis. Partial dissolution of minerals in meteorites by acid step leaching can in some cases cause fractionation of radiogenic isotopes of Pb. The occurrence of this fractionation seems to depend on the sample mineralogy and conditions of leaching, but the mechanism of fractionation is poorly understood and requires dedicated studies.

The main source of additional uncertainty related to both step leaching and chemical separation of Pb is related to analytical blanks. In many cases, uncertainty introduced by blank subtraction is the dominant component of the total uncertainty of Pb isotopic ratios, even with the current typical blank level of 0.5-1.0 picograms of Pb. Minimizing the effects of blank subtraction on uncertainty requires reducing the blank level, and reducing variability of the values and Pb isotope composition of the blanks, by identification and ranking of the blank components, and checking consistency between the total blank and the sum of partial blanks.

Another source of uncertainty introduced by Pb isotope analysis is fractionation of isotopes during evaporation from the filament (in TIMS) or in the sample introduction system (in MC-ICPMS). In both methods, the largest fractionation component is mass dependent, and can be corrected using various techniques, most effectively by using ²⁰²Pb-²⁰⁵Pb double spike. This spike is now widely used in meteorite analysis and in zircon U-Pb geochronology. Unfortunately, the availability of the ²⁰²Pb-²⁰⁵Pb double spike and its components is limited, and this could pose the problem in the future as the current stocks are running out.

Mass independent isotope fractionation is known to occur in both TIMS and MC-ICPMS. It can vary during analysis without direct correlation with mass dependent fractionation, and in such cases cannot be readily corrected using double spikes. The nature and extent of mass independent isotope fractionation in mass spectrometers await systematic study. The existing TIMS data suggest that mass independent fractionation of ²⁰⁷Pb/²⁰⁶Pb ratio depends on analytical conditions, and can be kept below 0.01%, and possibly below 0.005%, by the optimal choice of emitter and limiting the extent of sample evaporation to 60-70%.

The detector noise and uncertainty of inter-calibration in multicollector arrays can also make major contribution to the total uncertainty. Modern arrays of Faraday cups with high-Ohm or charge collection amplifiers provide ca. 3-4 times lower noise compared to conventional amplifiers with 10¹¹ Ohm resistors, and are suitable for analysis of samples

containing as little as 10-30 picograms of Pb. Further reduction of sample sizes might be possible with arrays of ion counters with high linearity and improved relative gain stability.

Chemical age dating of lunar zirconolite using electron microprobe

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Zirconolite (CaZrTi2O7) is an accessory mineral found in lunar basaltic [1-3] and granitic rocks [4]. It contains enough amounts of U, Th, and Pb but negligible amounts of common Pb [5], which enables to date its crystallization age. Zirconolite in lunar rocks typically exhibits a needle-like morphology with a narrow width of approximately 1-2 μm. The thinness of zirconolite makes it challenging to employ normal ion microprobe analysis for age dating. To overcome this limitation, electron microprobe analysis with its high spatial resolution (~1 μm at 15 keV accelerating voltage) has been employed for zirconolite dating [3, 4]. However, the precision of chemical dating using electron microprobe is lower compared to ion microprobe data. Recent advancements in trace element analysis using electron microprobe have shown potential for achieving higher precision in zirconolite dating. In this study, we present zirconolite crystallization age in a lunar granitic clast determined by electron microprobe with the MAN (mean atomic number) background and blank correction methods [6].

We studied a granophyric clast in the polished thin section of the DEW 12007 lunar meteorite. The clast consists of K-feldspar, silica, fayalitic olivine, and accessory phases including zircon, baddeleyite, zirconolite, tranquillityite, and apatite. Zirconolites exhibit a thin needle-like morphology (<~2 µm) with lengths ranging up to 100 µm. Mineral chemistry of zirconolite was analyzed using a field-emission electron probe microanalyzer (FE-EPMA; JEOL JXA-8530F) equipped with five wavelength dispersive X-ray spectrometers (WDS) at the Korea Polar Research Institute. Analytical conditions included an accelerating voltage of 15 kV, a beam current of 100 nA, and a beam size of 3 µm for standards and 1 µm for zirconolite. The MAN background correction and blank correction methods, implemented in the Probe for EPMA (PfE) software package, were employed to enhance data precision and reduce acquisition time. To establish precise MAN curves for all elements measured in this study, we selected 17 standard samples with average atomic numbers ranging from 18.7 to 35.2. X-ray peaks and high/low off-peak backgrounds were measured for 20 s and 10 s, respectively, from these standards. Care was taken to avoid potential interferences by conducting wavescans near

the peaks. For lunar zirconolite, only X-ray peaks were measured for specific durations: 20 s for Ti and Zr, 40 s for Ca and Fe, 100 s for Si, Al, and Y, 200 s for Ce, Cr, Mn, Mg, Nd, Sm, Dy, Ho, Er, Yb, Hf, and Nb, 300 s for Gd and Tb, 400 s for Th and Sc, 600 s for Tm and Pr, 700 s for La, 800 s for Eu, and 1000 s for U, Pb, Lu, and Ta. The detection limits for U, Th, and Pb were determined to be 30 ppm, 40 ppm, and 30 ppm, respectively. To get precisely determine concentrations of trace elements in zirconolite we used the 91500 zircon for blank correction using its known elemental concentrations.

The zirconolites in the granophyric clast exhibit average concentrations of 3402 ppm, 13307 ppm, and 7570 ppm for U, Th, and Pb, respectively. Utilizing the method proposed by [7], assuming no common Pb, the crystallization age of the zirconolites was determined to be 4404 \pm 120 (2 σ) Ma. This chemical age is consistent with the Pb-Pb age of zircon (4340.9 \pm 7.5 (2 σ) Ma) determined by SHRIMP [8]. Despite the extensive shock experienced by the granophyre containing the zirconolites, the agreement be-tween the chemical age and the Pb-Pb age from zirconolite and zircon grains suggests minimal Pb loss during the Moon's numerous shock events. The precision achieved in this study is significantly improved compared to previously reported chemical ages of lunar zirconolites measured with the electron microprobe [3, 4], thanks to the MAN background correction and blank correction methods with longer measurement times. Therefore, chemical age dating using the electron microprobe can be applicable to tiny U-Th-Pb bearing minerals in extraterrestrial materials, especially for return samples from Moon and Mars.

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Microanalysis and micromineralogy of Asian dust

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Mineral dust from arid sources migrates long distances across the oceans, reaching other continents. During transport, mineral dust interacts with electromagnetic radiation, atmospheric gases, liquids, and pollutants and finally becomes terrestrial and marine sediments. The mineralogy and microstructures of individual dust particles are fundamental to understanding the interactions between mineral dust and Earth environments. Many important properties in the Earth environment are related to the mineralogical nature of mineral dust. Pristine dust particles are heterogeneous mixtures of mineral grains of varying sizes, equivalent to a soil fragment blown to high altitude. Most chemical elements in dust occupy crystallographic sites in minerals. Each mineral has an inherent crystal structure and a chemical composition often varying in a limited range, resulting in characteristic physical and chemical properties. The properties and mixing of the constituent minerals of dust particles affect the interactions between mineral dust and Earth environments. The major analytical tools for investigating individual dust particles include electron microbeam methods such as scanning electron microscopy and transmission electron microscopy. The combined applications of electron microscopy, focused ion-beam milling, and energy dispersive X-ray spectrometry can identify constituent minerals and the microstructures of dust particles. Even the bulk mineral composition can be derived from the analyses of individual dust particles. This presentation summarizes mineralogical and microstructural properties of individual dust particles obtained by electron microscopic analyses of Asian dust migrating from Gobi Desert to the North Pacific, and discusses its implication for Earth environments.

Femtosecond laser ablation MC-ICPMS U-Th and U-Pb dating of Quaternary zircons from Jeju Island, Korea

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Laser ablation inductively coupled plasma mass spectrometry (ICPMS) emerged in the mid-1980s rapidly became a pivotal dating tool, akin to the ion microprobe. The introduction of femtosecond laser ablation system in the mid-2000s has significantly mitigated the analytical challenges associated with downhole fractionation. We here present the U-Th and U-Pb dating results of Quaternary zircons collected from Jeju Island, Korea, utilizing the femtosecond laser-connected Multi-Collector ICPMS installed at the Korea Basic Science Institute.

Zircon grains were separated from six trachyte lavas taken from outcrops near the Baengnokdam lake (JJ616-1), Yeongsil (JJ08-1), Chunwangsa (JJ09-1), Oraidong (JJ09-3), Sanbangsan (JJ615-1), and Wonmansa (JJ08-2). For the zircon U-Th dating, signal intensities were concurrently measured employing Faraday collectors (for ²³⁸U and ²³²Th) and ion counters (for 230 and 228 mass). The ²³⁸U/²³²Th ratio was corrected using the measured and recommended values of the 91500 zircon ([U] = 80.0 μ g/g, [Th] = 29.9 μ g/g) [1]. The contribution of molecular zirconium sesquioxide ions to the ²³⁰Th peak was stripped by monitoring the peak intensity of 228 mass [2]. The peak tail of ²³²Th, the relative sensitivity between U and Th, and the Faraday-ion counter efficiency were collectively corrected and calibrated under the assumption of Plešovice zircon [3] being in ²³⁸U-²³⁰Th secular equilibrium. After correction and calibration, we confirmed that the radioactivity ratios of (²³⁰Th/²³²Th) and (²³⁸U/²³²Th) for the 91500, FC-1, TEMORA 2, and LKZ-1 plotted on the equiline. Zircons from JJ616-1, JJ08-1, JJ09-1, and JJ09-3 yielded weighted mean 238 U- 230 Th ages of 28.7 ± 1.6 ka (n = 56/64, MSWD = 3.8), 81.8 \pm 10.9 ka (n = 11/12, MSWD = 1.6), 92.6 \pm 4.6 ka (n = 49/51, MSWD = 2.2), and 117.6 ± 8.2 ka (n = 48/50, MSWD = 3.2), respectively. The result for JJ08-1 zircon demonstrated consistency with the recommended value $(82 \pm 6 \text{ ka})$ [4].

The initial radioactive disequilibria resulting from Th/U and Pa/U fractionation in the

zircon-melt system, along with the presence of common Pb, exerts significant influence on the calculation of Quaternary zircon age. We corrected these effects employing a modified Tera-Wasserburg concordia diagram proposed by Sakata [5], assuming a common $^{207}Pb/^{206}Pb$ of 0.84 ± 0.05. Th/U partitioning was estimated based on the measured U and Th concentrations of whole-rock and zircon, and the $f_{Pa/U}$ ratio (= ([Pa]/[U])_{zircon}/([Pa]/[U])_{melt}) was assumed to be 3.50 ± 1.05. After applying these corrections, we obtained a weighted mean U-Pb age of Penglai zircon as 4230 ± 19 ka (n = 25/28, MSWD = 3.8), which exhibited marginal consistency with the recommended value of 4.4 ± 0.1 Ma [6]. JJ615-1 and JJ08-2 zircons yielded weighted mean U-Pb ages of 786 ± 5 ka (n = 26/28, MSWD = 0.66) and 744 ± 8 ka (n = 28/28, MSWD = 0.79), respectively.

Our data provide evidence that trachyte magmatism occurred in Jeju Island during the transitional period between the Early and Middle Pleistocene and the Late Pleistocene. The zircon samples analyzed in this study serve as reference age data for Quaternary geochronology studies.

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