Studies on Actinides and Fission Products Performed at the KURRI Hot Laboratory

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1. Objectives and Allotted Research Subjects

Studies on actinide and fission product nuclides with careful management are being more important for reprocessing, disposal, partitioning, and transmutation processes in the nuclear fuel cycle. Hot laboratory of KURRI is one of core facilities in Japan, in which various nuclides can be handled. This project enhances utilization of the KURRI hot laboratory by opening for fundamental and application studies related to radiochemistry, nuclear chemistry, environmental chemistry, geochemistry, and so on. Allotted research subjects are:

ARS-1 Complexation of actinides with organic substances (T. Sasaki et al.).

ARS-2 Solubility of actinide compounds in aqueous media (T. Kobayashi et al.).

ARS-3 Leaching of actinides and FPs from fuel debris (N. Sato et al.).

ARS-4 Neutron irradiation damage of vitrified waste matrices (T. Nagai et al.).

ARS-5 Ligand exchange reaction of actinides in molten salts (A. Uehara et al.).

ARS-6 Electrochemical behavior of uranium in pyroreprocessing system (Y. Sakamura et al.).

ARS-7 Structural study of f-elements in molten halides (H. Matsuura et al.).

ARS-8 Molecular dynamics simulation of uranyl ion in molten halides (T. Goto et al.).

ARS-9 Fundamental study of fission products for trans-actinide chemistry (Y. Kasamatsu et al.).

ARS-10 Isotope separation by using microreactor (R. Hazama et al.).

ARS-11 Optical properties of molten aluminum halides (T. Ohta et al.).

ARS-12 Precipitation of f-element oxides in molten halides (H. Sekimoto et al.).

ARS-13 Uptake of radiocesium and radiopotassium in plants (T. Kubota et al.).

ARS-14 Quantitative analysis of radionuclides in seawater (T. Ohta et al.).

ARS-15 Isotopic composition of radionuclides in environmental samples (Y. Shibahara et al.).

ARS-16 Noble gas mass spectrometry of neutron irradiated geological samples (H. Sumino et al.).

ARS-17 Radiometric Ar-Ar dating of neutron irradiated minerals and glasses (O. Ishizuka et al.).

ARS-18 Radiometric Ar-Ar dating of neutron irradiated lavas (N. Hirano et al.).

2. Main Results and Contents

ARS-1, 2, 3, and 4 were performed in order to deepen the knowledge of nuclear waste management issues. In ARS-1 and 2, stability constants and solubility products of actinides were obtained. In ARS-3, leaching kinetics of actinides and FPs from irradiated Zr alloy was clarified. In ARS-4, a structural change of borosilicate by neutron irradiation was found. ARS-5, 6, 7, and 8 were performed with the viewpoint of pyroreprocessing. In ARS-5 and 7, ligand exchange of F⁻ and Cl⁻ for U⁴⁺ and Nd³⁺ in molten halides was clarified. In ARS-6, effective diffusion coefficient of U⁴⁺ in porous Zr was determined. In ARS-8, atomic distances of UO₂²⁻ in LiCl melt were computed. Polarization of Cl⁻ around UO₂²⁻ was found.

ARS-9, 10, and 12 seek applications of molten salt systems for industrial use, for example, refining. ARS-11 studied optical properties of molten alkaline chlorides containing Al. Raman spectra obtained were interpreted by using ab initio method. ARS-12 focuses on recycling of rare earths. Solubility of Dy(III) under the coexistence of Dy oxide and oxychloride in chloride melts was discussed. ARS-10 studied isotope fractionation of Ca. A possible fractionation of ⁴⁸Ca/⁴⁰Ca was found. ARS-13, 14, and 15 studied on redox reactions in soils, plants, seawater, and so on. In ARS-13, distribution of radiocesium in plants was clarified. ARS-14 presented an effective preparation method of radiotracers which are useful for environmental science. ARS-15 suggested that precise isotopic analysis of Cs and Sr is helpful for a rapid source analysis of nuclear accident. ARS-16, 17, and 18 demonstrated that neutron irradiation at KUR is usable for the Ar-Ar and I-Xe dating of geological samples.

3. Summaries of the achievements

In this research, by using various unique facilities of KURRI for actinides and fission products, new and characteristic chemical, kinetic, structural, and thermodynamic data were obtained. These new information encompass solid chemistry, molten salt and solution chemistry, as well as nuclear reactions of f-elements and FPs. The results are useful either for scientific purpose or for technological purpose for nuclear science, environmental science, geoscience, and general industry.
INTRODUCTION:
A semi-empirical thermodynamic model was developed to estimate the apparent formation constants of metal ions with humic substances (HSs), humic and fulvic acids, over a wide range of solution conditions, i.e., pH, ionic strength, and HS and metal concentrations.

To understand the fundamental rules of metal complexation with HSs, many researchers have attempted to characterize the physical and chemical properties of HSs in soils, sediments, and natural waters. It has been determined that randomly cross-linked heterogeneous organic substances generally have similar distributions of a number of specific functional groups, including carboxyl, phenolic, and alcoholic groups. Towards the ultimate goal of characterizing natural HSs, researchers have proposed hypothetical HS chemical structures based on results obtained using several analytical methods.

The discrete fragment model has been proposed by our group; it decomposes the organic ligands into discrete fragments of functional groups and chelating bridges that connect the functional groups. The ligand fragments called as basic ligands were clipped from a "pragmatic" chemical structure of a humic acid (HA) proposed [1], which were distributed statistically in the HA framework. The fixed formation constant values of the metal ion with each ligand was taken from the literature; benzoic acid, phthalic acid, isophthalic acid, 1,2,3-benzenetricarboxylic acid, 1,2,4-benzenetricarboxylic acid, 2-hydroxybenzoic acid, phenol, butanedioic acid, and acetic acid. The steric effect of bidentate binding sites due to the additional stabilization by chelate formation was considered, while the electrostatic surface potential of the HA molecule in solution was not considered for simplification. The model has yielded satisfactory results for the apparent complex formation constant of trivalent europium with Aldrich HA under varied solution conditions, including pH, ionic strength, and the concentrations of metal ions and HA [2].

THEORETICAL:
The model was modified and applied to several kinds of metal ions including actinides, i.e., Th(IV), Pu(IV), and Np(V), according to following steps; 1) a number of datasets for acid dissociation of various HSs were analyzed to obtain the representative values for the abundance ratios of the basic ligands and the heterogeneity parameter of HSs, 2) the datasets for complexation of various multivalent metal ions with HSs were analyzed to obtain the representative values for the intramolecular chelating effect of the bidentate site fraction. In the case of tetravalent metal ions, the hydrolysis reactions are taken into account for the analysis of the experimental datasets [3].

RESULTS:
The present model fairly well reproduced the literature apparent formation constants of tetravalent Pu/Th (Fig.1), pentavalent Np, divalent Ca/Co, and trivalent Al/Eu with the hypothetical humic acid and of tetravalent Th, pentavalent Np, divalent Mg/Ca/Co/Mn/Ni/Cu/Zn/Pb, and trivalent Eu with the hypothetical fulvic acid under a wide range of pH, I, and initial HSs and metal concentration [3]. Some discrepancies between the calculated and experimental values were recognized and discussed; one is the I dependence of the values of some metal ions such as neptunium, and the other is the discrepancy observed for the system of ultra-trace amount of neptunium, suggesting further effects of not yet identified but much stronger binding sites in HS. Although the present hypothetical structure is only one example of HS, it provides a basis for further studies of the thermodynamic and kinetic parameters for complexation reactions.

REFERENCES:
Temperature Effect on the Solubility and Solid Phase of Tetravalent Metal Hydroxide


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INTRODUCTION:
The decay heat emission from vitrified high level radioactive waste in the repository will be transferred to groundwater aquifers through surrounding engineered and geological barrier systems. In the early failure scenario of the waste package, long-lived radionuclides including tetravalent actinides (An(IV)) leached in the groundwater are considered to be exposed to an elevated temperature environment up to 100°C [1]. For the safety assessment of geological disposal, it is required to evaluate a possible impact of elevated temperature on the solubility of An(IV). At 25°C, the steady-state solubility is generally controlled by amorphous hydroxide as solubility-limiting solid phase, and described using relevant thermodynamic constants [1]. However, the amorphous hydroxide was dehydrated and crystallized at elevated temperature [2]. Therefore, the thermodynamic estimation of An(IV) solubility needs to clarify the both of hydrolysis constants and solubility product (K_sp) at a given elevated temperature [3].

In the present study, the apparent solubility of zirconium hydroxide as chemical analogue for An(IV) and the crystallinity of the solid phase were investigated under several conditions of temperature (5 to 60°C). The temperature dependence of solubility product and the enthalpy change were discussed.

EXPERIMENTS:
Sample solutions by oversaturation method were prepared by adding NaOH or HClO_4 to the acidic Zr perchlorate solutions ([Zr] = 0.01 mol/dm^3 (M)). The ionic strength (I) was adjusted to be I = 0.5 by adding appropriate amount of NaClO_4. After aging the sample solutions in temperature chambers controlled at 5°C, 40°C and 60°C, the samples were transferred to the thermostat at 25°C, where Zr(OH)_4(s,60°C) represents the solid phase formed at 60°C. The obtained ΔH^° was slightly higher than the ΔH^° (~133.6 kJ/mol) for Zr(OH)_4(s,am) calculated from the standard enthalpy of formation [3]. Similar analysis was performed for the solubility after aging at 5 and 40°C, and a trend of ΔH^° for the solid phases formed at different temperatures suggested that the solid phase transformation is endothermic reaction within the investigated temperature range.

RESULTS:
The apparent solubility after aging at 40 and 60°C and measured at 25°C were lower than those kept at 25°C, indicating the progress of crystallization of initial amorphous hydroxide. The K_sp values after aging at different temperatures were determined from the analysis of the solubility dataset in Fig.1. After aging at 60°C, the solubility was measured at 5, 25, 40 and 60°C (Fig. 2 ) and the K_sp at different temperatures. Assuming no temperature dependence of enthalpy change (ΔH^°), the ΔH^° was calculated for Zr^{4+} + 4OH^- ⇌ Zr(OH)_4(s,60°C), where Zr(OH)_4(s,60°C) represents the solid phase formed at 60°C. The obtained ΔH^° was slightly higher than the ΔH^° (~133.6 kJ/mol) for Zr(OH)_4(s,am) calculated from the standard enthalpy of formation [3].

REFERENCES:
Research on the Behavior of Actinides and FPs in Fuel Debris

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INTRODUCTION:
After the LOCA of Fukushima Daiichi NPS, the melted core reacted with coolant at high temperature forming fuel debris containing fuel and structural materials such as zirconium. Under high temperature condition in the pressure vessel, several kinds of FPs and TRU were possibly released into the cooling water mixed with seawater and the air from the melted core and its fine debris. Information on the radionuclide behavior in fuel debris and surface seawater will be helpful to analyze the forthcoming analysis data about the contents of minor FPs and TRU in contaminated water, and to manage associated secondary wastes.

First, the simulated fuel debris composed of uranium and zirconium oxides as main constituents was prepared by heat treatment in reductive or oxidative conditions. Information on the radionuclide behavior in fuel debris and surface seawater will be helpful to analyze the forthcoming analysis data about the contents of minor FPs and TRU in contaminated water, and to manage associated secondary wastes. First, the simulated fuel debris composed of uranium and zirconium oxides as main constituents was prepared by heat treatment in reductive or oxidative conditions. Then the dissolution behavior of typical gamma-ray fission products and neutron activated nuclides as well as uranium in solid solutions was investigated by neutron irradiation and following leaching in the non-filtrated seawater. Dissolution behavior of MA was also studied by the used of MA doped simulated fuel debris.

EXPERIMENTAL:
Three types of UO₂-ZrO₂ solid solution samples with Zr concentration of 10, 50 and 90 mol% were prepared by mechanochemical and heat treatments under reductive and oxidative atmosphere. The sample was vacuum-sealed in quartz tube and irradiated for 20 min using the pneumatic transferring system (Pn-2) at KUR. For reducing the high radioactivity of short-lived nuclides, the sample was left in glove box, and then suspended in 30 ml of fresh seawater from Minamisoma city, Fukushima. After the aging time in the atmospheric condition at R.T., a 10 mL of supernatant was transferred to new sample tube after filtration with 0.45 μm (Advantec) or 3 kDa (Microcon, Millipore) membranes, followed by evaporation of the seawater at 363 K in order to prepare a solidified point-like source. For MA doped sample, similar preparation techniques were applied by using U₃O₈ powder with ²³⁷Np, ²⁴³Am and ²³⁶Pu. Gamma- and alpha-ray spectrometry were performed using a Ge detector and Si detector to determine the nuclides leached.

RESULTS:
Figure 1 shows the leaching ratios (R(\%)) of actinides to seawater. There, the clear time dependence cannot be seen in the leaching of Np, Am and Pu during 31 days leaching test. Also, their leaching ratios were suppressed in the very low extent (0.02 % or less). The leaching of these actinides are expected to be suppressed to very low extent regardless of the oxidation state in the solid phase since the solubilities of both M(III) and M(IV) for Am and Pu, and Np(IV) are very low at the pH of seawater. On the other hand, the Rₚ value was about 0.1 % during the leaching test. From this result, it is considered that the uranium dissolution from the simulated fuel debris was governed by the solubility limitation of UO₃ 2H₂O(cr), UO₂ 2H₂O (am) or maybe their intermediate phase as discussed in our previous study [1]. These results suggest that both dissolution and structure data are essential for fuel debris behavior. In further study, behavior of actinides and FPs from different types of fuel debris will be discussed.

REFERENCE:
PR11-4  Effect on Borosilicate Glass Structure by Neutron Irradiation

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INTRODUCTION: A high-level radioactive liquid waste including fission products, FPs, from a reprocessing process for spent nuclear fuels is processed into a solidified waste glass made by using a borosilicate glass as media. Many studies of the effect on borosilicate glass structure by irradiation have been carried out by irradiation of α ray, β ray, and γ ray which would be generated from FPs of the waste glass. However, that effect by a neutron irradiation has not been much evaluated. In this study, the borosilicate glass samples were irradiated by neutrons, and the glass structure change after the irradiation was measured by Raman spectrometry.

EXPERIMENTS: The borosilicate glass samples were prepared 2 compositions. The raw material reagents of SiO$_2$, H$_2$BO$_3$, Na$_2$CO$_3$, Li$_2$CO$_3$, and rare earth oxides as simulated FPs were placed in an alumina crucible and were melted at 1150°C in an electric furnace. After the molten samples were solidified by cooling to room temperature, they were cut into thin plates. In the irradiation, the glass samples of thin plate were set in a polyethylene tube and were irradiated under the condition of 1000 kW for 10 min in the Pn-2 of KUR. After the radioactivity of the samples was sufficiently attenuated, the Raman spectra of the glass sample were measured by using a laser Raman spectrometer, NRS-3100 of JASCO. For the effect on borosilicate glass by the nuclear reaction of $^7$Li, Peugeot, et al have evaluated the B-O structure by using NMR measurement and Raman spectrometry[1], our study was examined the Si-O structure.

RESULTS: As a structural change of the sample by the irradiation, an amount of Li would be increased by the $^7$Li($n$,α)$^4$Li reaction, and Li was expected to disconnect to the Si-O bridging structure. By evaluating the Raman shift of the Si-O structure, it was confirmed to be the effect on the borosilicate glass structure by the irradiation. The Raman shifts of Si-O structure of a silicate glass were in the wavenumber of 850-1200 cm$^{-1}$, and the peak positions of Raman shifts were different from the number of non-bridging oxygen, NBO, of the Si-O structure.[2] In this measurement of borosilicate glass, those Raman shifts were observed in 850-1250 cm$^{-1}$ and the measured spectra could be separated into Gaussian waves as shown in Fig. 1. The Raman peak of Q$^0$ structure without NBO appeared in 1140-1150 cm$^{-1}$, and those of Q$^1$, Q$^2$, and Q$^3$ structures with the NBO number = 1, 2, and 3 were in 1070-1090, 1000-1020, and 920-930 cm$^{-1}$ respectively. Comparing with the Raman shifts before and after irradiation, it could be observed that the peak heights of Q$^4$ and Q$^5$ decreased and those of Q$^2$ and Q$^3$ increased after the irradiation, as shown in Fig. 1. These height changes of Q$^4$, n=1-4, suggested the feasibility that a generated Li by the neutron irradiation disconnects the Si-O bridging structure in a borosilicate glass. However, this Si-O bridging structure is direct disconnected by γ ray included in the neutron irradiation and the additional experiments needs for understanding of the irradiation effect.

REFERENCES:
INTRODUCTION:
In the non-aqueous reprocessing process of spent nuclear fuels by the pyrometallurgical and the electrowinning methods, a spent fuel is dissolved into molten LiCl-KCl or NaCl-CsCl eutectic melt and dissolved uranium and plutonium ions are recovered as clear fuels by the pyrometallurgical and the molten NaCl-CsCl eutectic were investigated by absorption spectrum measurements.

EXPERIMENTAL:
All experiments were carried out under an argon atmosphere, in which humidity and oxygen impurity were continuously kept less than 1 ppm. The electronic absorption spectra of uranium ions in the melts were measured by using an UV/Vis/NIR spectrometer (V-570, JASCO Co.). The analytical light from a light source (a tungsten halogen lamp and D2O lamp) was guided to the electric furnace with quartz windows by using optical fibers, and the light passed through the sample in a quartz tube with a 10 mm light path inside the furnace. The light which traveled through the furnace was again guided to the spectrophotometer, and a monochromator was set in front of the detectors to decrease the background noise. The light intensity for the molten alkali chloride (I0) and that including uranium (I) was measured in the wavelength range of 300 – 2000 nm at 1 nm intervals. Wavelength was converted to wavenumber in this work. The molar absorptivity was calculated by using –log (I/I0) and total volume of the solution. All the experiments were performed at 923K ± 3K.

RESULTS:
Molar absorptivity of absorption spectra of U4+ in the presence of F− was plotted as a function of wave-number in Fig. 1. When an absorption spectrum of 0.106 M U4+ in the absence of F− was measured, molar absorptivities of each peak wavenumber at 14903, 16501, and 22123 cm−1 were observed. This result means that two species of complexes composed of U4+, Cl− and F− are equilibrated. However, when rF was over 9.5, another peak at 17800 cm−1 decreased with the increase of rF from 0.09 to 17 by adding NaF pellet as shown in Fig. 1. Absorption peaks corresponding to 14903, 16501, and 22123 cm−1 decreased with the increase of rF from 0.09 to 1.7 and isosbestic points at 13774, 15772, 16181, 17793, and 19305 cm−1 were observed. This result means that two species of complexes composed of U4+, Cl− and F− are equilibrated. However, when rF was over 9.5, another peak at 15847, 17331, and 19646 cm−1 were observed. This result means that another complex composed of U4+, Cl− and F− is formed. After 10 hours aging, red color precipitates were found on the bottom of the cell.

Fig. 1. Molar absorptivity of U4+ depended on the concentration of NaF in molten NaCl-CsCl eutectic at 923K. Concentration ratios of F− by U4+ (rF) are 0, 0.09, 0.17, 0.31, 0.47, 0.89, 1.3, 1.7, 2.6, 9.5, and 17.

When 9.36 × 10−3 M NaF was added in the melt, absorption peaks decreased. Molar ratio of fluorine by uranium (rF) added in the melt was changed from 0.09 to 17 by adding NaF pellet as shown in Fig. 1. Absorption peaks corresponding to 14903, 16501, and 22123 cm−1 decreased with the increase of rF from 0.09 to 1.7 and isosbestic points at 13774, 15772, 16181, 17793, and 19305 cm−1 were observed. This result means that two species of complexes composed of U4+, Cl− and F− are equilibrated. However, when rF was over 9.5, another peak was observed at 15847, 17331, and 19646 cm−1 were observed. This indicates that another complex composed of U4+, Cl− and F− is formed. After 10 hours aging, red color precipitates were found on the bottom of the cell.

REFERENCES:
INTRODUCTION: Analyses of the electrorefining process for the pyrometallurgical reprocessing of metallic fast reactor fuel using the multi diffusion layer anode model [1] have shown that (a) solubility of UCl$_3$ in LiCl-KCl melt, and (b) the diffusion coefficient of actinide ions in the porous Zr layer formed at the surface of the spent metallic fuel by selective dissolution of the actinides, have great influence on major performance, such as processing rate and separation between the actinides and Zr. In this study, chronopotentiometry (CP) was applied to evaluation of these important parameters at U-9wt%Zr alloy anode.

EXPERIMENTS: Modification of CP theory to be adapted to a situation, where the concentration reaches saturation by a constant current producing the species electrochemically, has been reported before [2]. Since diffusion coefficient of U(III) in LiCl-KCl is known [3], solubility of UCl$_3$ in LiCl-KCl was evaluated using this data and $\tau$ obtained by CP in this study. After formation of a porous Zr layer by selective anodic dissolution of U from the U-Zr alloy, CP was performed again. In this step, theoretically, the effective diffusion coefficient of UCl$_3$ in the porous Zr layer can be estimated using its solubility data which has been just evaluated in the previous step. The experimental setup and procedure have been also reported before [4]. All the experiments were carried out at 773 K, in a high-purity Ar atmosphere glove box in KURR hot cell laboratory.

RESULTS: The CPs obtained using U-Zr alloy before the formation of the porous Zr layer are shown in Fig. 1. The solubility of UCl$_3$ was evaluated to be 0.00449 mol-U/cm$^3$ so that its averaged diffusion coefficient determined from these CPs agrees with the value in literature ($1.45 \times 10^{-5}$ cm$^2$/s) [3]. Subsequently, CPs were measured after the formation of the porous Zr layer. In this case, the diffusion coefficient could not be evaluated directly from $\tau$ value, since the period until diffusion limit of U(III) varied in every measurement even with the same current density, as shown in Fig. 2. The reason for this behavior was considered that the decay of UCl$_3$ concentration gradient in the porous Zr layer caused by the CP measurement requires a long duration due to the expected lower diffusion coefficient and the large thickness of the layer. Such complicated condition and resulting behavior in the actual CP measurement cannot be explained using either the basic electrochemical theory [2] or simple multi-diffusion layer model [1]. Then, the series of the electrochemical operations, including the CP measurement at constant current density and the rest period in open circuit situation between the measurements, were digitally simulated by discretization of the diffusion layers around the U-Zr alloy into elements of 10 to 20 $\mu$m thickness using finite element method. The calculation result indicated that the transition time evaluated from CPs shown in Fig. 2 can be properly reproduced by assuming the effective diffusion coefficient of U(III) in the porous Zr layer to be 0.6 ~ 0.8 $\times 10^{-5}$ cm$^2$/s, which is consistent with the value $0.7 \times 10^{-5}$ cm$^2$/s evaluated from the analysis of the longer-term electrorefining experiments [1].

REFERENCES:
INTRODUCTION: Neodymium is one of the rare earth fission products and was used as the prototype of some trans uranium elements due to its similarity of electrochemical behavior. Also, neodymium is one of important materials since it has been widely utilized at magnets and electrochemical behavior. Also, neodymium is one of important trans uranium elements due to its similarity of electrochemical behavior.

RESULTS and DISCUSSION: Figure 1 shows the differential pulsed voltammograms of cathodic sweeps which exhibit mainly neodymium reduction peaks. On the contrary to previous measurements [1,2], the potential of neodymium reduction to metal was not shifted positively, however, drastic negative shift depending on fluoride addition did not occur as well. More strikingly, with increasing fluoride amount, the potential gap between Nd³⁺/Nd²⁺ and Nd⁴⁺/Nd decreased, thus disproportionation reaction may be restricted by addition of fluoride. The variation of oscillator strength of hypersensitive transition absorption of neodymium at ca. 589 nm depending on fluoride addition has been evaluated. This absorption peak has been considered to the indication of coordination symmetry around neodymium cation, i.e. 6 coordinated octahedral species, and the smaller value relates to more perfectly symmetric. One striking feature is that with increasing fluoride amount until ca. F/Nd = 2 in molten NaCl-CsCl-NaF, the value of oscillator strength once increased until F/Nd = 2, and decreases rapidly. While in molten LiCl-KCl-LiF, the value of oscillator strength decreases almost linearly.

EXPERIMENTS: All the electrochemical experiments using molten salts have been performed in an electric furnace which is built inside a glove box filled with an argon atmosphere in high purity using an electrochemical analyzer. Cyclic voltammetry, differential pulsed voltammetry and linear sweep voltammetry have been performed by using the electrodes as follows: working electrode: tungsten, counter electrode: pyrocarbon and reference electrode: silver wire dipped in molten LiCl-KCl electrolyte + AgCl (1 mol%) inside the borosilicate tube, respectively. Silica glass tube was used as a crucible. To observe the fluoride addition effect, 0 to 20 times amount of LiF to the concentration of neodymium was added to the molten salt. All measurements have been performed at 773 K. UV-vis spectroscopy of neodymium in molten NaCl-CsCl-NaF at 953 K has been carried out by using the spectrophotometer. A quartz cell with 10 mm of light path was used for the molten salt container, and experimental procedure was exactly the same as that described in the report of the last year. For the calculation of oscillator strength of hypersensitive transition and derivation of $Q_{4,46}$ parameters by the Judd-Ofelt analysis, density was assumed to be the additivity of molar volume of each component, and refractive index was temporary used from the value of KCl due to the non-availability of the data of CsCl.
Polarization Effect of Chloride Ions on Uranyl Ion in Molten LiCl

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INTRODUCTION: Molten salts are promising solvents for actinides in reprocessing of nuclear fuel. However, knowledge of chemical stability of ionic species in melts is still inadequate to maximize their potential abilities. Information on local structure around ionic species in melts may provide useful measures for their stability in melts. Molecular dynamics (MD) simulation is a powerful tool to elucidate such structures microscopically. In particular, recent MD simulations with polarizable ionic model (PIM)[1,2] have brought much progress in understanding of structure in ionic melts: they have successfully revealed more reliable picture of local structure in UCl3[2] which is comparable with those from XRD study. In this work, we have performed MD calculations of molten LiCl containing uranyl ion using PIM for chloride ions, and investigated the effect of polarization of Cl- ions on local structures around uranyl ion.

CALCULATION: MD calculations have been carried out using PIM for molten LiCl containing UO2$^{2+}$ ion. The system included 500, 502, and 1 ions for Li+, Cl-, and UO2$^{2+}$, respectively. MD calculation without polarization of Cl- ions has also performed, which is referred here to as RIM: rigid ion model. Furthermore, first principle MD simulation has been performed using the CPMD code[3] for the system with similar composition but smaller size. The temperature was set at 1073 K in all the calculations.

RESULTS: Figures 1 and 2 show radial distribution functions for U and Cl pair and U and Li pair, respectively, obtained from the present calculations. Table 1 summarizes intraionic distance between U and O in uranyl ion and interionic distance between U and Cl which are near neighbors with each other. These results clearly show effects of polarization of Cl- ions on the coordination structures around uranyl ion. That is, we have found that PIM can reproduce the results by first-principle MD simulation better than RIM.

Table 1 Intraionic distance between U and O in uranyl ion and interionic distance between U and Cl in molten LiCl containing uranyl ion

<table>
<thead>
<tr>
<th></th>
<th>Expt.</th>
<th>CPMD</th>
<th>PIM</th>
<th>RIM</th>
</tr>
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<tbody>
<tr>
<td>U=O</td>
<td>1.77 Å</td>
<td>1.80 Å</td>
<td>1.78 Å</td>
<td>1.77 Å</td>
</tr>
<tr>
<td>U-Cl</td>
<td>2.73 Å</td>
<td>2.64-2.71 Å</td>
<td>2.78 Å</td>
<td>2.94 Å</td>
</tr>
</tbody>
</table>

REFERENCES:
INTRODUCTION: Anomalous mass dependence was experimentally observed in uranium isotope fractionation by Fujii et al., in the late 80's[1] and Nishizawa et al., suggested that odd-even staggering may be due to the nuclear charge density difference in the middle of 90's[2] for the case of strontium. Calcium is congener of strontium and easy to handle to check the isotope effects[3,4].

EXPERIMENTS: Isotopic enrichment occurs according to the following chemical exchange reaction:

\[ 40^{\text{Ca}}^{2+} (aq) + 48^{\text{Ca}}L^{2+} (org) \rightarrow 4^{\text{Ca}}^{2+} (aq) + 40^{\text{Ca}}L^{2+} (org) \]

where \( L \) represents macrocyclic polyether(18-crown-6). As a result, \(^{40}\text{Ca}\) is enriched in the organic-phase (org) crown solution and the heavy isotopes of \(^{48}\text{Ca}\) tend to concentrate in the aqueous (aq) phase. The mass effect is observed by the thermal ionization mass spectrometer (TIMS) measurement of calcium isotope ratios for the mass range from 40-48 atomic mass unit (amu).

RESULTS: Unit mass enrichment factors of Sr and Ca isotope separation are summarized in Table 1. In general, a crown ether gives a large separation factor with more than ten times, compared with an ion exchange method and has an applicable ability of separation in reality.

<table>
<thead>
<tr>
<th>( t / \Delta M \ [\times 10^{-5}] )</th>
<th>Method and system</th>
<th>Temp. (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>51-17 (Sr)</td>
<td>Liquid-liquid extraction (LLE) with dicyclohexano-18-crown-6 (DC18C6). 2.3M-0.5M Sr in aqueous phase.</td>
<td>20±0.5</td>
<td>[2]</td>
</tr>
<tr>
<td>14 (Sr)</td>
<td>Crown-ether resin chromatography (CRC). 1.3m 0.1-0.01M Sr + 2M HCl</td>
<td>35±2</td>
<td>[5]</td>
</tr>
<tr>
<td>5.6 (Sr)</td>
<td>CRC. 1.3m 0.1M Sr + 3M HNO(_3)</td>
<td>35±2</td>
<td></td>
</tr>
<tr>
<td>2.3 (Sr)</td>
<td>α-hydroxyisobutyrate</td>
<td>Not specified</td>
<td>[6]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( t / \Delta M \ [\times 10^{-5}] )</th>
<th>Method and system</th>
<th>Temp. (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 (Ca)</td>
<td>LLE with DC18C6. 0.07M CHCl(_3)</td>
<td>25</td>
<td>[8]</td>
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<tr>
<td>36-15 (Ca)</td>
<td>LLE with HDEHP(di(2-ethylhexyl) orthophosphoric acid)</td>
<td>10-50</td>
<td>[9]</td>
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<tr>
<td>130 (Ca)</td>
<td>LLE with amalgam. 0.27-0.68M Ca/liter Hg</td>
<td>25</td>
<td>[10]</td>
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<tr>
<td>2.3 (Ca)</td>
<td>Ion exchange chromatography with Dowex50</td>
<td>room temp.</td>
<td>[11]</td>
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<tr>
<td>98 (Ca)</td>
<td>CRC(cryptand2B.2.2). 0.01M CaCl(_2)+CH(_3)OH/CHCl(_3)</td>
<td>20</td>
<td>[12]</td>
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<tr>
<td>63 (Ca)</td>
<td>CRC (18C6) 0.01M CaCl(_2)+CH(_3)OH/CHCl(_3)</td>
<td>20</td>
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<tr>
<td>2.8 (Ca)</td>
<td>Immodiacidophosphoric acid</td>
<td>0.95M NaCl+0.05M CaCl(_2)</td>
<td>25</td>
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<td>56-130 (Ca)</td>
<td>CRC (cryptand2B.2.2) CH(_3)OH/CHCl(_3)/H(_2)O</td>
<td>-21-21</td>
<td>[13]</td>
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<td>24 (Ca)</td>
<td>CRC (benzo-18C6). 0.02M Ca + 9M HCl</td>
<td>30</td>
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<td>76 (Ca)</td>
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<td>[15]</td>
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<td>8.9 (Ca)</td>
<td>CRC (benzo-15C5). 12M HCl (0.8mm ϕ, 1m)</td>
<td>50</td>
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</tr>
<tr>
<td>150 * (Ca)</td>
<td>LLE with DC18C6 0.07M CHCl(_3)</td>
<td>20</td>
<td>This work</td>
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</table>

Table 1. Unit mass enrichment factors of Sr and Ca isotope separation. *: Preliminary

REFERENCES:
PR11-10  Experimental and Calculated Optical Properties of Molten Aluminium Chloride Melts

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INTRODUCTION: Molten AlCl₃ and AlCl₃-AlCl₃ (A: alkaline metals) have been attractive targets of studies from both fundamental and application viewpoints, because of their relatively low melting points which lead to their effectiveness. The structure of the melts contains a variety of coordinations which have long been investigated and mainly consists of covalent bonding between Al-Cl. In this study, Raman scattering measurements are performed to investigate into their bonding structures, and the spectra are analyzed with ab initio simulations. We focus our study on CsCl-AlCl₃ binary and LiCl-KCl-CsCl-AlCl₃ ternary systems.

EXPERIMENTS: Raman scattering spectra obtained in KURRI were simulated by calculations with GAUSSIAN09 simulation package. Up to 2 ps trajectories of ions in the melts were calculated with a variant of first-principle molecular dynamics simulations, ADMP (Atom-centered Density Matrix Propagation). The computations of the ionic trajectories were performed for CsCl-AlCl₃ at 700 K.

RESULTS: As comprehensively reviewed in Ref. [1], up to 1 : 1 mixture of CsCl/AlCl₃ is expected to exclusively contain AlCl₄⁻ cluster as an anion. On the other hand, Al₂Cl₇⁻ clusters were contained 9.6% of the total anions in the whole snapshots, while AlCl₄⁻ clusters were 73.4%. These numbers of anion rates show that AlCl₄⁻ clusters are not always rigid, and Cl⁻ ions are exchanged among clusters.

Using Einstein relation for the mean square displacements versus time presented in FIG1, self-diffusion constants were computed to be $D_{Cs} = 1.216 \times 10^{-6}$ cm² s⁻¹, $D_{Al} = 1.530 \times 10^{-6}$ cm² s⁻¹ and $D_{Cl} = 2.671 \times 10^{-6}$ cm² s⁻¹, respectively. As far as we know, there is no direct reference experimental data for this system, while interdiffusion constant for NaCl-AlCl₃ mixture were reported to be $4.5 \times 10^{-6}$ cm² s⁻¹ at 413 K [2]. The square displacements for each individual atom are presented in FIG. 2. Al atoms, center of each anion clusters, exhibit both diffusing and static dynamics. A part of Cl atoms corresponds to Al atoms, both for two diffusing Al's and remaining non-diffusing two. Nevertheless, the rest of Cl's cannot be categorized to either of them. This result also supports that Cl⁻ ions are exchanged among clusters.

DISCUSSIONS: For CsCl-AlCl₃ mixture system, anion structure of isolate AlCl₄⁻ tetrahedra shift to corner-sharing two-tetrahedron structure, Al₂Cl₇⁻, dramatically at 1 : 1-ratio with increasing CsCl content. Our calculation seems to reproduce fluctuations in the structural rearrangement at that mixing ratio.

REFERENCE:

FIG. 1 Mean square displacements versus time for ADMP dynamics of constituent atoms at 700 K.

FIG. 2 Square displacements versus time for ADMP dynamics of Cs, Al and Cl atoms at 700 K.
INTRODUCTION: Development of recycling technique for neodymium magnet is essentially important to achieve sustainable society. Consequently, we propose and are investigating a new recycling process of neodymium magnet using B$_2$O$_3$ flux [1]. In the process, the neodymium magnet is melted together with sufficient amount of B$_2$O$_3$ in graphite crucible to form molten iron based alloy, B$_2$O$_3$ slag and Nd$_2$O$_3$-B$_2$O$_3$ slag, which is recovered and dissolved in molten salt. And then, Fe-Nd-B alloy is produced by electrolysis. For the process, thermodynamic properties such as solubility of rare earth oxide in molten salt is important information. In this study, precipitation behavior of dysprosium with adding oxide ion in CaCl$_2$-LiCl eutectic molten salt was investigated by spectrophotometry.

EXPERIMENTS: Solidified samples of CaCl$_2$-LiCl eutectic molten salt and 5 mol%Li$_2$O-(CaCl$_2$-LiCl)$_{en}$ molten salt were prepared through the following procedure. Li$_2$O, CaCl$_2$ and LiCl was weighted, mixed, co-melted at 700 °C in cylindrical quartz tube and quenched in Ar atmosphere. 3.01 g of CaCl$_2$-LiCl eutectic molten salt was inserted in a quartz optical cell and melted at 700 °C. The intensity of the transmitted light through CaCl$_2$-LiCl eutectic molten salt using a tungsten lamp and a spectrophotometer. Then, adding small amount of DyCl$_3$ in the CaCl$_2$-LiCl molten salt and measuring the intensity of the transmitted light through DyCl$_3$-(CaCl$_2$-LiCl)$_{en}$ molten salt was carried out repeatedly to obtain absorption spectra of Dy$^{3+}$ at 700 °C. Using the data on the intensity of the transmitted light, absorbance was evaluated.

RESULTS: Figure 1 shows the absorption spectra of Dy$^{3+}$ in DyCl$_3$-(CaCl$_2$-LiCl)$_{en}$ molten salt at 700 °C. There are three absorption peak depending on the concentration of Dy$^{3+}$ in the range of wavelength, $\lambda$, from 800 nm and 1600 nm; a strong absorption peak at 1296 nm and 2 weak absorption peaks at 918 and at 1121 nm. Figure 2 shows the absorption spectra of Dy$^{3+}$ in Li$_2$O-DyCl$_3$-CaCl$_2$-LiCl molten salt. The spectra were shifted upward and the difference between the top of the absorption peak and the absorbance on the tangential line between the feet of the peak at around 1296 nm became smaller with introducing O$^{2-}$. These indicates that the formation of DyOCl or Dy$_2$O$_3$(s) proceeded and the amount of Dy$^{3+}$ in molten salt decreased.

REFERENCE
Elucidation of the Uptake Route of Radionuclides in Deciduous and Coniferous Trees Using Radio Cesium and Radio Potassium in Annual Tree Rings

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Faculty of Engineering, Hokkaido University
¹ Research Reactor Institute, Kyoto University
² Professor Emeritus, Kyoto University

INTRODUCTION:
Although previous studies have measured the distribution of radionuclides in tree rings, the uptake route of ¹³⁷Cs originating from the fallouts of nuclear weapon tests and the Chernobyl accident has undoubtedly argued the roots¹-⁴. A number of researchers have also reported that ¹³⁷Cs and Pu are absorbed by trees through their bark and leaves; although ambiguously, conclusive evidence has been presented⁵.

Understanding the uptake route of radio cesium (radio-Cs) in the annual tree rings is important for a forest decontaminating in Fukushima. Thus, we investigated the fate of radio-Cs in the Fukushima forestry environment to understand its uptake route using following method: the behavior of radio cesium in the soil and the measurements of radio cesium in the annual tree rings of the deciduous tree konara and the coniferous tree sugi by gamma-ray spectrometry.

EXPERIMENTS
Our experiment is composed three objectives: 1) depth profile of ¹³⁷Cs, ¹³⁴Cs, and ⁴⁰K in the observed sites, 2) speciation of radio-Cs in soil, 3) measurement of ¹³⁷Cs and ⁴⁰K in tree rings

RESULTS:
The behavior of ¹³⁷Cs in the soil samples collected in Fukushima showed the following: (1) radio-Cs in the soil was primarily absorbed by soil minerals within the top 1-cm-depth from the surface; and (2) ¹³⁷Cs in soil was water insoluble and >95% of ¹³⁷Cs was bound to organic and residual matters. These observations suggest that the ¹³⁷Cs released from the Fukushima NPP was trapped in the surface soil and did not penetrate deeper into the soil. The results clearly show that radio-Cs in soil has not moved from the tree roots to the annual tree rings because the active root system rarely was found in the surrounding surface soil. The high ¹³⁷Cs concentration in the sapwood zone of konara coincided with the direction of the arriving radioactive plume in the sampling sites. Conversely, the concentrations of ¹³⁷Cs and ¹³⁴Cs in the annual tree rings of sugi showed non-directionality. As the radioactive Cs moved from the leaves to the tree trunk, the directionality of radio-Cs in the annual tree rings was eventually disappeared. The results of the present study indicate that ¹³⁴Cs and ¹³⁷Cs, detected in the tree rings, from the Fukushima NPP were directly absorbed from the atmosphere by the bark and leaves rather than the roots. Furthermore, the results suggest that the concentrations of radio-Cs in the trees in Fukushima would not further increase in the future.

On the basis of the distribution of radio-Cs in the annual tree rings of the both trees of konara and sugi, we propose the following guidelines for using contaminated wood from Fukushima when high concentrations ¹³⁷Cs have been detected in the trunk: (1) use the parts of wood where the ¹³⁷Cs concentrations are low, and (2) use the highest parts of the trees as sources of bio-ethanol and/or biomass, which correspond to the energy sources for the next generation.

REFERENCES:
Photon Activation Analysis of Alkali Earth Elements and Arsenic with Bremsstrahlung at the KURRI-LINAC

T. Kubota, T. Fujii, S. Fukutani, Y. Shibahara and T. Ohta

Kyoto University Research Reactor Institute

Graduate School of Engineering, Hokkaido University

INTRODUCTION: Photonuclear reaction induced by high energy photons can produce nuclides that are hardly produced in a nuclear reactor, for example, neutron deficient nuclides and carrier free isotopes through \((\gamma, n)\) and \((\gamma, p)\) reaction, respectively. High energy photon is generated in the bombardment of electrons of 30 MeV to platinum sheets at the KURRI-LINAC. We attempted to conduct activation analysis for silicate salt in the previous report [1]. However, Al-29 expected in \((\gamma, p)\) reaction was not observed. The results showed the investigation of effective reaction cross-sections was required for various kinds of target samples. In this report alkali earth elements are used as target sample in order to obtain carrier free alkali metal elements, and in addition the concentration of arsenic in seaweed is evaluated as a preliminary test instead of neutron activation [2].

EXPERIMENTS: The target samples were once heated to dehydration and disintegrate organic compounds; alkali earth salts were dried at 100°C; and seaweed (Hizikia fusiformis) was incinerated at 450°C. Each sample was encapsulated in a quartz tube [3]. The tube in an aluminum vessel was irradiated with photon generated by electron energy of 30 MeV at average current of 200 µA for 4 to 48 hours. Radioactivity, \(A\), induced by photonuclear reaction was measured by \(\gamma\)-spectrometry and provided the apparent cross-section, \(\theta\), which is determined by the following equation:

\[
A = M_0 \theta (\mu A) \left(1 - e^{-\lambda t}\right)
\]

where \(M_0\) (µA), \(\lambda\) and \(t\) were mole number of target nuclide, average electron beam current (micro-ampere), decay constant, and irradiation time, respectively.

RESULTS: Fig 1 shows the apparent cross-sections as a function of mass number. The cross-section of \((\gamma, n)\) reaction was larger than that of \((\gamma, p)\) reaction by one order of magnitude. While the former was the largest at heavy element, seems to be constant between mass number of 40 to 100. The latter was almost constant independent of mass number. For a light element \((\gamma, np)\) reaction was also observed; however, its cross-section was small. The measurement of activated seaweed shows the peaks of As-74 in Fig. 2. The cross-sections of some photonuclear reactions were obtained for isotope production and activate analysis, even though these values are empirical.

REFERENCES:
INTRODUCTION: For the analysis of radionuclide, the radiation measurement such as γ-spectrometry, β-spectrometry, and α-spectrometry were mainly performed. Although these methods have been used for the measurement of radioactive nuclide such as nuclear fuel materials and fission products released on the accident of Fukushima Dai-ichi Nuclear Power Plant, they may have disadvantage in the case of the analysis of radionuclide having the long half-life and/or that of isotopic composition including naturally occurring isotopes. Because the mass spectrometry has advantage for the analysis of the isotopic composition of the elements with high accuracy, this method may have the applicability for the analysis of radionuclide released on the accident of Fukushima Dai-ichi Nuclear Power Plant.

Although the amounts of radionuclide such as radioactive Cs and Sr released on this accident were very huge, the contaminated environmental samples show the small radioactivity per unit weight of the contaminated environmental samples, since the contaminated area is very wide. For the study of the recovery/analysis method of cesium and strontium, thus, the radioactive Cs and Sr were generated by the irradiation of natural uranium at KUR.

EXPERIMENTS: Radioactive Cs and Sr were generated by the irradiation of 10 mg of UO₂ of natural uranium at the Kyoto University Research Reactor with the neutron flux for 5.5×10¹² n/s cm⁻². The amounts of the major radionuclide of Cs and Sr generated by the irradiation for 3 hours were estimated as 7.4×10⁻¹¹ g (¹³⁷Cs) and 4.5×10⁻¹¹ g (⁶⁰⁰Sr). About 3 days later, the irradiated sample was dissolved with 8M HNO₃ and heated to dryness. The residues were immersed in 8 M HNO₃ and the insoluble residues were removed by centrifugation. TRU elements in sample solution were removed by the extraction-chromatography with UTEVA-resin [1], and the sample solution was evaporated to dryness. The residues was dissolved with 3 M HNO₃ solution. After the recovery of Sr by the extraction-chromatography with Sr-resin [2], Cs was recovered by using with ammonium phosphomolybdate (AMP) [3]. The sample solutions for the analysis of isotopic composition of Sr and Cs were obtained with the dissolving 1 M HNO₃ (10μL for Sr, 20 μL for Cs, respectively).

Isotopic compositions of Cs and Sr were measured with the TIMS (Triton-T1, Thermo Fisher Scientific). A 1 μL aliquot of each solution was loaded onto a rhenium single filament with a TaO activator [4]. Loading amount of ⁸⁹Sr and ¹³⁷Cs were 4.5×10⁻¹² g and 3.7×10⁻¹² g, respectively. Because of the loading amount of Sr and Cs, the mass spectra of radioactive Cs and Sr were obtained with a secondary electron multiplier detector (SEM).

RESULTS: In the measurement of radioactive Cs, ¹³⁷Cs, ¹³⁶Cs and ¹³³Cs were detected (Fig.1 (a)). ¹³⁷Cs was not detected, because of the amount generated by the irradiation at KUR. In this measurement, it was observed that the isotopic ratios of ⁶⁰⁰Sr/¹³⁷Cs and ¹³⁶Cs/¹³⁷Cs were 0.79 and 0.012, respectively. These mean that the several ten femto-gram of Cs would be detectable with the four orders of the significant figures.

In the measurement of radioactive Sr, ⁹⁰Sr, ⁹⁵Sr and ⁹⁰Sr were detected at the measurement 2.6 days later. The mass spectra of ⁹⁰Sr and ⁹⁵Sr were disappeared at the measurement of 31 days later and 374 days later, because of the half-life of ⁹⁰Sr (T₁/₂ = 9.5 h) and ⁹⁰Sr (T₁/₂ = 50.5 d). The obtained isotopic ratios were agreed with results of the estimation by using ORIGEN-II code [5]. This means that the several ten femto-gram of Sr would also be detectable.

It was confirmed that the recovery/analysis method of Cs and Sr have the applicability for the analysis of radioactive Cs and Sr released on the accident of Fukushima Dai-ichi Nuclear Power Plant. The loading amount of several pico-grams of radioactive Cs and Sr would bring the information of the isotopic ratio with the four orders of significant figure until the ten periods of half-live.

REFERENCES:
INTRODUCTION: Recent findings of subducted halogens and noble gases with seawater and sedimentary pore-fluid signatures in exhumed mantle wedge peridotites [1], as well as seawater-derived heavy noble gases (Ar, Kr, and Xe) in the convecting mantle [2], provide observations that allow us to investigate the processes that control the return of volatile and highly incompatible elements into the mantle. To verify whether and how such subduction fluids modify the composition of the mantle beneath subduction zones, we are investigating noble gas and halogen compositions of olivines in arc lavas from northern Izu subduction zone and those of seafloor sediments and basalts from NW margin of the Pacific plate. A combination of neutron irradiation and noble gas mass spectrometry (NI-NGMS), an extension of Ar-Ar and I-Xe dating methods, allows us to simultaneously determine trace amounts of halogens with naturally occurring noble gases by use of ultrahigh-sensitive noble gas mass spectrometry on neutron-irradiated samples [3,4].

EXPERIMENTS: The samples and standard samples for NI-NGMS, Hb3gr hornblende and the Shallowater meteorite were neutron-irradiated for six hours during a 5 MW operation of KUR by using the hydraulic conveyor to convert halogens (Cl, Br, and I) to corresponding noble gas isotopes. Noble gases in the unirradiated and irradiated samples were extracted selectively from fluid/melt inclusions using in vacuo crushing. The evolved noble gases were analyzed using mass spectrometry at The University of Tokyo [5,6].

RESULTS: MORB-like 3He/4He and halogen ratios of the olivines indicate insignificant contributions to the Izu arc magmas of radiogenic 3He and sedimentary-pore-fluid-like halogens, both of which are observed in the subduction fluids released from a slab at a depth of 100 km [1]. On the other hand, a clear difference in 40Ar/36Ar ratios between the Izu volcanic front and rear arc, and a comparison with those of the seafloor sediments and altered oceanic crusts suggest that Ar of sedimentary pore-water origin in the subducting slab is liberated continuously with depth and that it affects the noble gas composition of the magma generation region significantly. A small addition of the sediment-derived noble gases to the rear-arc magma is consistent with the slab melt contribution inferred from trace element and Pb-Sr-Nd-Hf isotope compositions [7].

The high I/Cl ratios of the seafloor sediments can account for the enrichment of I in subduction fluids relative to sedimentary pore-fluids [1], whereas contributions of halogens and noble gases from altered oceanic basalts are limited.

A simple mass balance calculation of Ar isotopes for the melt generation region beneath the Izu arc revealed that higher subduction flux of pore water other than direct incorporation with its host sediment/crust is necessary, and that serpentinized lithosphere in the subducting slab is regarded as the best candidate if the hydration of the lithosphere by pore fluids is operating in a closed system.

The significantly smaller contributions of subducted noble gases and halogens in the Izu arc magmas relative to those in the mantle wedge peridotites may result from a difference in the P-T condition of the slab in each subduction zone, or from dilution by mantle-derived halogens and He when the subduction fluid induced partial melting. The former implies a relatively small amount of the pore-water-derived subduction fluids would be released from a cold slab at a sub-arc depth resulting in further subduction of halogens, heavy noble gases and potentially water, to great depths in the mantle, which account for the seawater-like heavy noble gases observed in the convecting mantle [2].

REFERENCES:
INTRODUCTION: Submarine volcanic rocks are known to give ages different from their true eruption ages in some cases. This is due to the existence of excess $^{40}$Ar in the rapidly quenched glass or Ar loss and K remobilization caused by reaction with seawater or hydrothermal fluids. Stepwise-heating analysis in $^{40}$Ar/$^{39}$Ar dating is particularly useful for dating submarine volcanics.

Since this is the first time to use KUR for our laboratory, we investigated neutron flux gradient and production of interfering isotopes for $^{40}$Ar/$^{39}$Ar method by irradiating standard minerals and synthetic glasses as preparation for dating of unknown samples.

EXPERIMENTS: Samples were wrapped in an aluminum foil packet and the packets were piled up in a pure aluminum (99.5% Al) irradiation capsule (9 mm diameter and 30 mm long). The irradiation capsule was partitioned into 3 compartments to minimize the uncertainty of the sample positions at irradiation. The irradiation capsule was wrapped with 0.5 mm-thick Cd-foil before irradiation. The capsule was irradiated 2 hours at 5MW in Hyd facility of KUR. Analyses were conducted using $^{40}$Ar/$^{39}$Ar geochronology facility at the Geological Survey of Japan/AIST following the analytical procedure described in [1].

For the experiments described here, around 15 mg of sample was analyzed in each analysis. Due to alteration of poorly-crystallized part groundmass, basaltic samples were treated at 100°C on hot plate with stirrer in 6N HCl for 60 minutes and then 6N HNO$_3$ for 60 minutes to remove possible alteration products (clays and carbonates) prior to irradiation. This procedure effectively separated and concentrated fresh plagioclase in groundmass and of microphenocryst. After this acid treatment, these separates were examined under binocular microscope before packed for irradiation.

RESULTS: Two basaltic samples recovered from the northern margin of the Palau Basin, southernmost part of the Philippine Sea Plate, were studied. The West Philippine Basin and Palau Basin are supposed to have been the oldest oceanic basins in the Philippine Sea Plate. Accordingly, their origin and growth history can be a critical constraint on the tectonic reconstruction of the Philippine Sea Plate. These basins could have existed prior to the Izu-Bonin (Ogasawara)-Mariana arc (IBM arc), or formed as a consequence of subduction initiation along the IBM arc (e.g., backarc basins of the IBM arc). However, due to the paucity of geological and geophysical data from these basins, their origin and history are yet unclear.

YK10-14 and YK13-08 cruises by R/V Yokosuka investigated Palau Basin and southern part of West Philippine Basin obtained crucial geological and geophysical data [2] for reconstruction of the Philippine Sea Plate. 12 dredge hauls and 4 Shinkai submersible dives were made during these cruises. $^{40}$Ar/$^{39}$Ar dating of dolerite sample from the Palau Basin crust exposed at the Mindanao Fracture Zone at c. 130°E gave a plateau age of 40.4 Ma. This result implies that the spreading of the Palau Basin was still going on at 40.4 Ma. This age is within an age range of active spreading of the West Philippine Basin.

This year we conducted $^{40}$Ar/$^{39}$Ar dating of basaltic samples from 2 locations in the eastern part of the basin along the Mindanao Fracture zone. Fig. 1 shows age spectra for the 2 analyses. Sample 6K1358R11, which was collected by Shinkai 6500 at 4564 m deep gave a plateau age comprising of 63.8% of released gas. YK10-14 D3R14, which was collected further east along the Mindanao Fracture Zone by dredging also gave a well-defined plateau comprising of 96.3% of released gas. The plateau ages shown here are still temporary age because flux monitor measurement has not been completed yet. However, these data strongly imply that the age of formation of the Palau Basin closely matches with that of West Philippine Basin, and this result is crucial for tectonic reconstruction of this area. Final ages will also allow us to determine the direction and rate of seafloor spreading when the Palau Basin formed.

REFERENCE:
Ar–Ar Age Determination of Minamitorishima

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1 Geochemical Research Center, Tokyo University
2 Research Reactor Institute, Kyoto University

INTRODUCTION: Most of seamounts on the western Pacific Plate formed before 70 Ma in the so-called West Pacific Seamount Province (WPSP) which is characterized by relatively short seamount chains maybe indicating a significant short-lived hotspot system [1]. The geochronological studies of each Cretaceous seamount, on the other hand, show the long-lived main shield stage of volcanism, because a seamount remained above a hotspot for a long time (approximately 10 m.y. [2]). This may be attributed to either of the following two possibilities: 1) An abundant heat supply as in the superplume episode in the Early Cretaceous [3][4][5]. 2) Slow absolute motion of the Early Cretaceous Pacific Plate (3–6 cm/yr.) [6][7].

The research cruise using R/V Yokosuka equipped with the submersible SHINKAI 6500, was conducted around the Minamitorishima Island on May 2010 in order to know the detail history during the formation of the island, where volcanic rock samples have never been obtained before (Fig. 1). The shipboard multibeam acoustic surveys showing the detail bathymetry discovered the volcanic cones on seamount slope and the clusters of small conical volcanoes on surrounding abyssal plain (Oikawa and Morishita, 2009). Most of cones are several hundred meters in height and 1–10 km in diameter. We observed the stratigraphy of Minamitorishima using the submersible SHINKAI 6500. Highly vesicular lavas were sampled at the volcanic cone on the seamount slope. The olivine-bearing dense lavas, on the other hand, were obtained at the steep slope beneath the lava platform in bathymetry, implying main-shield stage lavas in contrast to volcanic cones probably erupted at the rejuvenated stage during the Minamitorishima’s formation.

EXPERIMENTS: Radiometric Ar–Ar dating is commonly used to determine the ages of submarine lavas, because the traditional K–Ar dating is impossible to remove the alteration part in such rocks [8]. The rock-samples prepared for dating were crushed to 100-500 μm grains, and leached by the 1N HNO3 at 70-60 °C for one hour. The leached samples were irradiated by neutrons in a reactor to produce 39Ar from 39K during a few hours. During the irradiation, samples were packed with EB-1 biotite flux monitors [9], K2SO4 and CaF2 as correcting factors in an aluminum capsule. They are shielded by Cd foil in order to reduce neutron-induced 40Ar from 40K [10]. Then, radiogenic 40Ar, daughter nuclide of radioactive 40K and parent, 39Ar in stead of 40K, were simultaneously analyzed using a mass-spectrometer with an extraction technique of multi-step heating of approximately every 50 to 100 °C between 500 to 1500 °C.

RESULTS: The irradiations of sample in KUR were done in May, 2014. We are going to analyze the irradiated samples after cooling. We note that the Minamitorishima is just only “island” in WPSP in spite of many of larger volcanic edifices of seamount and guyot than Minamitorishima. We have a hypothesis of different process and age to make the island in WPSP, awaiting future analytical results.

REFERENCES: