Cosmogenic ^{45}Sc in Gibeon iron meteorite by radioanalytical neutron activation analysis

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Summary. Cosmogenic nuclides in many fragments of Gibeon iron meteorite have been studied by Honda and co-workers. They observed that their concentrations varied by 5 orders and found that Gibeon gives two different exposure ages using pair of stable noble gas isotopes and radionuclide. To assess one possible cause for the difference, namely loss of partial noble gases due to atmospheric heating of the incoming meteoroid, concentrations of non-volatile and stable cosmogenic ^{45}Sc of Gibeon were determined by radiochemical neutron activation analysis (RNAA). For RNAA, a radiochemical procedure using extraction chromatography was developed to separate Sc from an iron meteorite. Concentrations of ^{45}Sc in 7 fragments ranged from 0.0064 to 0.11 ppb and correlated with cosmogenic ^4He concentrations. This correlation suggests that noble gases in Gibeon were not lost during the fall to the earth.

1. Introduction

Meteorites and lunar rocks have cosmic ray induced stable and radionuclides called cosmogenic nuclides. These nuclides play important roles in the determination of a cosmic-ray exposure (CRE) ages and terrestrial ages, and in the estimation of cosmic ray intensity. Assuming that cosmic ray intensity was constant, the contents of cosmogenic stable nuclides are proportional to the duration of irradiation by cosmic rays, *i.e.* to the CRE age.

The first fragment of the Gibeon iron meteorite was found in Namibia in 1836, since then total of 21 tons of the meteorite have been recovered [1]. Honda *et al.* [2] have been determined the concentrations of several cosmogenic nuclides including stable noble gas isotopes and several radionuclides in many fragments of Gibeon. The concentrations of these nuclides vary by 5 orders of magnitude from fragment to fragment, and systematic correlations among cosmogenic nuclides are observed. The observed trends probably reflect shielding differences, *i.e.*, differences in the numbers of cosmic rays that reached different parts of the meteoroid while it was in space. And they divided

samples studied into two groups with different CRE age estimated from stable noble gas isotopes; Group G1 with 4×10^8 years and Group G2 with an average CRE age of 1.5×10^7 years. There are two possible reasons that Gibeon shows two different exposure ages; 1) Gibeon has a multi-stages exposure history, and 2) part of cosmogenic noble gases escaped from the meteorite body during its fall to the earth [3]. Non-volatile stable cosmogenic nuclides may be helpful for looking into the second possible mechanism.

In general, it is extremely difficult to detect stable cosmogenic nuclides except of noble gases above the background of non-cosmogenic component that meteorites incorporated when their parent bodies formed. Iron parent bodies, however, contain very low concentrations of geochemically lithophile elements such as Sc. Thus Sc detected in the metal phases of iron meteorites should be mainly cosmogenic in origin. We determined the concentration of ^{45}Sc in several Gibeon fragments by radiochemical neutron activation analysis (RNAA). The production rate of ^{45}Sc should be relatively high mainly because mass number of the product ^{45}Sc is fairly close to that of the principal target element, Fe. Since monoisotopic Sc is one of the elements for which the application of mass spectrometric methods is difficult, analysis of ultra trace Sc is a most suitable application of RNAA.

Wänke and König [4] and Honda *et al.* [5] previously reported Sc concentrations in iron meteorites by RNAA. Wänke and König separated Sc by electrochemical and precipitation methods and detected β -rays from ^{46}Sc produced from (n, γ) reaction with a Geiger counter [4]. Honda *et al.* used cation exchange and precipitation method to separate Sc and detected γ -rays from ^{46}Sc with a Ge detector [5]. In the present work a separation procedure using extraction column chromatography [6, 7] was developed to remove completely the major radioactive nuclides produced by neutron irradiation and which might interfere with the detection of ^{46}Sc .

2. Experimental

2.1 Radioactive tracer experiment for radiochemical procedure

Extraction column chromatography was applied by Minowa and Ebihara to purify rare earth elements (REEs) including

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trace Sc. They reported that REEs in HCl were not adsorbed on TRU resin (Eichrom Technologies, Inc.) and Sc was adsorbed from both 4 M and 2 M HCl but not from 1 M HCl [6]. Therefore we applied their procedure to RNAA of Sc in iron meteorites and also evaluated its ability to remove several elements interfering γ -spectrometry of weak ^{46}Sc .

Radioactive tracers produced by (n, γ) or (γ, n) reaction were used for evaluation of elution behaviors of Sc, Mn, Fe, Co, Ni, and Ir in extraction column chromatography. ^{54}Mn , ^{59}Fe , ^{60}Co and ^{192}Ir are major activity produced in an iron meteorite sample after neutron irradiation. At first 3 ml of 4 M HCl containing proper activities of ^{46}Sc , ^{54}Mn , ^{59}Fe , ^{60}Co , ^{56}Ni and ^{192}Ir was prepared. Amount of carrier for these nuclides were less than 7.5 μg except of Mn, Fe and Ni. ^{54}Mn has no carrier because it was produced by $^{56}\text{Fe}(n, p\gamma n)$ reaction. Assuming that Fe is not removed sufficiently by a solvent extraction before an extraction column chromatography, amount of Fe carrier of ^{59}Fe was 2.3 mg corresponding to about 1/500–1/1000 of meteorite sample (1–2 g). For Ni, the carrier weight was 6.4 mg.

3 ml of 4 M HCl solution having radiotracers was loaded onto 1 ml of TRU resin column (5 mm i.d. and 42 mm length). The column was washed with 15 ml of 4 M HCl, and then 10 ml of 1 M HCl followed by 5 ml of H_2O were loaded to elute Sc. Each 5 ml of eluent was subjected to γ -ray spectrometry.

The amount of Sc adsorbed on TRU resin in 4 M HCl was determined by a column method using ^{46}Sc tracer. Three 4 M HCl solutions containing ^{46}Sc and different amount of Sc carrier were loaded to 1 ml of TRU resin columns. After feeding additional 10 ml of 4 M HCl and 5 ml of 1 M HCl, the eluates were subjected to γ -spectrometry.

2.2 Determination of Sc concentration in iron meteorites

1–2 g of Gibeon fragments were etched with dil. HNO_3 to remove surface contamination. The samples were wrapped in two layers of polyimide Capton® films and irradiated at JRR-4 T-pipe ($\phi_{\text{th}} = 5.3 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1}$ and Cd ratio = 3.8) for 1 h or at JRR-3 HR ($\phi_{\text{th}} = 9.6 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1}$ and Cd ratio = 8) for 2 h. After irradiation, the samples were etched again with dilute aqua regia to remove terrestrial Sc contamination on their surface completely. Samples were dissolved in 4 M HNO_3 with 5 to 10 mg of Sc carrier, and then heated to dryness. The residue was finally dissolved in 4 M HCl. Iron was extracted by 30 ml of methyl isobutyl ketone from 10 ml of 4 M HCl solution 4–6 times until HCl solution became green in color. The hydrochloric acid solution remaining after solvent extraction was heated to dryness, then the residue was dissolved in 2 ml of 4 M HCl. For reasons explained below, iron remaining in this solution was reduced to Fe^{2+} by adding 5 ml of 4 M HCl containing 5 g of ascorbic acid followed by extraction chromatography using 6 ml of TRU resin column (10 mm i.d.). After loading the sample solution, 30 ml of 4 M HCl containing ascorbic acid and additional 30 ml of 4 M HCl without ascorbic acid was fed, and then Sc was eluted with 30 ml of 1 M HCl. Scandium in 1 M HCl was recovered as scandium tartrate by adding ammonium tartrate and NH_3 aq. to make alkaline. The chemical yield of Sc was determined gravimetrically

after γ -ray spectrometry with Ge detector. For determination of Sc, 889 keV γ -ray from ^{46}Sc was used because natural ^{214}Bi emits 1120 keV γ -ray that interferes with 1121 keV γ -ray from ^{46}Sc .

3. Results and discussion

3.1 Elution behavior of Mn, Fe, Co, and Ir for extraction chromatography

Elution behaviors of Sc, Mn, Fe(III), Co, and Ir in HCl solution for TRU resin were shown in Fig. 1. More than 95% of Mn and Co were eluted within first 5 column volumes of 4 M HCl, thus Mn and Co were found not to be adsorbed on TRU resin with 4 M HCl. About 70% of Ir was eluted with 10 column volumes of 4 M HCl and after that remaining Ir was also eluted with additional 4 M and 1 M HCl little by little. Because no Sc and Fe were observed in eluate of 4 M HCl, Sc and trivalent Fe was confirmed to be adsorbed strongly on TRU resin with 4 M HCl. With 5 column volumes of 1 M HCl, Sc and Fe(III) were eluted completely from TRU resin. It is concluded that Sc cannot to be separated from Fe(III) by extraction chromatography using TRU resin with HCl solution.

Behaviour of Ni was studied using 4M HCl containing only ^{56}Ni , ^{57}Ni and their daughter nuclides ^{56}Co and ^{57}Co by a similar way described above. 100% of ^{56}Ni and 99% of ^{56}Co were observed in the eluate of 4 M HCl loading solution. It is concluded that Ni was not adsorbed on TRU resin from 4 M HCl like Co and Mn.

To separate iron, Fe^{3+} was reduced to Fe^{2+} by adding ascorbic acid to the solution containing Sc, Mn, Fe(III), Co and Ir, and elution behavior of Fe(II) was evaluated by the same procedure above. As shown in Fig. 2, 98% of Fe(II) as well as Mn and Co was eluted after the addition of 5 column volumes of 4 M HCl. About 30% of Ir was retained on TRU resin after elution with H_2O . Because Sc was not eluted with 4 M HCl but was eluted with 1M HCl, Sc was concluded to be separable from Fe(II) by using TRU resin.

Fig. 1. Elution behavior of Sc, Mn, Fe(III), Co, and Ir for TRU resin with HCl. Both Sc and Fe(III) were eluted with 5 column volumes of 1 M HCl.

Fig. 2. Elution behavior of Sc, Mn, Fe(II), Co, and Ir for TRU resin with HCl. Fe(II) was not adsorbed on TRU resin with 4 M HCl. 4 M HCl contains ascorbic acid.

The amount of Sc adsorbed on 1 ml of TRU resin was evaluated by loading three separate 4 M HCl solutions containing Sc carrier of 0.40, 2.0, and 6.0 mg each with ^{46}Sc onto 1 ml of TRU resin and then eluting the Sc with 1 M HCl. Measuring γ -rays in each eluent, 0.39 ± 0.1 , 0.88 ± 0.01 and 0.93 ± 0.01 mg of Sc respectively were found to be adsorbed on 1 ml of TRU resin. Thus it is concluded that TRU resin adsorbs 0.91 mg Sc/ml resin from 4 M HCl.

3.2 Sc in Gibeon iron meteorite

Scandium concentrations in 7 fragments having different ^4He concentration were determined. Chemical yields of Sc were about 40–80%. Low chemical yields were due to addition of too much (about 9 mg) of Sc carrier. This mass exceeded the capacity of the resin in the column (5 ml) by a factor of two. As shown in Fig. 3, ^{60}Co , whose activity was the same as that of natural ^{40}K , was contaminated in final Sc precipitates. ^{192}Ir was also contaminated, and in several samples ^{59}Fe was detected. Interference due to ^{192}Ir was not severe because its main γ -rays are lower energy than those of ^{46}Sc . Contamination of ^{59}Fe is probably due to incomplete reduction of Fe^{3+} .

In this study about 6 ppt of Sc can be determined with a relative error of 10% and a detection limit of Sc concentration attained 0.4 ppt, assuming 2 g of sample, irradiation for 2 h, and 80% of chemical yield. With irradiation for longer time and reduction of contamination of ^{60}Co and ^{59}Fe through an additional purification step, the detection limit could be lowered. In NAA of Sc using the $^{45}\text{Sc}(n, \gamma)^{46}\text{Sc}$ reaction, the $^{46}\text{Ti}(n, p)^{46}\text{Sc}$ reaction would prevent to determine Sc. Since Ti is geochemical lithophile element as well as Sc, its concentration is estimated to be also very low like Sc. The contribution from Ti was neglected.

In this work 0.0064–0.11 ppb of ^{45}Sc concentrations were obtained in 7 fragments. Iron meteorites often contain silicate and other types of inclusions, which might increase background levels of Sc. No such inclusions were visible on the surface of the fragments. To date, the concentrations re-

Fig. 3. Gamma-ray spectrum of scandium tartrate recovered from 1.7 g of fragment irradiated for 1 h at JRR-4. Chemical yield was 69% and Sc concentration was determined to be 0.0064 ppb. Gamma-ray peaks not shown nuclides are originated from natural radionuclides.

Fig. 4. Correlation between ^{45}Sc and ^4He in iron meteorites. Lozenge symbols show Gibeon in this work and by Honda *et al.* [5] and circular symbols show other iron meteorites by Honda *et al.* [5]. “G1” in the figure means G1 group of Gibeon and lozenge symbols not shown arrows are belonging to G2 group.

ported for geochemically siderophile and chalcophile trace elements in Gibeon vary by a factor of two at most. Few concentrations of lithophile elements have been reported.

It is not until that large variation of elemental concentration such as Sc in Gibeon fragments was observed. Therefore most observed ^{45}Sc was concluded to be cosmogenic origin. It is proved that ^{45}Sc concentration showed good correlation with cosmogenic ^4He concentrations as shown in Fig. 4. Concentrations of ^4He in the fragments were measured on a noble gas mass spectrometer (modified-VG5400) at the laboratory for Earthquake Chemistry, University of Tokyo. In Fig. 4 ^{45}Sc and ^4He concentrations in other iron meteorites determined by Honda *et al.* [5] are also plotted by open symbols. The correlation between ^{45}Sc and ^4He observed in Gibeon shows no difference from that in other iron meteorites. And no systematic difference between sub-group G1 (longer exposure age) and G2 (shorter exposure age) of Gibeon was observed. The average atomic

ratios of $^{45}\text{Sc}/^4\text{He}$ for Gibeon G1 group, Gibeon G2 group, and other meteorites were 0.063 ± 0.022 , 0.071 ± 0.031 , and 0.055 ± 0.026 , respectively (errors are standard deviations, 1σ). These atomic ratios are consistent within their errors. Thus it is concluded that noble gases did not escape from meteorite body during the fall. Two stages of irradiation are suggested to explain the two different exposure ages. Generally iron meteorites have longer irradiation ages than stony meteorites, and it is understood that iron meteorites are hard to break in the space.

The lowest ^{45}Sc concentration was 6.4 ± 1.5 ppt in this work. Honda *et al.* obtained lower concentration, 2 ± 1 ppt in Campo del Cielo iron meteorite [5]. Since good correlation between ^{45}Sc and ^4He was observed down to 2 ppt of ^{45}Sc , the concentration of non-cosmogenic original ^{45}Sc included at the time of formation of the parent body of Gibeon is inferred to be less than 2 ppt. It is roughly estimated that ^{45}Sc original level is less than 1 ppt, which is 200 times lower than the one estimated by Wänke and König [4]. The original concentration of ^{45}Sc as lithophile element provides a constraint on the environment at the time of iron parent body formation. Further analysis is required.

4. Conclusion

The concentrations of ^{45}Sc in Gibeon iron meteorite were determined by RNAA. A good correlation between ^{45}Sc and cosmogenic ^4He was found, which agrees with one previously reported for several iron meteorites. No systematic

difference both between Gibeon G1 group with longer exposure age and G2 group with shorter age, and between Gibeon meteorites and other iron meteorites were observed. Thus Gibeon did not experience loss of noble gases either in the space or during fall to the earth. It is concluded that multi stage exposure resulted in two different CRE ages.

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References

1. Buchwald, V. F.: In: *Handbook of Iron Meteorites, their History, Distribution, and Structure*. University of California Press (1975).
2. Honda, M., Nagai, N., Nagao, K., Bajo, K., Takaoka, N., Oura, Y., Nishiizumi, K.: Irradiation histories of iron meteorites. *J. Phys. Soc. Jpn.* **78**(Suppl. A), 12 (2009).
3. Nord, R., Zaehring, J.: *Geochimii I Analiticeskoy Chimii*. Akad. Nauk (1972), p. 59.
4. Wänke, H., König, H.: *Studies on Meteorites*. Max-Planck Inst. Chem., Mainz (1960), p. 19.
5. Honda, M., Nagai, H., Takaoka, N., Yamamuro, K., Kume, T., Takahashi, A., Akizawa, S.: Scandium 45 in meteoritic irons. *Proc. NIPR Symp. Antarct. Meteorites* **1**, 197 (1988).
6. Minowa, H., Ebihara, M.: Separation of rare earth elements from scandium by extraction chromatography. Application to radiochemical neutron activation analysis for trace rare earth elements in geological samples. *Anal. Chim. Acta* **498**, 25 (2003).
7. Nomura, M., Sato, M., Amakawa, H., Oura, Y., Ebihara, M.: Precise determination of Sc in natural waters by neutron activation analysis coupled with preconcentration of Sc. *Anal. Chim. Acta* **553**, 58 (2005).