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Determination of Trace Amount of Manganese in High-purity Iron

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Trace amount of manganese in high-purity iron samples was determined by INAA using Tc-Pn at KUR, ICP-MS, and ICP-AES. It was confirmed that the INAA using Tc-Pn was able to determine several tens of ppb Mn as an impurity in iron samples without correcting a contribution of the ^{56}Mn produced by the fast neutron-induced reaction on ^{56}Fe. Based on the results, the INAA using Tc-Pn was applied to the determination of trace amount of manganese in some fragments of the Gibeon iron meteorite in order to estimate cosmogenic ^{55}Mn in those fragments.

1. Introduction

Manganese is one of the most sensitive elements for instrumental neutron activation analysis (INAA).[1] In determining trace amount of manganese in samples like iron meteorites by INAA, a contribution of the ^{56}Mn produced by the fast neutron-induced reaction ^{56}Fe(n,p)^{56}Mn must be corrected.[1] In this work, we confirmed that several tens of ppb of manganese in high-purity iron samples can be determined by INAA using the thermal column pneumatic transport system (Tc-Pn) at Kyoto University Reactor (KUR) without correcting a contribution of the ^{56}Mn produced by the fast neutron-induced reaction. Tc-Pn is utilized to minimize contributions of epithermal and fast neutrons effectively.

Manganese contents in iron meteorites are very low; they were measured in a range of 40 to 90 ppb using radiochemical neutron activation analysis (RNAA).[2] In the Gibeon iron meteorite, depth profiles of cosmogenic nuclides (^{10}Be) and stable nuclides (^{3}He, ^{4}He) were measured by Honda et al.[3–6] They reported that ^{10}Be in the fragments from the deeper part of this iron meteorite is much lower than those from the surface.[3,4] In this work, we applied the INAA using Tc-Pn to the estimation of the amount of cosmogenic ^{55}Mn in the fragments from the deeper part and from the surface of the Gibeon iron meteorite.

2. Experimental

2.1. Determination of trace amount of manganese in high-purity iron samples. High-purity iron samples, JSS003-5, JSS009-2, JSS001-4, and JSS001-5 (JSS009-2 is an iron oxide sample, and the others are metallic ones) are commercially available from the Japan iron and steel federation, and the impurity contents in those samples are indicated in the attached certificates.[7–10] Before irradiation of the samples, the surfaces of JSS001-4 and JSS001-5 were leached with dilute nitric acid to remove contaminants which adhered to those surfaces in sample-manufacturing. By leaching, the sample weight was reduced to about 75%. About 250 mg of each high-purity iron sample was irradiated with manganese comparators. The manganese comparators were prepared from manganese standard solution. The neutron irradiation was carried out for 60 min using Tc-Pn at KUR, whose thermal and fast neutron fluxes are reported to be 4×10^{11} n cm^{-2} s^{-1} and 8×10^{7} n cm^{-2} s^{-1}, respectively.[11] After irradiation, γ rays of ^{56}Mn (846 keV) emitted from each sample were measured by a low background Ge detector.

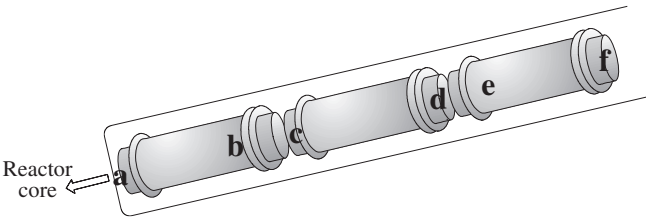

Figure 1. Six positions where Cd-ratios were measured in the thermal column at KUR.

To evaluate the effect of epithermal and fast neutron induced reactions at some irradiation positions in Tc-Pn, the Cd-ratios of gold were measured at six positions shown in Figure 1. The ratios at the positions from "a" to "f" were 220, 230, 250, 230, 150, and 140, respectively. Based on the ratios obtained, all the irradiations of iron samples were performed between "a" and "d".

Besides INAA, inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) were also utilized to determine the amount of manganese in the same samples in order to compare the results with those obtained by INAA. For ICP-MS and ICP-AES, it is necessary to separate bulk iron from the samples to prevent the mass matrix effect of ^{56}Fe. The iron samples of 100–350 mg were dissolved in conc. HNO_3 or aqua regia. The iron was separated by anion exchange (DOWEX 1-X8, 100–200 mesh) and solvent extraction using diisopropylether. The solution after iron-separation was subjected to ICP-MS and ICP-AES. The yield in this chemical separation was estimated to be more than 90% using ^{56}Mn radiotracers in a separate experiment.

2.2. Determination of manganese in the Gibeon iron meteorite. We applied the neutron activation analysis using Tc-Pn to the determination of trace amount of manganese in five fragments of the Gibeon iron meteorite: G. 003, G. 102, G. 105, G. 2001, and G. 99. Neutron irradiations for all the fragments were carried out in the same manner as those for the high purity-iron samples. Since iron meteorites contain heterogeneously inclusions like troilite (FeS) which contains 300–800 ppm of manganese as an impurity,[2,12] it seems to be necessary to remove such inclusions thoroughly in the determination of trace amount of elements represented by manganese

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TABLE 1: Result of Mn content

Sample	INAA	ICP-MS	ICP-AES	Certified Value
JSS003-5 (metal)	25.5 ± 0.3 ppm	25.2 ± 0.6 ppm	25.1 ± 0.1 ppm	27 ± 1 ppm[a]
JSS009-2 (oxide)	750 ± 15 ppb	884 ± 30 ppb	830 ± 8 ppb	<2 ppm[b]
JSS001-4 (metal)	26 ± 2 ppb	65 ± 3 ppb	[e]	30.6 ± 5.5 ppb[c]
JSS001-5 (metal)	25 ± 1 ppb	[e]	[e]	30 ± 10 ppb[d]

[a]Reference 7. [b]Reference 8. [c]Reference 1. [d]Reference 10. [e]See text of sec. 3.1.

TABLE 2: Mn concentrations in five fragments of the Gibeon iron meteorite

Sample	Surface-leaching after NAA / times	Weight / g	Mn concentration / ppb	^{10}Be content / dpm kg^{-1}
G. 003	0	0.4239	507 ± 45	
G. 003	1	0.3993	330 ± 33	0.00007[a]
G. 003	2	0.3826	333 ± 44	
G. 102	0	0.1772	101 ± 15	0.00016[a]
G. 102	1	0.1597	82 ± 21	
G. 105	0	0.2490	401 ± 36	0.0005[b]
G. 105	1	0.2340	414 ± 43	
G. 2001	0	0.2518	645 ± 34	0.49[b]
G. 99	0	0.1239	154 ± 14	1.17[a]
G. 99*	0	0.1159	942 ± 28	

[a]Reference 6. [b]Reference 13.

in iron meteorites.[2] In this work, to investigate the effect of the inclusions, the fragments of G. 003, G. 102, and G. 105 were leached with acid after neutron irradiations. G. 102 and G. 105 were leached once ultrasonically with 1.5 N HNO_3 for 2 min, and G. 003 twice.

3. Results and Discussion

3.1. High-purity iron samples. The contents of manganese in the high-purity iron samples measured by INAA, ICP-MS, and ICP-AES are listed in Table 1. The certified values of manganese contents in these samples are also included. The INAA results agreed with the certified values for all the samples within experimental uncertainties, indicating that the contribution of the ^{56}Mn produced by fast neutrons was negligibly small in this irradiation condition. The contribution of the fast neutron induced reaction was estimated to be <1 ppb Mn in JSS001-4 and <5 ppb in JSS001-5 by subtracting the certified values from the INAA results.

The results from ICP-MS and ICP-AES were consistent with the certified values for JSS003-5 and JSS009-2, while for JSS001-4 and JSS001-5, which have only 0.03 ppm Mn, we could not obtain the results consistent with the certified values. The contamination in the chemical treatment seemed to affect the determination of trace amount of manganese.

Consequently, it was confirmed that the INAA using Tc-Pn can determine trace amount of manganese in high-purity iron samples more exactly and easily than the other methods. Therefore, the INAA using Tc-Pn was applied to the determination of manganese in the iron meteorite.

3.2. Cosmogenic ^{55}Mn in the Gibeon iron meteorite. The manganese contents in five fragments of the Gibeon iron meteorite determined by NAA are summarized in Table 2, which includes the results of some fragments leached once or twice after neutron irradiation. Cosmogenic ^{10}Be in these fragments measured by Honda et al.[3,4,6,13] are also indicated in Table 2. It is expected that the Gibeon fragments with lower ^{10}Be content tend to be less exposed by cosmic rays and to have lower cosmogenic ^{55}Mn. However, the Gibeon fragments with lower ^{10}Be do not always have lower manganese contents as indicated in Table 2. G. 003 with the lowest ^{10}Be has higher ^{55}Mn content than G. 102, while G. 99 with the highest ^{10}Be has lower ^{55}Mn than G. 003 and G. 105. The observed trend of manganese contents in these fragments can be probably explained by the inclusions contained in the Gibeon iron meteorite. It seems that the manganese content measured in each fragment is affected by relatively high contents of manganese in troilite.

Among three fragments leached after irradiation, only the manganese content of G. 003 was reduced by 30% after one-time leaching, indicating that the leaching removed troilite. Both G. 99 and G. 99* were cut off from different parts of the same fragment. The difference in manganese contents between two parts can also be explained by the troilite included heterogeneously in the fragment. For the determination of cosmogenic ^{55}Mn in the Gibeon fragments, it is required to remove inclusions completely.

4. Conclusion

Trace amount of manganese as an impurity in four kinds of high-purity iron samples was determined by three analytical methods. About 30 ppb Mn in the iron samples could be determined by INAA using Tc-Pn at KUR without correcting a contribution of the ^{56}Mn produced by the fast neutron-induced reaction. Neutron activation analysis using Tc-Pn was applied to the determination of ^{55}Mn in five fragments of the Gibeon iron meteorite. From the measurements for those fragments with surface-leaching, it was found that manganese derived from the troililte inclusions interfered in the estimation of cosmogenic ^{55}Mn in the Gibeon fragments. The complete removal of such inclusions will lead to estimation of cosmogenic ^{55}Mn in the Gibeon iron meteorite.

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