

Mössbauer Spectroscopic Characterization of Iron Species in the Test Samples of 4A and 4B for the Second HASPET Competition

By

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Abstract: It was revealed in the preset Mössbauer investigation that four iron-bearing minerals were contained in both the unknown samples named “4A” and “4B” for the second HASPET competition; they are olivine, pyroxene, kamacite and troilite. For purpose of the identification, Mössbauer spectra were measured for mineral samples being ensured to be what it is. It was concluded that the samples of 4A and 4B should be meteorite materials; the former be a stony meteorite while the latter be an iron meteorite from our ⁵⁷Fe-Mössbauer measurement and analysis.

1. INTRODUCTION

Iron is one of the most important elements from geochemical and cosmochemical viewpoints. It is well known that iron has various valence (oxidation) states from +1 to +6, leading to plenty of iron species in terrestrial or extraterrestrial materials (Greenwood and Earnshaw, 1984; Cox, 1995). What is the chemical states of iron in the materials? How about the proportion of each fraction of the iron species contained in the material? These two questions are expected to be key-factors to identify a geo- and/or cosmochemical sample because they should be related closely to the formation origin and weathering history of the sample. The mineralogical and geochemical applications of the ⁵⁷Fe-Mössbauer spectroscopy have developed for iron-bearing materials, possibly giving us information on the physical and chemical states of iron (Tominaga and Minai, 1984; McCammon, 1995; Constantinescu et al., 1997). A recent remarkable topic of the application was ⁵⁷Fe-Mössbauer exploration of the Mars with MINOS II by a collaboration of NASA and a German group (Klingelhofer, 2004). The Mössbauer hyperfine parameters provide information on the valence states, the symmetry of coordination, and the magnetic environments, which are obtained from three hyperfine parameters of isomer shift (IS), quadrupole splitting (QS), and internal magnetic field (H_f), respectively (Dickson and Berry, 1986; Murad and Cashion, 2004). In the case that there are existed several components of iron species, we can observe a spectrum as the superimposition of each component and obtain the relative abundances of the iron species by deconvolution. It should be emphasized that a ⁵⁷Fe-Mössbauer spectrum can be measured non-destructively under in-situ condition for a small amount of samples, approximately a few-tens milligram. If necessary, the samples used for Mössbauer measurements can be returned or reused for the other kinds of analysis after the investigation. From such advantages the spectroscopy could be greatly suitable to the analysis of rare and precious materials, for example, the samples to be returned from Itokawa by the Hayabusa mission in 2007. The test samples of 4A and 4B reached us on December 6, 2004. In the present article, the results of Mössbauer spectroscopic examinations for the two unknown samples distributed for the competition are reported. Some minerals and a standard reference material sample were also analyzed for comparison.

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2. EXPERIMENTAL

2.1. Sample materials

Each sample (about 100 mg) mailed to us on December of 2004 was inspected by eyes at first. Both the samples are dark-grey (nearly black). The sample 4A was seen as powder while the 4B was composed of small grains with the size of 0.2 to 1.0 mm. The powder of 4A was submitted to Mössbauer measurements without further treatment. Although the grains for the 4B sample were tried to be crashed and milled into fine powders using an agate mortar with a pestle, the milling was not effectively carried out due to the hardness of the grains, which allowed us to speculate that it contained metals, alloys, or metallic compounds as a major component. The sample weights and thicknesses for the measurements are summarized in Table 1. It had been suggested from the first series of the preliminary ^{57}Fe -Mössbauer measurements that the test samples contained some kinds of iron-bearing minerals, leading us to the measurements for some minerals and a chemical reagent as reference samples. Those minerals were obtained from Hori Mineralogy Co. as listed in Table 1. Commercially available iron(II) sulfide FeS was purchased from Kishida Chemical Co. A standard soil sample was also measured for semi-quantitative estimation of iron content of the test samples, which was issued as "JSAC 0411" by the Japan Society of Analytical Chemistry.

2.2. Mössbauer measurements and analysis

Mössbauer spectra were measured with Mössbauer spectrometers of Model MD-222B and Model MDF-500F fabricated by Topologic Systems, Inc. against a Mössbauer source of 370-MBq or 925-MBq ^{57}Co in Rh foil. Measurement temperatures were ranged from 80.0 to 293.0 K regulated by using an Oxford cryostat DN-1726 with a temperature controller ITC-601. Each spectrum was measured for the duration time of a few days. The curve fitting of spectra were performed by means of a non-linear least-square method, a commercially available Mössbauer analysis program named MossWinn 3.0i developed by Klencsar of University of Kaposvar, Hungary (Klencsar, 2005), with a personal computer, assuming that all the spectra were composed of Lorentzian-shaped absorption peaks. A Lorentzian peak, characteristic to absorption or emission of nuclear transition energy, has the following three quantities; the peak position, and intensity, and line-width. In the present fitting procedure, the isomer shift (IS), quadrupole splitting (QS), and internal magnetic field (H_f) could be calculated from the peak positions while the relative peak area was calculated using the peak intensity and the line-width. The IS values and Doppler velocity scale were calibrated with respect to the centroid of sextet of metallic iron (α -Fe) at room temperature.

Table 1. Samples submitted to ^{57}Fe -Mössbauer measurement.

Name	Sampling site	Weight mg	Thickness mg/cm ²
4A	unknown	27.9	63.1
4B	unknown	38.2	53.1
olivine/forsterite	Pakistan	10.9	23.6
pyroxene/augite	Czech	29.5	29.5
pyroxene/enstatite	Sli Lanca	7.1	15.1
pyroxene/enstatite	Tanzania	49.1	49.1
FeS(troilite)	chemical reagent ^{*1}	44.5	44.5
standard soil sample	JSAC 0411 ^{*2}	52.9	52.9

*1. Chemical reagent of iron(II) sulfide (FeS) was commercially available from Kishida Chem. Co. which contained troilite of about 40 wt%, estimated by our Mössbauer measurement.

*2. This standard sample was purchased from the Japan Society for Analytical Chemistry(JSAC), which had been prepared using volcanic ash soil sampled in Naruko-cho, Miyagi Prefecture. The content of iron reported by JSAC was 3.300 wt%.

3. RESULTS

^{57}Fe -Mössbauer spectra measured at the temperatures of 80.0, 150.0, 170.0, 220.0 and 293.0 K for the test samples of 4A and 4B were shown in Figs. 1 and 2, respectively. The spectra of 4A and 4B were successfully fitted by assuming that there were four and three components, respectively, as seen in the figures, the characterizations of which are described in the following discussion section (4-1). The obtained Mössbauer hyperfine parameters and the relative areas are summarized in Tables 2 and 3. The Mössbauer spectra and hyperfine parameters for the minerals are shown in Fig. 3 and Table 4. The temperature dependences of the Mössbauer parameters and the area of each component are illustrated for the samples of 4A and 4B in Figs. 4 to 7.

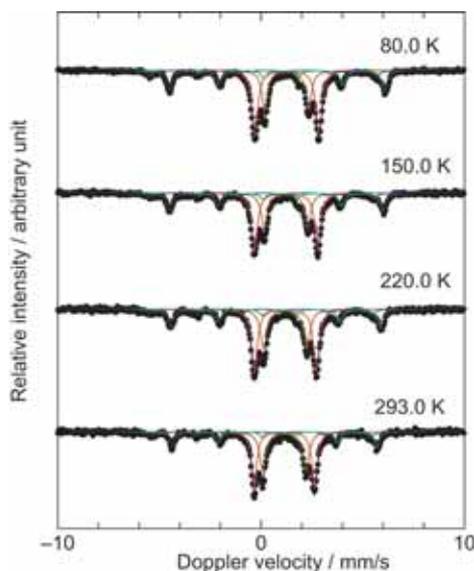


Figure 1. ^{57}Fe -Mössbauer spectra at 80.0, 150.0, 220.0, and 293.0 K for the test sample of 4A. Red curves set for a DB(O) (olivine) component, brown for a DB(I) (pyroxene), blue for a SX(H) (kamacite), and green for a SX(L) (troilite).

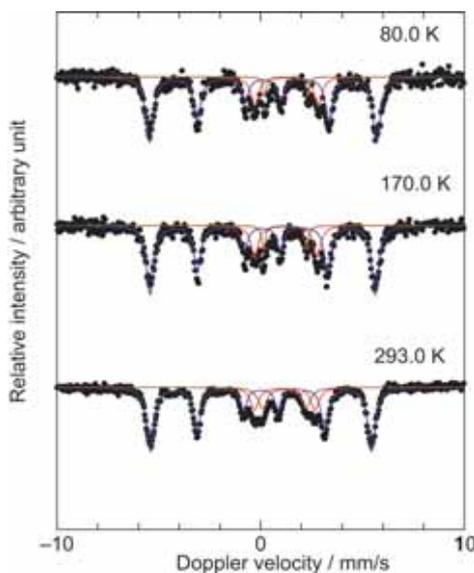


Figure 2. ^{57}Fe -Mössbauer spectra at 80.0, 170.0, and 293.0 K for the test sample of 4B. Red curves set for a DB(O) (olivine) component, brown for a DB(I) (pyroxene), and blue for a SX(H) (kamacite).

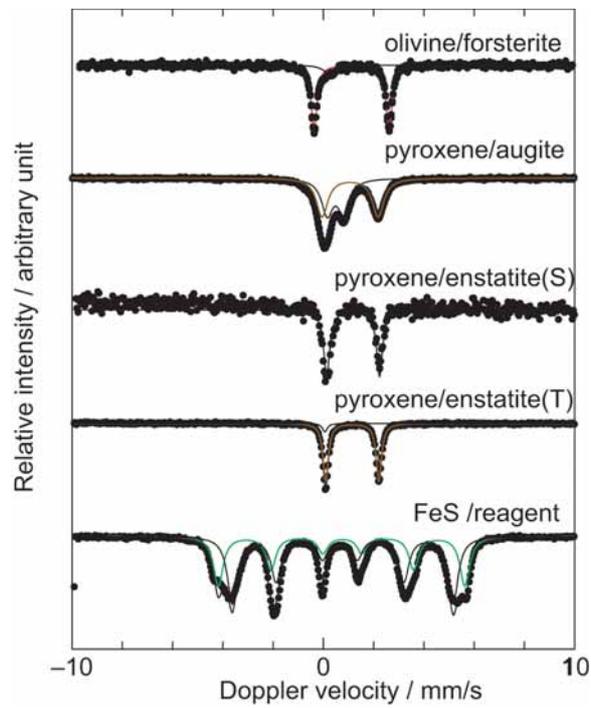


Figure 3. ^{57}Fe -Mössbauer spectra at 293.0 K for mineral samples and FeS reagent: Red curves set for a DB(O) (olivine) component, brown for a DB(I) (pyroxene), and green for a SX(L) (troilite)

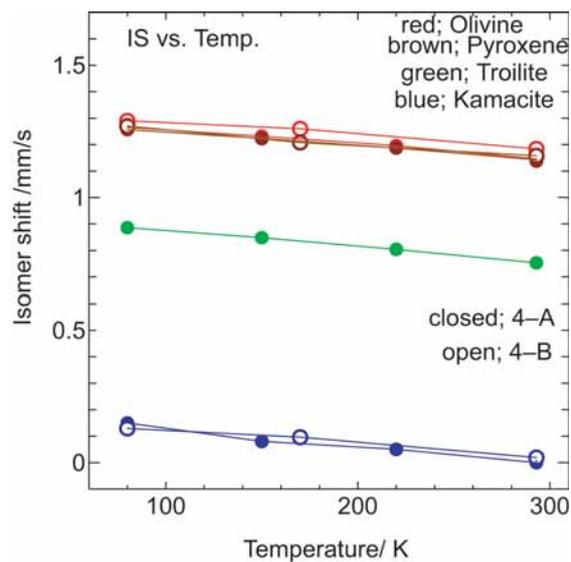


Figure 4. Temperature-dependence of isomer shifts of olivine, pyroxene, kamacite, and troilite in the test samples 4A and 4B.

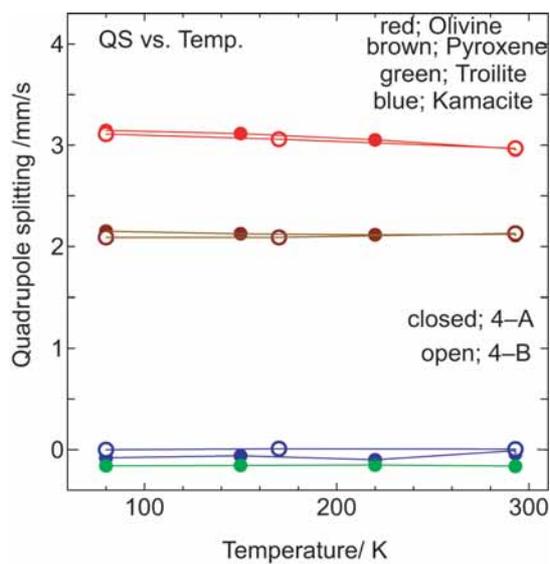


Figure 5. Temperature-dependence of quadrupole splittings of olivine, pyroxene, kamacite, and troilite in the test samples 4A and 4B.

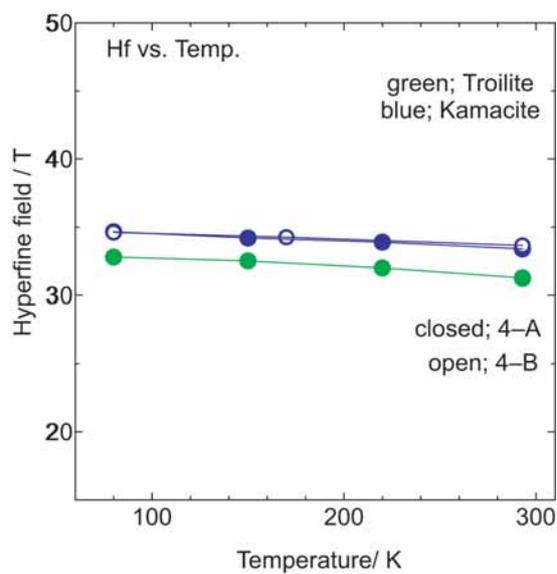


Figure 6. Temperature-dependence of hyperfine fields of kamacite and troilite in the test samples 4A and 4B.

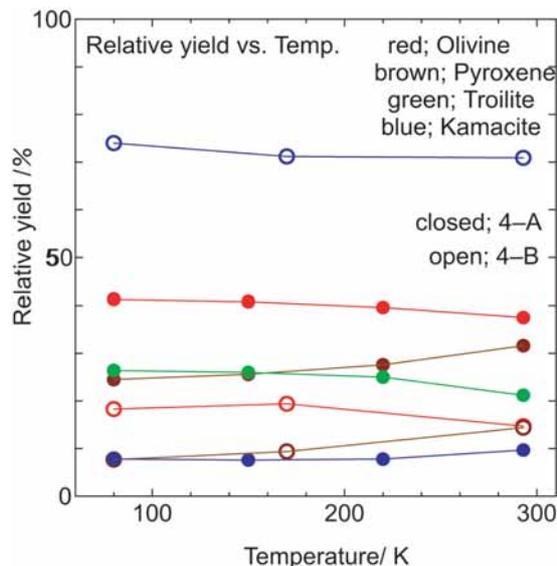


Figure 7. Temperature-dependence of relative yields of olivine, pyroxene, kamacite, and troilite in the test samples 4A and 4B.

4. DISCUSSION

4.1. Assignments of the iron-bearing components for the test samples of 4A and 4B

As shown in Figs. 2 and 3, our Mössbauer analysis revealed the following points:

1. The 4A sample should contain four iron species, corresponding to two doublets and two sextets in the Mössbauer spectra, which are denoted as DB(O), DB(I), SX(H), and SX(L) in the present report.
2. The 4B sample should contain three iron species. The three species are correspondent to two doublets and one sextet in the spectra. The parameters of the two doublets are found to be fairly agreed with those of DB(O) and DB(I) in the sample 4A. The sextet parameter of the 4B sample is greatly close to that of SX(H) in the 4A.
3. Therefore, it is just 4 iron species that we have to reveal what it is in both the samples of 4A and 4B; i.e., DB(O), DB(I), SX(H), and SX(L).
4. The abbreviations of DB(O), DB(I), SX(H), and SX(L) made tentatively here mean “outer doublet”, “inner doublet”, “sextet with a higher H_f ”, and “sextet with a lower H_f ”, respectively.

The Mössbauer parameters of IS and QS for DB(O) and DB(I) are close to those for olivine and pyroxene, respectively, reported previously (Akasaka and Shinno, 1992; McCammon, 1995; Calogero et al., 1999). The results of our measurements of several minerals gave confirmative assignments. Both the IS and QS values obtained for DB(O) of the test samples of 4A and 4B are found to agree to those of forsterite, a kind of olivine, as shown in Table 4. As to DB(I), comparison of the parameters of IS and QS for the test samples (Tables 1 and 2) and the minerals (Table 3) leads us to an important finding of much more excellent assignment with those for orthopyroxene than clinopyroxene.

The IS and QS parameters, being nearly zero, of SX(H) observed here could ascribe it to metallic iron or iron-bearing alloy such as Fe-Ni, kamacite according to the literatures (McCammon, 1995; Calogero et al., 1999). We know that there can be taenite as another Fe-Ni alloy mineral. However, the hyperfine magnetic field H_f of 33-34 T at 293.0 K in our measurement was agreement with one for kamacite (33.8 T) but not with one for taenite (28.9 T) (McCammon, 1995). The iron species corresponding to SX(L) might be resumed to be troilite in a similar way. The IS and H_f values obtained here were found to be very close to those of troilite in literatures. These values were also agreed with those for FeS in this study. The QS parameter was also observed to be in a relative wide range (-0.8 to 0.15 mm/s) of troilite reported previously. Our assignments are summarized in Table 5.

Table 2. Mössbauer parameters obtained for the test sample 4A.

mm/s	IS*	QS	H _f	Γ	A
mm/s	mm/s	mm/s	T	mm/s	%
80.0 K					
DB(O)/olivine	1.265 (1)	3.147 (2)		0.346 (3)	41.3
DB(I)/pyroxene	1.257 (2)	2.151 (3)		0.346 (5)	24.5
SX(H)/kamacite	0.15 (1)	-0.08 (2)	34.66 (7)	0.41 (3)	7.8
SX(L)/troilite	0.886 (2)	-0.160 (5)	32.80 (2)	0.337 (7)	26.4
150.0 K					
DB(O)/olivine	1.232 (1)	3.115 (3)		0.344 (5)	40.8
DB(I)/pyroxene	1.223 (2)	2.126 (5)		0.365 (8)	25.6
SX(H)/kamacite	0.08 (2)	-0.06(3)	34.2 (1)	0.45 (6)	7.6
SX(L)/troilite	0.848 (4)	-0.156 (7)	32.52 (2)	0.34 (1)	26.0
220.0 K					
DB(O)/olivine	1.196 (1)	3.053 (3)		0.342 (5)	39.6
DB(I)/pyroxene	1.187 (2)	2.116 (6)		0.380 (9)	27.6
SX(H)/kamacite	0.05 (2)	-0.10 (3)	33.9 (1)	0.42 (6)	7.8
SX(L)/troilite	0.804 (4)	-0.152 (8)	32.00 (3)	0.36 (1)	25.0
293.0 K					
DB(O)/olivine	1.146 (1)	2.963 (4)		0.307 (6)	37.5
DB(I)/pyroxene	1.143 (2)	2.121 (6)		0.37 (1)	31.6
SX(H)/kamacite	0.000 (1)	-0.01 (2)	33.4 (1)	0.47 (6)	9.7
SX(L)/troilite	0.753 (5)	-0.162 (9)	31.27 (3)	0.30 (1)	21.2

*Relative to α -iron.**Table 3.** Mössbauer parameters obtained for the test sample 4B.

mm/s	IS*	QS	H _f	Γ	A
mm/s	mm/s	mm/s	T	mm/s	%
80.0 K					
DB(O)/olivine	1.29 (1)	3.11 (3)		0.48 (5)	18.3
DB(I)/pyroxene	1.27 (1)	2.09 (2)		0.25 (4)	7.7
SX(H)/kamacite	0.129 (4)	0.00 (1)	34.61 (3)	0.44 (1)	74.0
170.0 K					
DB(O)/olivine	1.26 (1)	3.06 (2)		0.49 (5)	19.4
DB(I)/pyroxene	1.208 (9)	2.09 (2)		0.28 (4)	9.4
SX(H)/kamacite	0.096 (3)	0.009 (7)	34.26 (3)	0.41 (1)	71.2
293.0 K					
DB(O)/olivine	1.184 (8)	2.97 (3)		0.51 (4)	14.7
DB(I)/pyroxene	1.158 (8)	2.13 (3)		0.53 (4)	14.4
SX(H)/kamacite	0.019 (2)	0.005 (5)	33.65 (1)	0.433 (6)	70.9

*Relative to α -iron.**Table 4.** Mössbauer parameters obtained at 293 K for minerals.

mm/s	IS*	QS	Γ	A
mm/s	mm/s	mm/s	mm/s	%
olivine from Pakistan				
doublet	1.125 (1)	2.989 (2)	0.273 (3)	89.0
singlet	0.20 (2)		0.60(5)	11.0
pyroxene from Czech				
outer doublet	1.064 (2)	2.231 (4)	0.551 (5)	52.7
inner doublet	0.484 (2)	0.663 (4)	0.547 (7)	47.3
pyroxene from Sri Lanca				
doublet	1.185 (4)	2.103 (8)	0.29 (1)	100
pyroxene from Tanzania				
doublet	1.151 (2)	2.115 (4)	0.253 (2)	93.6
singlet	0.06 (2)		0.24 (3)	6.4

*Relative to α -iron.

Table 5. Assignments of iron species observed in the Mössbauer spectra at 293 K for the 4A and 4B test samples.

mm/s*	IS* mm/s	QS T	H _f	Mineral	Chemical formulae
DB(O)	1.146(1) 1.184(8)	2.963(9) 2.97(3)		olivine	(Mg,Fe) ₂ Si ₄
DB(I)	1.143(2) 1.158(8)	2.121(6) 2.13(3)		pyroxene	(Mg,Fe) ₂ Si ₂ O ₆
SX(H)	0.000(1) 0.019(2)	-0.01(2) 0.005(5)	33.4(1) 33.65(1)	kamacite	FeNi
SX(L)	0.753(5)	-0.162(9)	31.27(3)	troilite	FeS

*Relative to α -iron.

The first line sets for the test sample of 4A, and the second one for the 4B. The component of SX(L) was observed for the 4A, not in the 4B. According to the literatures (McCammion, 1995; Calogero et al., 1999), the Mössbauer parameters were reported as follows;

For olivine, IS are in the range from 1.14 to 1.16 mm/s, QS; 2.94 to 2.99 mm/s.

For pyroxene, IS; 1.13 to 1.16 mm/s, QS; 2.09 to 2.10 mm/s.

For kamacite, IS; about 0 mm/s, QS; about 0 mm/s; H_f; 33.4 to 34.0 T.

For troilite, IS; 0.75 to 0.81 mm/s, QS; -0.8 to 0.15 mm/s (wide range !); H_f; 31.3 to 31.6 T.

The parameters for olivine and pyroxene were obtained in the present work, showing a good agreement with those cited above (see Table 4).

4.2. Identification of the test samples 4A and 4B

Four minerals of olivine, pyroxene, kamacite, and troilite found in the test samples are popular as iron-bearing components of meteorite samples (Calogero et al., 1999). When measuring a Mössbauer spectrum of the sample of 4A at the first stage of this work, we noticed that the overall absorption profile is closely resemble to those reported for meteorites (Endo et al., 1994; Bland et al., 1998). After our further measurements and comparison with reported data, it was revealed that the 4A sample showed the similar spectral feature not only in the line shapes but also in the peak positions. Tables 1 and 2 and Fig. 7 show that the major components for the sample 4A are iron-bearing silicate minerals of olivine and pyroxene, and that the main component for the sample 4B is Fe-Ni alloy of kamacite. It was concluded at the final stage of the present HASPET work that the test samples of 4A and 4B can be ascribed to some kinds of meteorite. Perhaps, the 4A sample would be a stony meteorite containing iron-bearing silicates as major components while the 4B sample would be an iron meteorite made mainly from metallic iron and/or alloy such as Fe-Ni. The Mössbauer spectra of the 4A sample was resemble to those for the Antarctica meteorites reported by Endo et al. (1994) as described above. However, there has been recognized to be a different feature in the spectra between the previous results and ours. It was proved that the meteorites contained Fe³⁺ species with a substantial yield of a few-tens percentage while no or negligible amounts of ferric component was found in our Mössbauer spectrum of the 4A sample. This implies that the 4A, if it is a meteorite sample, might relatively be fresh and/or not be oxidized (or weathered) before and after the falling.

4.3. Temperature dependence of Mössbauer spectra fro the test samples of 4A and 4B

The spectral line-shape was not dependent on temperature as seen in Figs. 1 and 2. Temperature dependences of the Mössbauer parameters are summarized in Tables 1 and 2, and also illustrated in Figs. 4 to 7. Slight decrease of IS on temperature, observed for each component in Fig. 4, are due to the second-order Doppler shift effect. There was found a little decrease of H_f with increasing temperature in kamacite and troilite in Fig. 6. This might be caused by magnetic-moment fluctuation due to thermal agitation. No or little change in the Mössbauer line-shape with temperature suggested the particles of kamacite or troilite should be not enough fine so that they could show super-paramagnetic character. The mean of the particle sizes would be approximately more than several-tens nanometer.

4.4. Semi-quantitative estimation of iron content in the sample of 4A from the Mössbauer measurements

It is sometimes difficult to determine quantitatively the iron content in a material by Mössbauer spectroscopy. The peak

area, of course, reflects the amount of an iron species existing in the sample, but not proportional exactly to the amount because of the difference in the recoilless fractions, that is, the absorption intensities per iron atom, of various iron species. We dared to determine the iron content of the 4A sample by comparing the total absorption area with that of the standard sample (JSAC-0411, issued by the Japan Society of Analytical Chemistry) containing a known amount of iron (3.300 wt%), giving an iron content of ca. 15 wt%.

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