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Fe-Bearing Phases in Antarctic Carbonaceous Chondrites Yamato-82162 and Yamato-86720: a Mössbauer study

by

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In this paper we report on variable temperature Mössbauer spectroscopy measurements on samples of carbonaceous chondrites Yamato 82162 and Yamato 86720. Transmission Mössbauer spectra were taken through the temperature range 4.2 K to 300 K. The Mössbauer spectra at room temperature indicate in both meteorites the presence of a magnetically splitted component and two quadrupole doublets corresponding to paramagnetic Fe^{2+} and Fe^{3+} compounds.

Key-words: Antarctic meteorites; Carbonaceous chondrites; Mössbauer spectroscopy.

I - INTRODUCTION

The carbonaceous chondrites of type CI have elemental abundance close to those of the solar atmosphere (apart from highly volatile elements like H and noble gases), and are therefore regarded as the most primitive solar system material available for study. The major fraction of these meteorites consists of extremely fine (< 1 μm) grains of a variety of Fe-bearing phases such as Fe-rich phyllosilicates, ferrihydrite, magnetite, Fe-Ni metal, troilite, pyrrhotite, Fe-rich olivine and Fe-Mg carbonate. The occurrence and relative abundance of these phases serve as important indicators to decipher the physical-chemical conditions in which these primitive meteorites were formed.

The carbonaceous chondrites Yamato-82162 (Y-82162) and Yamato-86720 (Y-86720) were recovered from the bare ice fields of the Yamato mountains, in Antarctica, by the Japanese Antarctic Research Expedition in 1982 and 1986 respectively [1]. The oxygen isotopic characteristics of these meteorites are CI-like [2], but the details of mineralogy and chemistry are different from those of ordinary CI or CM chondrites [3,4,5], suggesting that these meteorites experienced unique formation history compared to other CI and CM chondrites.

In this paper we present the results of our ^{57}Fe Mössbauer spectroscopy measurements of Y-82162 and Y-86720. This technique is useful especially to identify Fe-bearing compounds and to estimate their relative abundance in bulk samples regardless of their grain size. It can be also useful to study local atomic environments around Fe atoms, which can be correlated with thermal metamorphic process of the meteorites. Our primary purposes of these measurements are to identify fine-grained Fe compounds and to know relative abundance of Fe compounds in these meteorites. Thereby, we will compare the Mössbauer spectroscopy data with the results obtained by mineralogical and petrographical studies and will infer the formation history of these meteorites.

II - PREVIOUS STUDIES ON MINERALOGY AND PETROLOGY

1 - Yamato-82162

Y-82162 consists largely of fine-grained, Mg-Fe phyllosilicate-rich matrix and lesser amounts of Ni-bearing Fe-sulfides, magnetite, Mg-Fe-rich carbonates, and Ca-phosphates [3,6]. Magnetite commonly occurs in characteristic framboidal, platy, and spheroidal morphologies. The presence of these minerals is consistent with Y-82162 being CI type. However, this chondrite shows several mineralogical features that apparently differ from non-Antarctic CI chondrites as follows: a) it has much higher abundance of coarse phylosilicates and Fe-sulfides than non-Antarctic CI chondrites, and b) it has no veins of sulfates and carbonates. These features suggest that it has been derived from different primary materials and has experienced a different aqueous alteration history from non-Antarctic CI chondrites.

Transmission electron microscope (TEM) studies reveal that the Y-82162 matrix contains abundant fine grains of olivine in addition to phyllosilicates [3,7]. The abundance of olivine contrasts with non-Antarctic CI chondrites which contain virtually no anhydrous silicates. The observed micro textures suggest that the matrix phyllosilicates, which contain hydroxyl or water in their structures, were dehydrated and altered to olivine by heating. Therefore, this meteorite probably has been affected by mild thermal metamorphism. These results indicate that Y-82162 has experienced a distinct late history from the non-Antarctic CI chondrites.

2 - Yamato-86720

The petrographic, scanning electron microscope (SEM) and TEM studies of Y-86720 [4,6,7] indicate that it is petrographically closer to CM than to CI chondrites. However it shows many mineralogical and chemical features distinct from the known CM chondrites. Y-86720 has a very high abundance of Fe-sulfides, which are mostly troilite, but some are slightly metal deficient and thus may be pyrrhotite. Ca-Mg carbonates and Fe-Ni metal are present in minor amounts, but magnetite is absent. The chondrules and aggregates were completely replaced by optically translucent materials presumably phyllosilicates, suggesting that this meteorite has experienced extensive aqueous alteration. The matrix consists largely of fine grains of Mg-Fe olivine, a nearly amorphous Si-Mg-Fe-rich material, and an Fe-rich material; the latter may be ferrihydrite. The textures suggest that the olivine and the Si-Mg-Fe rich material were produced by alteration of phyllosilicates by heating. The mineralogical comparison shows that the degree of thermal metamorphism is higher in Y-86720 than in Y-82162 [4,6].

III - EXPERIMENTAL

The samples of the meteorites were ground into a powder and Mössbauer absorbers were prepared in a Plexiglas sample holder. Transmission Mössbauer spectra were taken using a ^{57}Co/Rh source through the temperature range 4.2 K< T < 300 K. These measurements were made with source and absorber at the same temperature. Calibration was done from a α-Fe spectrum. In this work all the isomer shifts are given relative to metallic iron.

IV - RESULTS

1 - Yamato-82162

Figure 1 shows the Mössbauer spectra (MS) of Y-82162 from room temperature (RT) down to liquid He temperature (4.2 K). The spectrum at RT indicates mainly the presence of a magnetically splitted component, due to iron in sulfides and two quadrupole doublets attributed to paramagnetic Fe^{2+} and Fe^{3+} compounds. In addition , we found a second magnetic sextet in a very low proportion (5%).

At low temperatures, in the range between 40 K and 13 K, the fitting of all spectra shows a very well behavior of the Mössbauer parameters for all phases already identified in the RT spectrum, as can be seen in Table I.

At 4.2 K a drastic transition is observed, and the best fitting was obtained considering the presence of the phases previously identified and a large contribution from paramagnetic phases. This contribution is taken into account in terms of a doublet with a line width of Γ=1.45 mm/s, which is obviously due to the contribution of several paramagnetic modified phases which can only be resolved at 4.2 K.

It is interesting to observe in Table I, that below 25 K a line broadening occurs for the paramagnetic components. For Fe^{3+} the line width is constant (Γ= 0.50 mm/s) up to 25 K, increasing to Γ= 0.72 mm/s at 13 K but going back to Γ=0.54 mm/s at 4.2 K. A similar behavior is seen for the Fe^{2+} component. The linewidth remains constant (Γ= 0.59 mm/s in average) up to 25 K and increases to 0.82 mm/s at 13 K. At 4.2 K the Fe^{2+} contribution splits into two components. One with a small line width and a small relative proportion and the other is a very broad doublet (Γ=1.45 mm/s) which accounts for all contributions from Fe^{2+} compounds seen only at that temperature. The magnetic component shows very similar Mössbauer parameters in all the temperature ranges.

2 - Yamato-86720

The results obtained for Y-86720 can be seen in figure 2 and Table II. The fitting of the spectra from RT up to 25 K is similar to that of Y-82162. They show the same contributions from a magnetic phase and from Fe^{2+} and Fe^{3+} paramagnetic compounds.

In contrast to the narrow line width found for the Y-82162 RT spectrum, that of Y-86720 shows very broad lines for the paramagnetic as well as for the magnetic phases. Below RT up to 25 K a decrease of all line widths is observed followed by a continuous increase up to 4.2 K. A second magnetic phase with an internal magnetic field of 250 kOe appears at 4.2 K, in a small proportion (8%). From the relative spectral areas (see Table II) we can interpret that this phase results from the contribution of an Fe^{2+} compound previously unidentified [8], that will be discussed below.

We have to emphasize the behavior of the line width of the magnetic component with temperature. The lines are very broadened up to 7 K, becoming very sharp at 4.2 K ($\Gamma = 0.42$ mm/s). In addition, a large broadening of the Fe^{2+} paramagnetic compounds is observed which is similar to that of Y-82162.

V - DISCUSSION

The Mössbauer spectroscopy measurements indicate the presence of a very well resolved magnetic phase in both meteorites; the magnetic signature can be ascribed to Fe in troilite, thus being consistent with that troilite is abundant in both meteorites. The relative proportion of the magnetic phase remains almost constant with temperature, and the apparent increase of the outer lines of the spectra (see figs. 1 and 2) can be explained by the increase of the line width due to a paramagnetic component. The Mössbauer parameters at RT for the paramagnetic component in both meteorites are in accordance with Fe^{2+} in olivine [9]. However in the case of Y-86720, even at RT, we observed a much broader line, which indicates a significant amount of some other compound or compounds besides olivine, which are discussed below.

The Fe^{3+} doublet observed at RT in the spectrum of Y-86720 can be attributed to a superparamagnetic component, probably ferryhidrite [3,7]. However the Fe^{3+} doublet in Y-82162 can not be ascribed to such a superparamagnetic component but probably to an overlap of a different compound or compounds such as Fe and Mg carbonates and magnetite [3].

We found in the spectra of both meteorites a small amount of a magnetic component with a hyperfine field of 250 kOe. This magnetic component was observed at RT in the spectrum of the Y-82162 sample, while in that of the Y-86720 it was only seen at 4.2 K. From that result we conclude that the corresponding compound, whatever it is, is present in Y-86720 as small particles, being responsible for the superparamagnetic signature. Identification of this component in such complex spectra is not easy; however, although definite identification can not be performed only based on the Mössbauer results, we suggest some possibilities vis-a-vis the mineralogical studies [3,4], as follows: a) this component can be related to Fe-rich superparamagnetic clusters in olivine. Clustering of Fe ions has been previously observed in lunar [10], terrestrial and synthetic olivines [11]. These previous studies showed clear evidence of superparamagnetic relaxation effects arising from clusters of Fe ions and also an influence of thermal history on the cluster size distribution; b) it can be correlated with non-stoichiometric slightly metal deficient pyrrhotite; c) it can also be related to Cu-Fe sulfide. The occurrence of cubanite ($Cu_2Fe_3S_5$) was reported to occur in non-Antarctic CI chondrites [12]. However the Mössbauer hyperfine parameters obtained for this component do not correspond to such a Cu-Fe sulfide but are more close to chalcopyrite or to an intermediate compound between chalcopyrite and cubanite.

The line widths of the magnetic and paramagnetic Fe components in the Y-82162 spectrum are less broadened than those in the Y-86720 spectrum (Tables I and II). This difference in line broadening may reflect a more homogeneous Fe distribution for Y-82162 than for Y-86720, which is consistent with a less metamorphosed material in Y-82162 than in Y-86720. The Mössbauer measurements also indicate that the amount of olivine in Y-82162 is almost half of that in Y-86720, which is also in good agreement with that Y-82162 was less metamorphosed (phyllosilicates were less transformed to olivine) than Y-86720.

The fact that ferryhidrite was not detected in our spectra for Y-82162 may be explained by the lack of the late aqueous alteration in this meteorite as suggested by Tomeoka et al. [4]. In the case of Y-86720, however, the Mössbauer measurements show the presence of an Fe^{3+} doublet that can be attributed to ferryhidrite. If that is the case, the presence of ferryhidrite in Y-86720 appears to be inconsistent with that Y-86720 has experienced more intense thermal metamorphism than Y-82162, because ferrihydrite dehydrates readily to hematite or goethite at temperatures below 100 C [13,14]. Therefore ferrihydrite, if any, was probably formed after thermal metamorphism was completed. However, whether the ferrihydrite was formed before or after the meteorite fell on the earth remains uncertain.

In conclusion, the present Mössbauer spectroscopy measurements clearly show that a variety of Fe compounds are present in Y-82162 and Y-86720. Both chondrites contain large amounts of troilite and olivine as major Fe carriers. Y-82162 contains no superparamagnetic phase such as ferrihydrite, while Y-86720 contains a significant amount of such phase. Both meteorites contains a previously unidentified magnetic component having a hyperfine field of 250 kOe. The major Fe compounds are mostly consistent with those identified by the mineralogical studies. Our measurements also support the view that these chondrites were affected by thermal metamorphism, and that Y-82162 was less metamorphosed than Y-86720.

Acknowledgments

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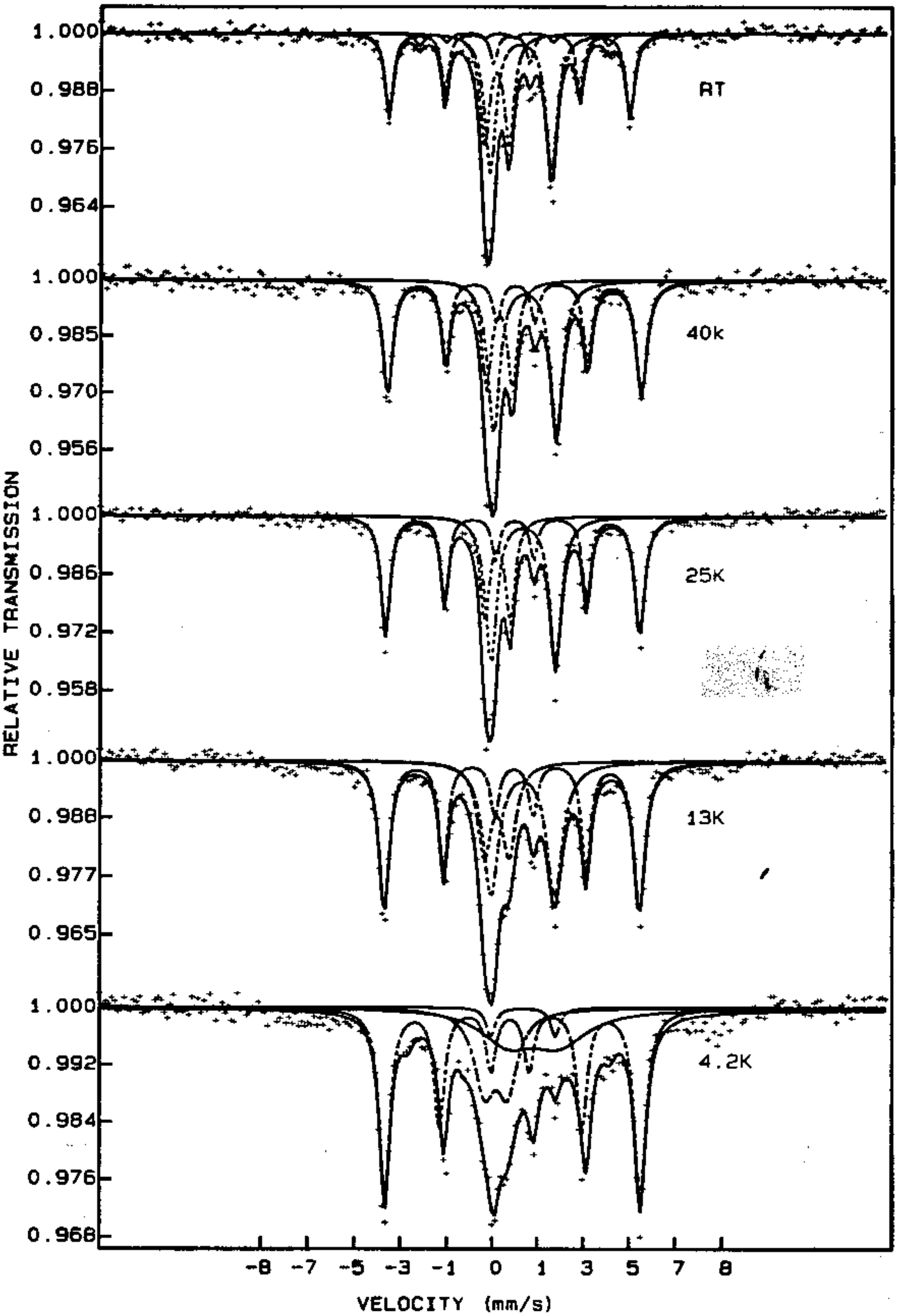
FIGURE CAPTION

Figure 1 - Mössbauer spectra for the Yamato 82162 meteorite at various temperatures.

Figure 2 - Mössbauer spectra for the Yamato 86720 meteorite at various temperatures.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0.976
0.964
RT
1.000
0.985
0.970
0.956
40k
1.000
0.986
0.972
0.958
25K
1.000
0.988
0.977
0.965
13K
1.000
0.992
0.984
0.976
0.968
4.2K
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-7
-5
-3
-1
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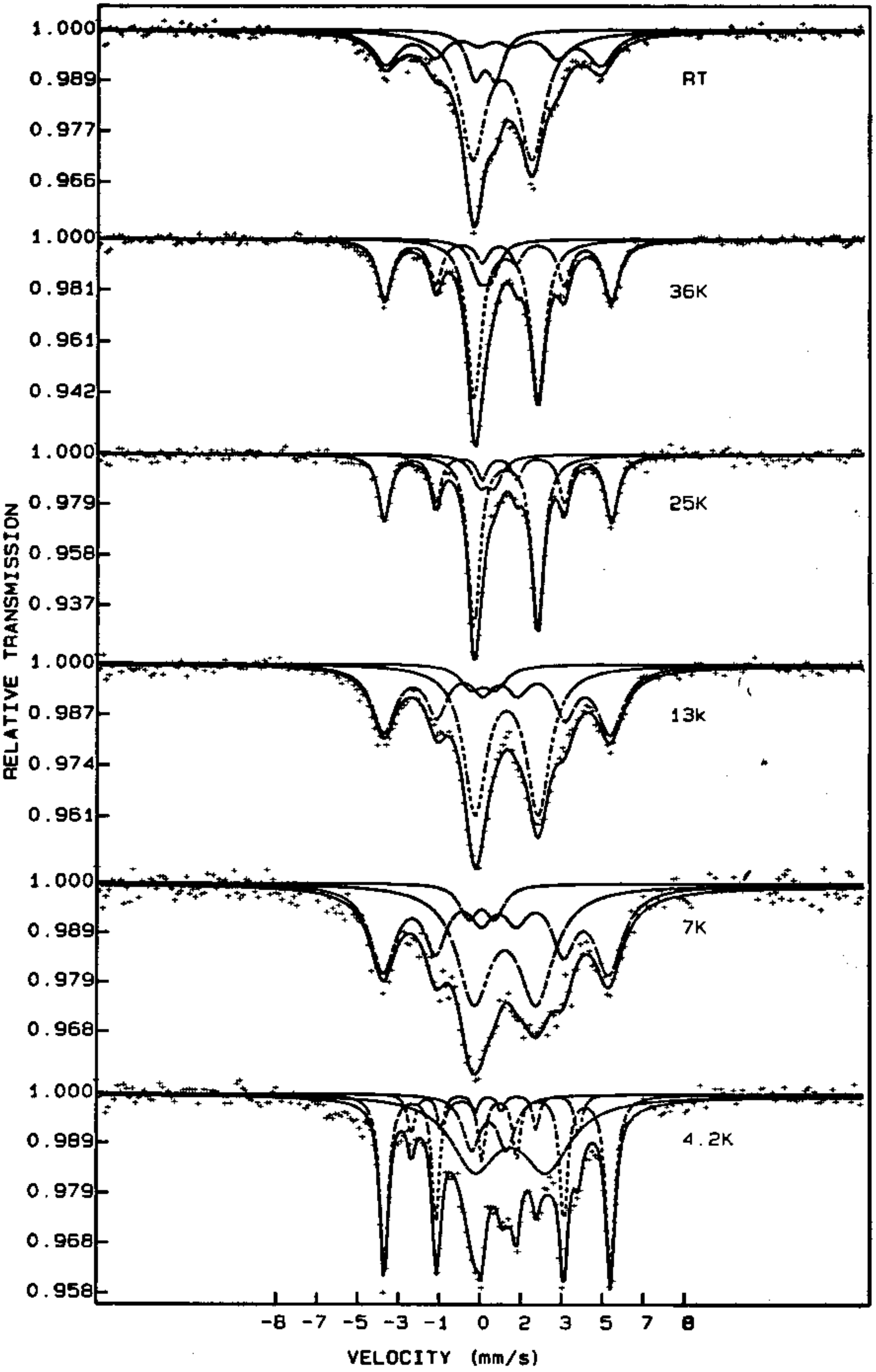
1
3
5
7
8
VELOCITY (mm/s)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0.977
0.966
RT
1.000
0.981
0.961
0.942
36K
1.000
0.979
0.958
0.937
25K
1.000
0.987
0.974
0.961
13k
1.000
0.989
0.979
0.968
7K
1.000
0.989
0.979
0.968
0.958
4.2K
RELATIVE TRANSMISSION
-8 -7 -5 -3 -1 0 2 3 5 7 8
VELOCITY (mm/s)

Temp. (K)		Γ(mm/s) ($\pm$0.02)	IS(mm/s) ($\pm$0.02)	Δ(mm/s) ($\pm$0.02)	HF(KOe) ($\pm$3.0)	Area(%)
RT	Fe^{3+}	0.50	0.17	1.07		26.1
	Fe^{2+}	0.57	1.21	2.68		38.1
	Troilite	0.35	0.73	-0.17	313.1	30.8
		0.35	0.59	0.55	249.7	5.0
40K	Fe^{3+}	0.51	0.26	1.14		21.1
	Fe^{2+}	0.61	1.37	2.74		37.1
	Troilite	0.42	0.89	-0.17	328.1	41.8
25K	Fe^{3+}	0.49	0.23	1.12		21.3
	Fe^{2+}	0.59	1.35	2.81		36.4
	Troilite	0.39	0.88	-0.20	328.7	42.3
13K	Fe^{3+}	0.72	0.22	1.09		20.3
	Fe^{2+}	0.82	1.36	2.78		34.0
	Troilite	0.45	0.89	-0.20	329.9	45.7
4.2K	Fe^{3+}	0.54	0.18	1.06		27.7
	Fe^{2+}	0.23	1.35	2.81		4.5
	Fe^{2+}	1.45	1.81	2.23		31.5
	Troilite	0.25	0.88	-0.17	329.2	31.8
		0.30	0.97	0.59	265.4	4.5

Table I - Mössbauer parameters for the Y-82162 meteorite at various temperatures. Γ is the linewidth at half height, IS is the isomer shift relative to α-Fe, Δ is the quadrupole splitting, HF is the internal hyperfine magnetic field, and Area is the relative spectral area. The line intensity ratios I_2/I_1 and I_3/I_1 were fixed to 0.66 and 0.33, respectively, during the fitting.

Temp. (K)		Γ(mm/s) (±0.02)	IS(mm/s) (±0.02)	Δ(mm/s) (±0.02)	HF(KOe) (±3.0)	Area(%)
RT	Fe^{3+}	0.93	0.29	1.01		13.2
	Fe^{2+}	1.45	1.12	2.86		57.2
	Troilite	1.25	0.71	-0.18	315.3	29.6
36K	Fe^{3+}	0.91	0.23	0.60		12.0
	Fe^{2+}	0.82	1.25	3.09		51.3
	Troilite	0.69	0.84	-0.16	331.5	36.7
25K	Fe^{3+}	0.87	0.34	0.73		10.8
	Fe^{2+}	0.68	1.25	3.08		52.4
	Troilite	0.57	0.86	-0.17	332.5	36.8
13K	Fe^{3+}	1.25	0.16	1.20		7.0
	Fe_2^+	1.33	1.29	3.05		49.7
	Troilite	1.15	0.86	-0.25	331.3	43.3
7K	Fe^{3+}	1.05	0.16	1.28		6.8
	Fe^{2+}	1.97	1.29	3.02		45.1
	Troilite	1.27	0.87	-0.23	330.5	48.1
4.2K	Fe^{3+}	1.02	0.46	1.70		12.2
	Fe^{2+}	2.76	1.49	3.49		43.2
	Troilite	0.42	0.86	-0.18	331.3	36.4
		0.35	0.56	0.28	248.7	8.2

Table II - Mössbauer parameters for the Y-86720 meteorite at various temperatures. Γ is the linewidth at half height, IS is the isomer shift relative to α-Fe, Δ is the quadrupole splitting, HF is the internal hyperfine magnetic field, and Area is the relative spectral area. The line intensity ratios I_2/I_1 and I_3/I_1 were fixed to 0.66 and 0.33, respectively, during the fitting.

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