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Precise Determination of the Mn-53/Mn-55 Isotopic Ratio in the ALH77250 Iron Meteorite

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Abstract The natural radiogenic nuclide ^{53}Mn is found in iron meteorites. In order to determine the half life of ^{53}Mn, the ^{53}Mn/^{55}Mn isotopic ratios in the ALH77250, which has high ^{53}Mn concentration, were measured precisely by the thermal ionization mass spectrometer. The average of the isotopic ratios, when the measured ion currents of ^{55}Mn were greater than 1×10^{-12} A and the interference of ^{53}Cr to ^{53}Mn was less than 10%, was $(5.977\pm0.032)\times10^{-5}$ $(2\sigma_m)$. With combination of the X-ray measurements of ^{53}Mn, a new precise half life will be determined.

Key words: Mn-53, ALH77250, iron meteorite, isotopic ratio, half life

1. Introduction

Manganese-53 is one of the most useful natural radioactive nuclide for meteorite chronology. It is mainly produced in iron meteorites by cosmic rays with the reactions of ^{56}Fe(n, p3n), ^{54}Fe(n, 2n), or ^{56}Fe(p, a) (Honda *et al.*; 1961, Millard, 1965; Imamura *et al.*, 1969), and called as a cosmogenic nuclide (e.g. Yabuki and Shima, 1989; Nishiizumi, 1987). But it is also known as one of extinct nuclides, which are once existed in the early solar system but already decayed due to short half lives compared with the age of the solar system (4.56×10^9 yr). The decay daughter isotope ^{53}Cr is detected in the calcium, aluminum-rich inclusions in many carbonaceous chondrites and other meteorites, and it is used for formation age determination and decipher early history of the solar system (e.g. Birck and Allegre, 1988; Lugmair and Shukolyukov 1998). However, current value of the half life of ^{53}Mn (3.7×10^6 yr) is determined in 1971 (Honda and Imamura, 1971) and even the latest report is in 1972 (Wölfle *et al.*, 1972). Thus we re-evaluate the half life of ^{53}Mn and started to determine a new precise value. Here we report the measurements of the ^{53}Mn/^{55}Mn isotopic ratios which are of the order of 10^{-5} within 1% error, which is an important part to determine the half life.

2. Experiments

2.1 Sample Solutions

The Mn standard solution (Johnson-Matthey) was used for checking of the ^{55}Mn ion beam at mass spectrometry. The method of the extraction of Mn from iron meteorites will be reported elsewhere and thus described here briefly. First, iron meteorites were dissolved in 1 : 2 HNO_3. Then, the solutions were dried up and converted to 7 M HCl solutions. With diisopropyl ether, Fe was extracted out. From the aqueous fraction, Mn was separated using anion and then cation exchange columns. The extracted Mn solutions were purified several times by the modified method of Honda and Imamura (1971). The method was tested by the Canyon Diablo iron meteorite and then applied to the ALH77250 iron meteorite, which has high concentration of ^{53}Mn (493 dpm/kg; Setoguchi, 2001).

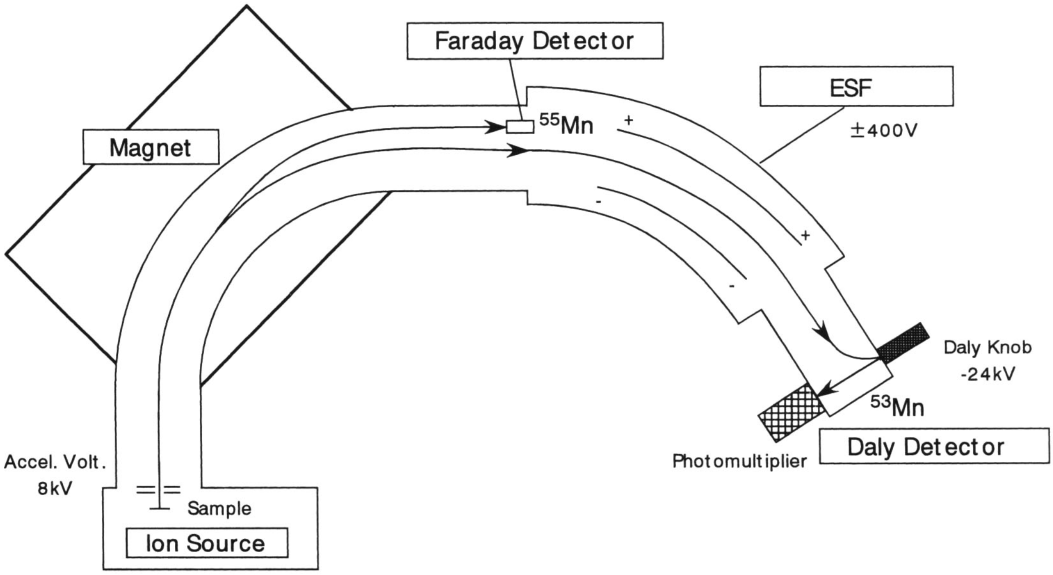

Fig. 1. A schematic diagram of a Micromass Sector 54–30 mass spectrometer. While ^{55}Mn is measured by the Faraday detector system, ^{53}Mn is measured by the Daly detector system through the electrostatic filter (ESF), which is operated in ion counting mode.

2.2 Instrumentation

A Micromass Sector 54–30 thermal ionization mass spectrometer at the National Science Museum was used for this study. A schematic diagram of the mass spectrometer is shown in Fig. 1. Seven Faraday cup collectors and a Daly detector system are placed at the end of the magnet and at the end of the electrostatic filter (ESF), respectively. While ^{55}Mn is measured by the Faraday detector system, ^{53}Mn is measured by the Daly detector system through the ESF. The Daly detector system is operated in the ion counting mode, which can count each ^{53}Mn ion and can measure the ion beam current of as low as 1×10^{-18} A. Measuring ^{55}Mn at a Faraday detector (up to 1×10^{-10} A) and ^{53}Mn at the Daly detector, extreme isotope ratios of ^{53}Mn/^{55}Mn at the order of 10^{-5} can be measured within 1% analytical errors.

2.3 Mass Spectrometry of Mn

A rhenium ribbons were prebaked with 4.8 A filament current. Silica gel was placed on the ribbon in order to enhance the beam intensity of Mn and to reduce that of organic compounds. About 1 μg of Mn was loaded onto the ribbon and then the sample was covered by the phosphoric acid. The ^{53}Mn/^{55}Mn ratios were determined via three sequences (Fig. 2) as in Yoneda *et al.* (1995). Sequence 2 measured ^{53}Mn at the Daly detector and ^{55}Mn at the H2 Faraday cup detector simultaneously. The sequences 1 and 3 were to determine the Cr interference on ^{53}Mn. The natural isotopic ratio of ^{53}Cr/^{52}Cr for the correction was assumed since contribution of spallation-produced ^{53}Cr is reported to be negligible (Shima and Honda, 1966).

Two separate measurements which used different filaments were performed. At each measurement, several sets of isotopic ratios in different filament currents were measured.

3. Results and Discussion

3.1 Faraday-Daly Gain Calibration

Just before the ^{53}Mn/^{55}Mn isotopic ratio measurements, the gain difference between Faraday and Daly collectors were measured by Faraday-Daly gain calibration. This calibration was performed by measuring the same ^{55}Mn ion beam of $\sim10^{-13}$ A by Faraday and Daly collectors alter-

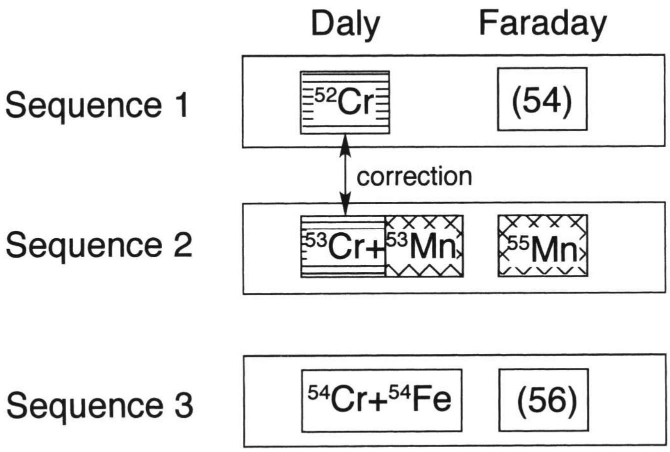

Fig. 2. The sequences for the $^{53}Mn/^{55}Mn$ measurements. At the sequence 2, ^{53}Mn and ^{55}Mn are measured simultaneously. The amount of the interference of ^{53}Cr on ^{53}Mn is calculated from the ^{52}Cr intensity at the sequence 1. The sequence 3 monitors Cr and other (such as Fe) interferences.

Table 1. Results of Faraday-Daly gain calibration.
Measurement #1

Run	Filament current (A)	Mn-55 (×1E-13 A)	Daly/Faraday (×1E-14 A)	Standard error (%)
1	1.780	2.0	86.18	0.07
2	1.780	3.0	86.63	0.02
3	1.780	4.0	86.82	0.08
4	1.750	3.3	87.36	0.03
5	1.720	2.6	87.74	0.11
6	1.700	2.2	87.77	0.11
7	1.700	2.2	87.59	0.03
8	1.725	3.1	87.30	0.09
9	1.650	1.4	88.05	0.06

Measurement #2

Run	Filament current (A)	Mn-55 (×1E-13 A)	Daly/Faraday (×1E-14 A)	Standard error (%)
1	1.810	2.2	84.09	0.04
2	1.810	2.6	84.36	0.04
3	1.810	2.9	84.63	0.01
4	1.814	3.4	85.15	0.02
5	1.814	3.5	85.37	0.03
6	1.800	3.1	85.95	0.04
7	1.790	2.8	85.97	0.01
8	1.780	2.5	86.17	0.03
9	1.770	2.3	86.24	0.02
10	1.790	2.8	85.98	0.02
11	1.800	3.2	85.78	0.03
12	1.810	3.4	85.71	0.03

Each run consists of 5 mesurement cycles.

nately. The results are shown in Table 1. The best values, 87.59 and 85.98, are used for the measurement #1 and #2, respectively. Using the ^{232}Th beam, the Faraday-Daly gain factor variation was less than 0.5% during the 8-hour measurements (Yoneda *et al.*, 1995). The difference between the gain factors of two measurements is due to the slight difference of the settings of the mass spectrometer.

3.2 $^{53}Mn/^{55}Mn$ Isotopic Ratio

The results of 2 separate measurements are listed in Table 2. The ion beam intensities of ^{55}Mn measured by the Faraday detector were from ~1 to 500×10^{-14} A, and those at mass 53 (mixture of ^{53}Mn and ^{53}Cr) measured by the Daly detector were from ~3 to 300×10^{-18} A, giving an isotopic ratio of $\sim6\times10^{-5}$. The correction of the ^{53}Cr interferences on ^{53}Mn calculated from the intensity of ^{52}Cr were normally small (less than 10% of the total intensity at the best condition). The average of each run, which is calculated from 10 ratios (except measurement #1 run 4) at the same filament current, are plotted against the filament currents in Fig. 3. The mass fractionation effect with the filament current, hence the

Table 2. Results of the Isotopic measurements of Mn-53/Mn-55.
Measurement #1

Run	Filament current (A)	Cr-52 (×1E-14 A)	Mn-53+Cr-53 (×1E-14 A)	Mn-55 (×1E-14 A)	Cr-54+Fe-54 (×1E-14 A)	53Mn/55Mn (×1E-6)	Cr-53/(Mn-53+Cr-53) (%)	Avarage (×1E-6)	Standard error (%)
1	2.145	0.08887	0.01808	140.495	0.00359	56.959	55.74	58.922	0.914
		0.07236	0.01598	137.235	0.00327	56.654	51.35		
		0.05833	0.01434	134.240	0.00281	57.550	46.12		
		0.04553	0.01278	131.531	0.00223	57.910	40.40		
		0.03686	0.01210	128.562	0.00207	61.576	34.55		
		0.03035	0.01085	125.431	0.00188	59.078	31.72		
		0.02535	0.01019	122.470	0.00188	59.760	28.20		
		0.02213	0.00961	119.502	0.00158	59.427	26.11		
		0.01886	0.00933	117.100	0.00154	61.410	22.92		
		0.01657	0.00857	113.633	0.00144	58.901	21.92		
2	2.175	0.00496	0.00724	112.689	0.00103	59.216	7.78	61.029	0.673
		0.00447	0.00752	110.751	0.00101	63.318	6.75		
		0.00390	0.00709	106.987	0.00097	62.181	6.23		
		0.00359	0.00659	103.208	0.00090	59.917	6.18		
		0.00295	0.00655	99.399	0.00094	62.574	5.11		
		0.00261	0.00617	96.501	0.00089	60.861	4.80		
		0.00209	0.00597	94.206	0.00085	60.816	3.97		
		0.00187	0.00571	90.015	0.00068	61.045	3.72		
		0.00171	0.00535	86.148	0.00073	59.887	3.62		
		0.00151	0.00517	82.667	0.00060	60.470	3.31		
3	2.250	0.00157	0.00572	89.648	0.00061	61.832	3.12	59.420	1.098
		0.00145	0.00519	85.286	0.00058	58.955	3.17		
		0.00144	0.00502	81.283	0.00055	59.727	3.25		
		0.00133	0.00488	75.942	0.00053	62.318	3.08		
		0.00137	0.00465	72.769	0.00051	61.836	3.33		
		0.00137	0.00371	61.978	0.00039	57.391	4.18		
		0.00129	0.00429	70.011	0.00048	59.170	3.42		
		0.00133	0.00389	65.127	0.00041	57.441	3.89		
		0.00123	0.00394	64.153	0.00036	59.237	3.55		
		0.00120	0.00375	64.177	0.00040	56.288	3.63		
4	2.500	0.35233	0.04227	38.129	0.01008	60.751	94.52	39.714	19.957
		0.33806	0.03944	31.155	0.00929	35.566	97.19		
		0.30979	0.03573	26.663	0.00835	22.569	98.32		
		0.27936	0.03249	20.273	0.00779	39.968	97.51		

Table 2. Results of the Isotopic measurements of Mn-53/Mn-55 (continued).
Measurement #2

Run	Filament current (A)	Cr-52 (×1E-14 A)	Mn-53+Cr-53 (×1E-14 A)	Mn-55 (×1E-14 A)	Cr-54+Fe-54 (×1E-14 A)	53Mn/55Mn (×1E-6)	Cr-53/(Mn-53+Cr-53) (%)	Avarage (×1E-6)	Standard error (%)
1	2.150	0.25660	0.04312	212.414	0.00808	66.042	67.47	64.491	1.307
		0.24350	0.04223	212.067	0.00842	68.935	65.38		
		0.24020	0.04063	211.592	0.00871	63.310	67.03		
		0.22823	0.03891	210.720	0.00787	61.835	66.51		
		0.21353	0.03820	209.715	0.00726	66.690	63.39		
		0.20266	0.03643	208.780	0.00746	64.420	63.08		
		0.19171	0.03438	207.637	0.00692	60.879	63.23		
		0.18503	0.03428	207.104	0.00682	64.210	61.21		
		0.17610	0.03383	206.704	0.00640	67.058	59.03		
		0.16654	0.03156	206.013	0.00629	61.533	59.83		
2	2.175	0.09483	0.02674	257.018	0.00000	62.222	40.20	62.138	0.693
		0.08992	0.02627	256.308	0.00000	62.718	38.81		
		0.08805	0.02592	255.406	0.00000	62.413	38.51		
		0.08193	0.02584	255.372	0.00000	64.802	35.95		
		0.08004	0.02501	253.529	0.00000	62.861	36.29		
		0.08089	0.02438	252.264	0.00000	60.273	37.63		
		0.07681	0.02381	250.244	0.00000	60.349	36.58		
		0.07188	0.02380	248.755	0.00000	62.899	34.25		
		0.06563	0.02262	248.749	0.00001	61.005	32.90		
		0.06114	0.02227	247.975	0.00001	61.836	31.14		
3	2.200	0.03909	0.02313	306.959	0.00000	60.910	19.17	61.371	0.520
		0.03639	0.02273	304.543	0.00000	61.099	18.15		
		0.03519	0.02278	302.757	0.00000	62.073	17.51		
		0.03368	0.02180	300.789	0.00000	59.788	17.52		
		0.02956	0.02208	298.642	0.00000	62.703	15.18		
		0.03133	0.02195	297.933	0.00001	61.737	16.19		
		0.02873	0.02180	297.059	0.00000	62.406	14.95		
		0.02693	0.02131	295.569	0.00000	61.783	14.33		
		0.02571	0.02098	293.728	0.00001	61.490	13.90		
		0.02455	0.02025	292.548	0.00000	59.719	13.74		
4	2.250	0.02114	0.02747	424.372	0.00000	59.083	8.73	59.798	0.259
		0.02152	0.02762	419.943	0.00000	59.972	8.83		
		0.01877	0.02656	415.254	0.00000	58.844	8.01		
		0.01652	0.02634	408.418	0.00000	59.916	7.11		
		0.01634	0.02535	390.641	0.00000	60.146	7.31		
		0.01511	0.02482	384.896	0.00000	60.037	6.90		
		0.01542	0.02459	382.489	0.00000	59.722	7.11		
		0.01453	0.02486	385.081	0.00001	60.283	6.63		
		0.01376	0.02419	379.212	0.00000	59.670	6.45		
		0.01287	0.02384	371.105	0.00000	60.311	6.12		
5	2.300	0.04754	0.03746	520.598	0.00000	61.610	14.39	60.823	0.337
		0.04209	0.03624	512.763	0.00000	61.364	13.17		
		0.03661	0.03404	494.381	0.00000	60.459	12.20		
		0.03743	0.03394	479.104	0.00000	61.972	12.51		
		0.03189	0.03144	460.116	0.00000	60.468	11.50		
		0.03064	0.03068	454.062	0.00000	59.912	11.33		
		0.02937	0.02979	439.623	0.00001	60.179	11.18		
		0.02573	0.02939	434.910	0.00000	60.857	9.93		
		0.02433	0.02855	424.409	0.00001	60.772	9.66		
		0.02343	0.02806	418.994	0.00000	60.637	9.47		

Table 2. Results of the Isotopic measurements of Mn-53/Mn-55 (continued).
Measurement #2 (continued)

Run	Filament current (A)	Cr-52 (×1E-14 A)	Mn-53+Cr-53 (×1E-14 A)	Mn-55 (×1E-14 A)	Cr-54+Fe-54 (×1E-14 A)	53Mn/55Mn (×1E-6)	Cr-53/(Mn-53+Cr-53) (%)	Avarage (×1E-6)	Standard error (%)
6	2.350	0.01850	0.02883	440.098	0.00000	60.752	7.28	59.230	0.455
		0.01544	0.02637	414.709	0.00000	59.364	6.64		
		0.01374	0.02547	397.589	0.00001	60.139	6.12		
		0.01267	0.02440	386.342	0.00000	59.446	5.89		
		0.01138	0.02286	371.609	0.00000	58.044	5.65		
		0.01009	0.02239	357.878	0.00001	59.359	5.11		
		0.00907	0.02150	346.232	0.00001	59.137	4.78		
		0.00787	0.02099	338.677	0.00001	59.335	4.25		
		0.00752	0.01993	329.389	0.00000	57.917	4.28		
		0.00720	0.01934	314.951	−0.00001	58.812	4.22		
7	2.400	0.00461	0.01912	315.103	0.00000	59.015	2.74	59.482	0.495
		0.00398	0.01852	299.527	0.00001	60.312	2.44		
		0.00351	0.01753	285.610	0.00001	59.974	2.27		
		0.00316	0.01684	275.183	0.00001	59.894	2.13		
		0.00307	0.01553	250.106	0.00000	60.688	2.24		
		0.00264	0.01350	225.649	0.00000	58.511	2.22		
		0.00236	0.01248	210.513	0.00000	57.994	2.15		
		0.00217	0.01174	191.023	0.00000	60.154	2.09		
		0.00195	0.01067	174.387	0.00001	59.905	2.07		
		0.00167	0.00966	162.268	−0.00001	58.372	1.96		
8	2.500	0.00292	0.00562	84.853	0.00052	62.353	5.89	59.847	0.774
		0.00290	0.00527	81.597	0.00059	60.551	6.23		
		0.00272	0.00483	76.976	0.00044	58.709	6.39		
		0.00245	0.00435	68.553	0.00040	59.384	6.39		
		0.00247	0.00435	67.088	0.00039	60.694	6.43		
		0.00203	0.00398	62.688	0.00036	59.762	5.78		
		0.00221	0.00398	61.127	0.00034	61.047	6.29		
		0.00204	0.00356	57.812	0.00036	57.590	6.49		
		0.00195	0.00285	45.275	0.00025	57.985	7.78		
		0.00185	0.00232	34.918	0.00023	60.395	9.07		
9	2.700	0.00636	0.01125	175.443	0.00073	60.024	6.41	59.848	0.755
		0.00614	0.01045	165.709	0.00068	58.841	6.66		
		0.00575	0.01017	165.204	0.00058	57.589	6.41		
		0.00543	0.00980	150.683	0.00051	60.942	6.28		
		0.00495	0.00915	143.485	0.00039	59.825	6.14		
		0.00455	0.00819	126.719	0.00032	60.543	6.30		
		0.00390	0.00680	106.855	0.00025	59.521	6.51		
		0.00360	0.00650	100.591	0.00024	60.549	6.28		
		0.00311	0.00544	87.460	0.00020	58.147	6.49		
		0.00294	0.00558	83.933	0.00016	62.500	5.97		
10	2.850	0.00325	0.00167	20.646	0.00011	63.265	21.98	57.399	4.866
		0.00345	0.00140	15.918	0.00012	63.341	27.93		
		0.00316	0.00092	11.764	0.00013	48.016	38.81		
		0.00303	0.00085	8.757	0.00010	57.337	40.63		
		0.00305	0.00075	6.247	0.00010	63.893	46.45		
		0.00297	0.00064	4.353	0.00008	70.086	52.49		
		0.00284	0.00050	3.011	0.00009	60.684	63.78		
		0.00287	0.00044	2.008	0.00011	54.792	74.75		
		0.00271	0.00038	1.363	0.00008	52.481	81.09		
		0.00251	0.00032	0.898	0.00009	40.099	88.79		

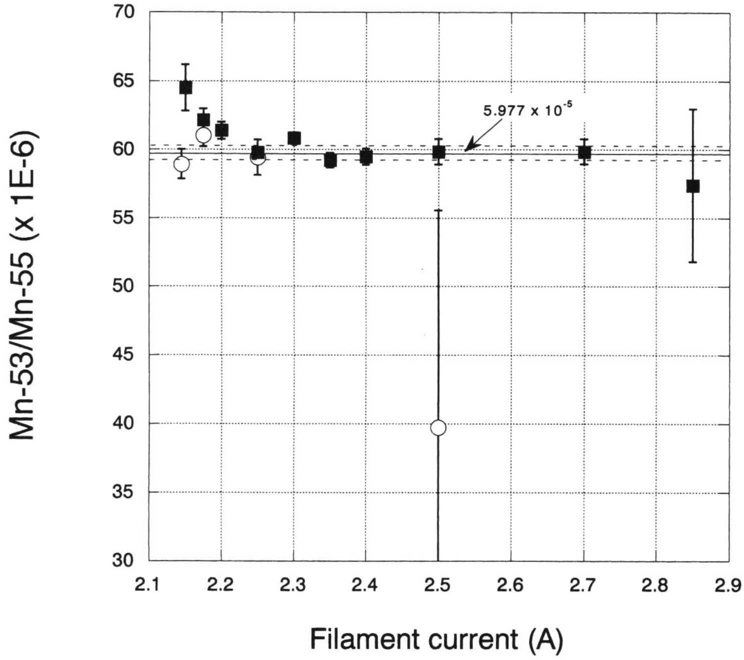

Fig. 3. The results of the $^{53}Mn/^{55}Mn$ ratios of measurement #1 (open circles) and measurement #2 (solid squares) plotted against the filament currents. Error bars represent the standard errors ($2\sigma_m$).

temperature, are not seen during the measurements. For the calculation of the total average of the isotopic ratios, only the data, when the measured ion currents of ^{55}Mn were greater than 1×10^{-12} A and the interference of ^{53}Cr to ^{53}Mn was less than 10%, were used. The obtained average was $(5.977\pm0.032)\times10^{-5}$ (errors are $2\sigma_m$).

3.3 Half life of ^{53}Mn

The half life of ^{53}Mn ($T_{1/2}$) can be calculated from the equation (1):

$$T_{1/2}=\frac{\ln 2\times N(^{53}\mathrm{Mn})}{A(^{53}\mathrm{Mn})} \quad (1)$$

where, $N(^{53}Mn)$ is number of ^{53}Mn atoms and $A(^{53}Mn)$ is decay rate. $N(^{53}Mn)$ is can be calculated from the isotopic ratio $^{53}Mn/^{55}Mn$ and the content of Mn in the sample. $A(^{53}Mn)$ is determined by X-ray countings with a LEPS counter. Preliminary results of these measurements were reported by Oura *et al.* (2002). With 0.09289 Bq and 19.14 μg Mn in the sample, a new half life of ^{53}Mn, 3.0×10^6 y, was calculated. This new value is about 20% shorter than the current value 3.7×10^6 y and the relative analytical errors of the new value, 5%, is smaller than those of the current value, 10%. However, the errors are still large comparing with the isotopic ratio measurements for meteorite chronology. Additional X-ray measurements and efforts to reduce uncertainties are in progress. Details will be published elsewhere.

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