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journal homepage: www.elsevier.com/locate/nimbAMS measurement of ^{53}Mn and its initial application at CIAE

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ABSTRACT

The determination of cosmogenic ^{53}Mn in terrestrial archives has important applications, such as burial ages, exposure age and erosion rates. Accelerator mass spectrometry (AMS) is the most sensitive technique to detect minute amounts of ^{53}Mn . ^{53}Mn measurements were developed at the China Institute of Atomic Energy (CIAE) using the ΔE -Q3D equipped AMS system. This approach was recently optimized with the goal to reach the sensitivity required for AMS measurements of ^{53}Mn in deep-sea ferromanganese crust (DSFC) samples. Based on these improvements of sample preparation, current beam transmission and so on, ^{53}Mn in two samples of DSFC was measured by AMS. The ratios of $^{53}\text{Mn}/\text{Mn}$ corresponding to an age of 3.77 ± 0.42 and 13.73 ± 2.74 Ma by ^{129}I dating method are $(5.01 \pm 2.15) \times 10^{-13}$ and $(1.90 \pm 0.96) \times 10^{-13}$. The ratios are close to the experimental reference values, deduced from the previous research. The experimental progress, performances and results are presented in this contribution.

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1. Introduction

The long-lived nuclide ^{53}Mn with a half-life of 3.7 ± 0.4 Ma [1] is produced in extraterrestrial matter, e.g. dust particles, by various nuclear reactions of cosmic rays, particularly *in situ* in the surface layer of rocks by cosmic rays via spallation of the primary target element iron. ^{53}Mn is also produced via spallation of the iron by the removal of a proton and two neutrons on the Earth's surface. The determination of the cosmogenic radionuclide ^{53}Mn on Earth has many interesting applications in scientific areas. Examples include the measurement of ^{53}Mn concentrations in deep sea ferromanganese crusts (DSFC), which gives insight into the flux of extraterrestrial matter onto Earth, the intensity of cosmic radiation and it allows also the dating of terrestrial formations [2]. ^{53}Mn is also used for the measurement of erosion rates over a time scale of millions of years, and dating over tens of millions years, well beyond the upper limit of $^{10}\text{Be}/^{26}\text{Al}$ dating [3].

However, the potential of ^{53}Mn dating has not been fully explored, due to the lack of an appropriate method for the determination of ^{53}Mn . Two methods for highly sensitive AMS

measurements of ^{53}Mn have been developed, i.e., gas-filled magnet (GFM) at Technische Universität München (TUM) [4] and the Australian National University (ANU) [3], and ΔE -Q3D at CIAE [5], and relevant applications were developed in geoscience [6,7]. In addition, previous studies indicated that compared to the MnO_2 sample material/ MnO^- ion extraction approach, the use of MnF_2 sample and MnF^- ion extraction gave much better suppression from the interfering isobar ^{53}Cr which improved the sensitivity for AMS measurement of ^{53}Mn [8,9]. For further optimizing the experimental technique at CIAE and exploring potential applications of ^{53}Mn , the procedures in sample preparation and the AMS measurement for a DSFC samples were refined at CIAE. The experimental progress, performances and results are presented in this paper.

2. Methods

2.1. Description of DSFC sample

The ideal reservoirs for ^{53}Mn of extraterrestrial origin and deposited on Earth are DSFC [2]. The determination of the ^{53}Mn contents in dated layers of DSFCs may reveal the extraterrestrial ^{53}Mn flux over a very long time period. One of the DSFC, namely

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CXD08-1, was available for ^{53}Mn analysis. It was collected from the Pacific, located at $19^{\circ}96'47''\text{N}$, $172^{\circ}91'78''\text{E}$ and from a depth of 1908 m. A photo of the sample is shown in Fig. 1. CXD08-1 is a crust of about 8 cm thickness and has a knobby surface texture. The vertical section was laminated. The upper zone of 0–4.5 cm depth is dense, loose in the middle, but dense again from ~5.5 cm depth to bottom.

2.2. Extraction of manganese from DSFC

The samples used in this work were the layers of 5–10 mm and 15–20 mm of CXD08-1, labeled CXD08-1-2# and CXD08-1-4#. The samples were cleaned, crushed and sieved. Particles with sizes of 100–200 μm were collected. The particles were transferred into an Erlenmeyer flask, repeatedly rinsed and leached using 18 M Ω water in order to eliminate the potential contamination of metal ions. About 50 mg grains of each sample were dissolved in HCl to yield a solution containing 8–10 mg Mn. Since the Mn concentration in this DSFC was high (about 20%), no ^{55}Mn carrier was added. The solution of MnCl_2 was filtered with quantitative filter paper to remove insoluble materials. Manganese was recovered from the sample solutions by precipitation as $\text{MnO}(\text{OH})_2$ via the addition of NaOH. The $\text{MnO}(\text{OH})_2$ was deposited by centrifugation at 4000 rpm for 20 min and washed three times with bi-distilled water followed by centrifugation at 4000 rpm for 10 min. The sample was then dried at 100 $^{\circ}\text{C}$ for 24 h in a vacuum oven to produce MnO_2 , which was finally chemically treated for the removal of chromium and transformed into MnF_2 by the procedure detailed in Sections 2.3 and 2.4, respectively, for the AMS measurement.

2.3. Chemical suppression of chromium

The main interference ions for AMS measurement of ^{53}Mn come from its stable isobar ^{53}Cr . Thus, it is important to minimize the content of chromium in samples. In this work, all samples were chemically treated for the removal of chromium. The procedure was similar as described in Ref. [7]. Briefly, the MnO_2 (purchased from Alfa Aesar Company with 99.99% purity) was dissolved completely in concentrated hydrochloric acid (conc. HCl). The resulting MnCl_2 solution was loaded on an AG-1- \times 8 anion exchange resin (100–200 mesh) column. Cr and Mn were then eluted by 10 M HCl and 7 M HCl, successively. The anion exchange chromatography was repeated three times. Manganese was precipitated as $\text{MnO}(\text{OH})_2$ by adding NaOH. The $\text{MnO}(\text{OH})_2$ was centrifuged, washed, and then dried at 100 $^{\circ}\text{C}$ for 24 h in vacuum oven to

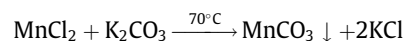
produce MnO_2 , which was finally transformed into MnF_2 by the procedure detailed in Section 2.4 for AMS measurement. The chemical yield of Mn for this procedure was about 75%, and the content of residual ^{53}Cr in Mn sample should be several ppm by estimate.

2.4. MnF_2 preparation

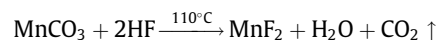
The following procedure was developed for MnF_2 preparation of all samples:

- (1) The MnO_2 powder was dissolved in concentrated hydrochloric acid. The reaction equation is as follows:

$$\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 \uparrow + 2\text{H}_2\text{O}$$
- (2) Afterwards, the resulting black-green solution was heated on a heating plate for 4 h at about 90 $^{\circ}\text{C}$ to remove Cl_2 .
- (3) Manganese was recovered from the sample solution by the precipitation of MnCO_3 via the addition of K_2CO_3 . The bottle containing the sample was heated in a water bath to 70 $^{\circ}\text{C}$ for several hours in order to flocculate MnCO_3 . The reaction equation is as follows:



- (4) After centrifugation at 4000 rpm for 20 min, the supernatant liquid was decanted. The precipitate of MnCO_3 was washed three times with 18 M Ω water followed by centrifugation at 4000 rpm for 10 min.
- (5) The MnCO_3 was dried at 100 $^{\circ}\text{C}$ and then transferred to a Teflon beaker. Hydrofluoric acid (HF, 48%) was added and the reactants heated at 110 $^{\circ}\text{C}$, until MnCO_3 was dissolved completely. The solution was then evaporated to dryness. The residue was heated in an oven for 2 h at 120 $^{\circ}\text{C}$ to obtain MnF_2 as a pink colored powder.



The MnF_2 sample was mixed with a similar volume of high purity (99.99%) silver powder, which served as a thermal and electrical conductor. Finally, the powder was pressed into the Al sample holders of 40-sample NEC MC-SNICS ion source for AMS measurement.

2.5. AMS analysis

The ^{53}Mn measurements were performed on the HI-13 Tandem Accelerator equipped with a $\Delta\text{E-Q3D}$ detection system [10] at China Institute of Atomic Energy. The negative molecular ions of MnF^- were injected into the HI-13 Tandem Accelerator. The typical negative ion current at the low-energy Faraday Cup (FC) was about 200 nA for $^{55}\text{MnF}^-$ ions. Terminal voltages of 11.1 and 11.5 MV were used for ^{55}Mn and ^{53}Mn , respectively, which provided the same magnetic rigidity for the two isotopes when transported to the FC located in front of the detection system for the optimization of measurement conditions and to the $\Delta\text{E-Q3D}$ detection system for events detection, respectively. Foil (3 $\mu\text{g}/\text{cm}^2$ carbon) stripping was employed at the accelerator terminal to break up the molecular ions and produce atomic ions with high positive charge states. Manganese (also chromium) ions with charge state 11^+ were selected by the analyzing magnet. By means of the switching magnet the particles were transported further to the $\Delta\text{E-Q3D}$ detection system for the isobar separation of ^{53}Mn and ^{53}Cr and counting of ^{53}Mn .

A stack of very homogeneous Silicon Nitride (Si_3N_4) membranes (from Silson Ltd./UK) with a total thickness of 4.0 μm (four 1 μm

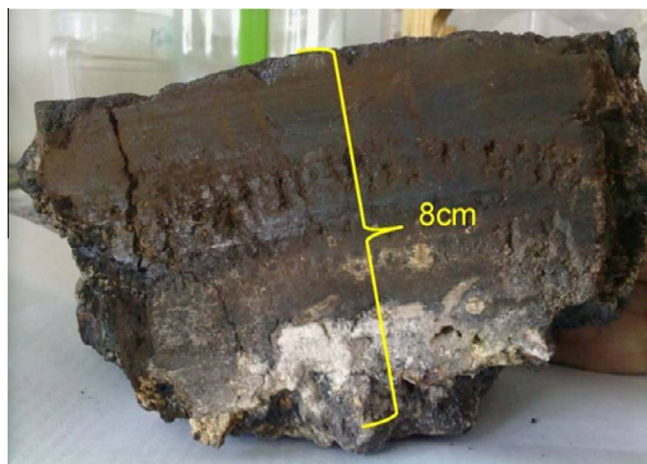


Fig. 1. A photo of deep sea ferromanganese crust sample CXD08-1.

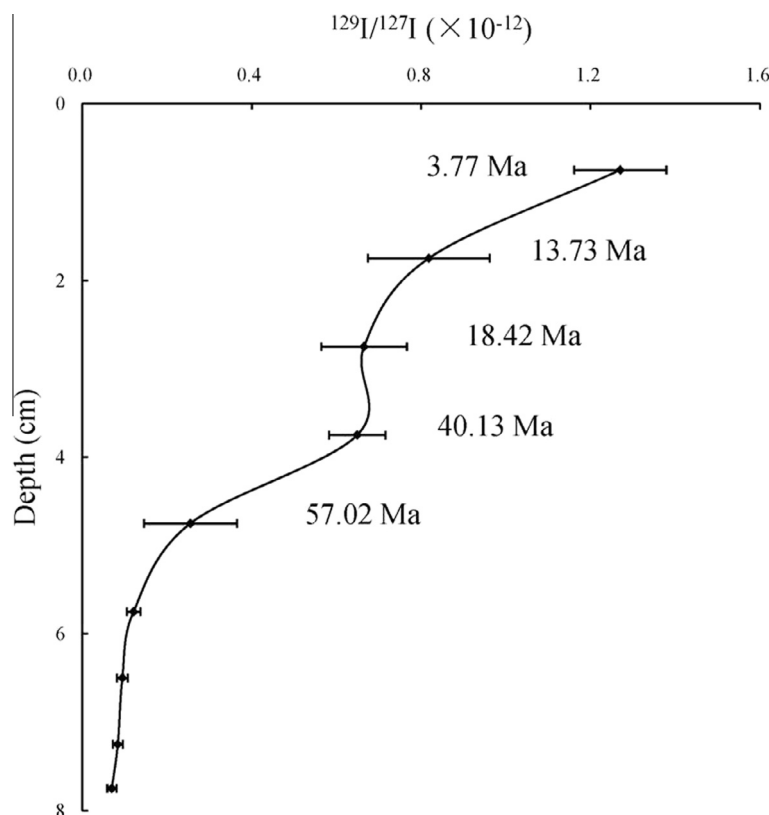


Fig. 2. Distribution of depth profile of $^{129}\text{I}/^{127}\text{I}$ ratio in CXD08-1.

foils) was mounted at the entrance of the Q3D [11] as a passive absorber to produce different energy losses for ^{53}Mn and ^{53}Cr . After leaving the Si_3N_4 membrane, the $^{53}\text{Mn}^{18+}$ and $^{53}\text{Cr}^{18+}$ ions with energies of about 100.43 MeV and 102.14 MeV, respectively, were analyzed by the Q3D magnetic spectrometer. The isobars of ^{53}Mn and ^{53}Cr were then separated in their beam trajectories by the magnetic field of the Q3D magnetic spectrometer according to their different residual energies. In order to increase the detection efficiency for ^{53}Mn and further separate the isobaric interference of ^{53}Cr , a Multiple-Anode Ionization Chamber (MAIC, four anodes in this work) with an entrance window of $100\text{ mm} \times 40\text{ mm}^2$ Mylar foil and the gas medium of 38 mbar propane was mounted at the accurately located position of the Q3D focal plane to record ^{53}Mn events. Based on the difference in energy losses of ^{53}Cr and ^{53}Mn ions in the propane, ^{53}Cr and ^{53}Mn can be further identified with the MAIC.

3. Results and discussion

CXD08-1-2#, CXD08-1-4#, one chemical blank and one CIAE Reference Sample (CIAE RS) with a reference $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of 3.90×10^{-12} , were analyzed for $^{53}\text{Mn}/^{55}\text{Mn}$ ratios. The average ages of CXD08-1-2# and CXD08-1-4# were deduced by the ^{129}I dating method and calculated by the following equation to be 3.77 ± 0.42 and 13.73 ± 2.74 Ma [12], respectively. The depth profile of $^{129}\text{I}/^{127}\text{I}$ in CXD08-1 is shown in Fig. 2.

$$t = \frac{T_{129}}{\ln 2} \ln \frac{^{129}\text{I}_i}{^{129}\text{I}_m}$$

where, t is the age of a crust sample; T_{129} the ^{129}I half-life, 1.57×10^7 a; $^{129}\text{I}_m$ the ratio of $^{129}\text{I}/\text{I}$ in the sample measured by AMS at CIAE; $^{129}\text{I}_i$ the initial value of natural $^{129}\text{I}/\text{I}$ for dating, $(1.50 \pm 0.15) \times 10^{-12}$, which is the pre-anthropogenic input ratio of $^{129}\text{I}/\text{I}$ in the marine system [13].

The CIAE RS was produced by chemical dilution of a TUM Reference Sample (TUM RS), with a quoted isotope ratio of $^{53}\text{Mn}/^{55}\text{Mn} = 3.30 \times 10^{-9}$, which was provided by the TUM AMS group. All samples used were chemically treated for the removal of chromium. The CIAE RS was first measured for the optimization of measurement conditions. The results of $^{53}\text{Mn}/^{55}\text{Mn}$ ratios for all samples were obtained by simultaneously measuring the currents of $^{55}\text{MnF}^-$ ions on the low-energy offset Faraday cup, and the count rate of ^{53}Mn recorded by the MAIC (after a proper treatment by software gates and background subtraction). The results of the energy loss signal from anode 4, ΔE_4 , versus that from anode 2, ΔE_2 , are shown in Fig. 3.

As shown in Fig. 3, for the CIAE RS and DSFC samples, the number of ^{53}Mn counts can be reliably extracted with appropriate gates on the various anode signals from the detector. No ^{53}Cr event exists in ^{53}Mn window in the coincidence spectra of the Blank sample, as shown in Fig. 3h. The ratio of $^{53}\text{Mn}/^{55}\text{Mn}$ for the Blank is $< 3.00 \times 10^{-14}$, estimated by only one event in the ^{53}Mn window and CIAE RS normalization, implying that the ^{53}Cr interference can be significantly reduced by chemical procedure. Preliminary results for these samples are presented in Table 1. The results of $^{53}\text{Mn}/^{55}\text{Mn}$ ratios for all samples were obtained by simultaneously measuring the beam currents of $^{55}\text{MnF}^-$ ions on the low-energy offset FC, and the count rate of ^{53}Mn recorded by the MAIC after a proper treatment by software gates and background subtraction.

A ^{53}Mn depth profile of three layers of 0–3, 5–10 and 10–20 mm of a similar DSFC which originates from Mona Pihoa in the South Pacific (19°S , 149°W) at a depth of about 1300 m, corresponding to the $^{53}\text{Mn}/\text{Mn}$ ratios of 6.6×10^{-13} , 4.0×10^{-13} , 2.2×10^{-13} , respectively, has been measured with AMS method, corresponding to age spans of 0–2.8, 3.7–5.9, and 5.9–13 Ma estimated by Knie et al., using cobalt dating [14]. Table 1 shows our results of the measured $^{129}\text{I}/\text{I}$ and $^{53}\text{Mn}/\text{Mn}$ ratios. The results indicate that the chemical procedure for removing chromium also reduced the iron

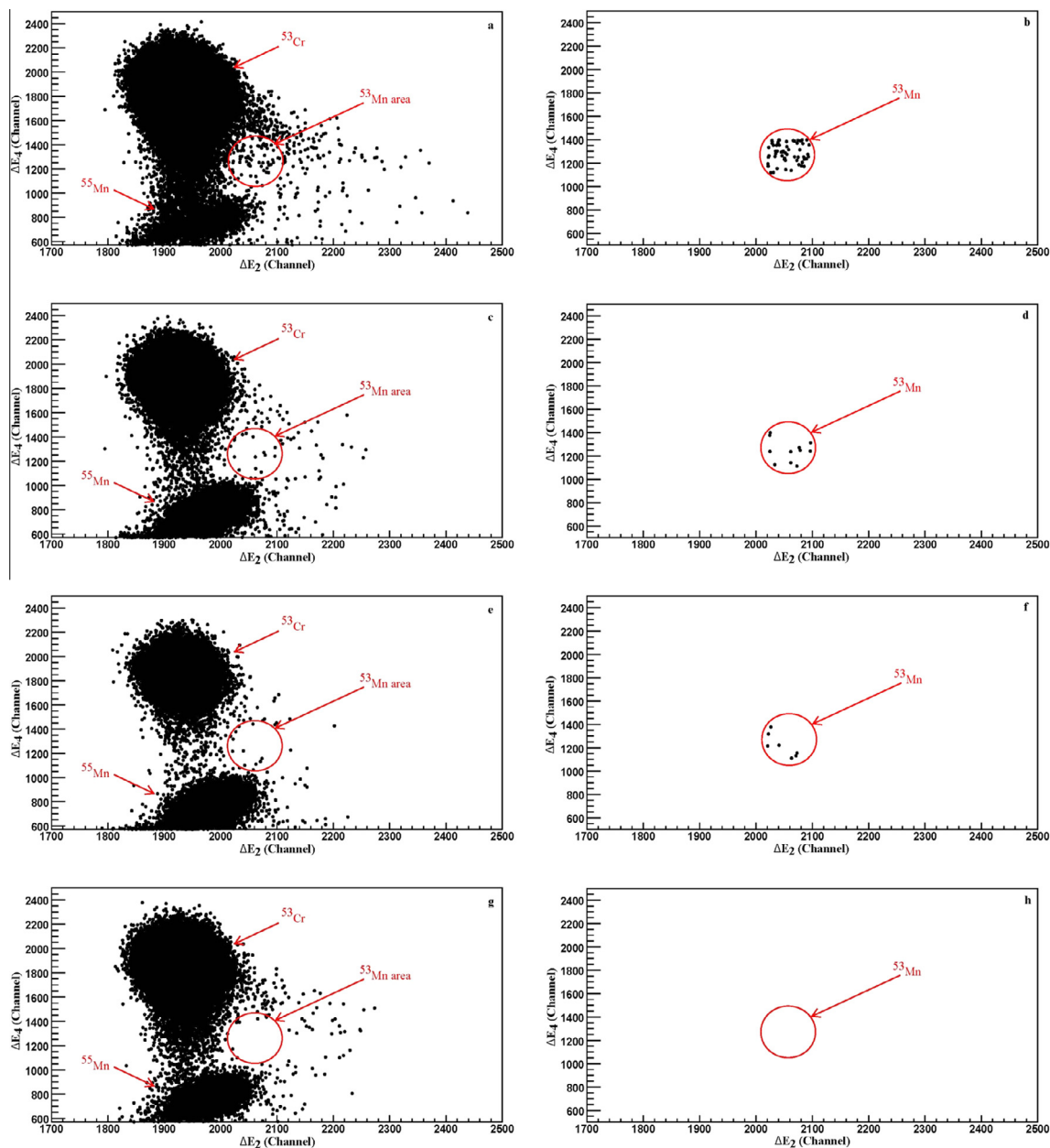


Fig. 3. Two-dimensional spectra of ΔE_2 vs ΔE_4 for CIAE RS, two ferromanganese crust and one blank samples by MnF^- extraction from MnF_2 sample. a for a standard sample with $^{53}\text{Mn}/^{55}\text{Mn} = (3.9 \pm 0.5) \times 10^{-12}$, counting time 1800 s; c for a sample of CXD08-1-2#, counting time 4000 s; e for a sample of CXD08-1-4#, counting time 6000 s; g for a sample of F_Blank, counting time 5000 s; b, d, f, and h are for the same samples as for a, c, e, and g, respectively, taken with coincidence gated at ^{53}Mn .

Table 1

AMS results of $^{53}\text{Mn}/\text{Mn}$ in DSFC samples.

Sample	Layer (mm)	$^{129}\text{I}/\text{I}$ [12]	Average age (Ma)	^{53}Mn count	$^{53}\text{Mn}/\text{Mn}$	
					Measured ratio	Normalized ratio
CIAE RS		$(5.00 \pm 0.11) \times 10^{-12}$		60	$(3.73 \pm 0.48) \times 10^{-12}$	3.90×10^{-12}
CXD08-1-2#	5–10	$(1.27 \pm 0.14) \times 10^{-12}$	(3.77 ± 0.42)	11	$(4.79 \pm 2.06) \times 10^{-13}$	$(5.01 \pm 2.15) \times 10^{-13}$
CXD08-1-4#	15–20	$(8.18 \pm 1.63) \times 10^{-13}$	(13.73 ± 2.74)	7	$(1.82 \pm 0.92) \times 10^{-13}$	$(1.90 \pm 0.96) \times 10^{-13}$
Blank		$<1.00 \times 10^{-14}$		0	$<2.87 \times 10^{-14}$	$<3.00 \times 10^{-14}$

The quoted uncertainties of RS are counting statistics only.

The quoted uncertainties of CXD08-1-2# and CXD08-1-4# include the statistical error and RS's error propagation.

Chemical blanks, instead of the "crust blank", were used in the ^{129}I and ^{53}Mn measurements.

content substantially. The clear signal above the background, determined from blank measurement, can be seen in the samples of layers 5–10 and 15–20 mm. The ratios of $^{53}\text{Mn}/\text{Mn}$ corresponding to an age of 3.77 ± 0.42 and 13.73 ± 2.74 Ma

estimated by ^{129}I dating method [12] are $(5.01 \pm 2.15) \times 10^{-13}$ and $(1.90 \pm 0.96) \times 10^{-13}$ measured by AMS. The ratios are close to the experimental reference values of about 5.1×10^{-13} and 1.5×10^{-13} , which can be deduced from the ratios of (4.0 ± 1.6)

and $(2.2 \pm 0.8) \times 10^{-13}$ corresponding to an age of 3.7–5.9 and 5.9–13 Ma, respectively, in Ref. [14]. Therefore, the ratios of $^{53}\text{Mn}/\text{Mn}$ give a corroboration of our results of ^{129}I dating. Further studies are needed on the systematic analyses of more layers of DSFC samples for ^{53}Mn and other cosmogenic nuclides, such as ^{60}Fe to verify our initial experiment results.

4. Summary

A method for AMS measurement of ^{53}Mn has been established at CIAE, two layer samples of DSFC were analyzed by AMS at CIAE, and encouraging results were obtained. The initial results show that ^{53}Mn is a very important and significant nuclide, and the application field of ^{53}Mn AMS has a strong potential of further expansion. However, further improvements are needed in increasing beam current (presently about 200 nA) and transmission efficiency (presently about 6%) in order to further reduce the uncertainty. Based on the development of ^{53}Mn experimental method, the AMS measurement method of ^{60}Fe will be established as soon as possible at CIAE, and further application of the two nuclides, such as the search for supernova-produced nuclides on earth, will be carried out in the near future.

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