

AMS Measurement of  $^{53}\text{Mn}$  at CIAE \*

DONG Ke-Jun(董克君)<sup>1</sup>, HE Ming(何明)<sup>1</sup>, LI Chao-Li(李朝历)<sup>1</sup>, HU Hao(胡豪)<sup>1</sup>, LIU Guang-Shan(刘广山)<sup>2</sup>,  
 CHEN Zhi-Gang(陈志刚)<sup>2</sup>, LI Zhen-Yu(李振宇)<sup>1</sup>, WU Shao-Yong(武绍勇)<sup>1</sup>, LIU Jian-Cheng(刘建成)<sup>1</sup>,  
 YOU Qu-Bo(游曲波)<sup>1</sup>, JIN Chun-Sheng(金春生)<sup>1</sup>, WANG Xiang-Gao(王祥高)<sup>3</sup>, SHEN Hong-Tao(沈洪涛)<sup>4</sup>,  
 GUAN Yong-Jing(管永精)<sup>3</sup>, YUAN Jian(袁坚)<sup>1</sup>, JIANG Shan(姜山)<sup>1\*\*</sup>

<sup>1</sup> China Institute of Atomic Energy, P.O. Box 275(50), Beijing 102413

<sup>2</sup> College of Oceanography and Environmental Science, Xiamen University, Xiamen 361005

<sup>3</sup> College of Physics Science and Technology, Guangxi University, Nanning 530004

<sup>4</sup> College of Physics and Technology, Guangxi Normal University, Guilin 541004

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The long-lived isotope  $^{53}\text{Mn}$  cosmogenically produced *in situ* is a very useful indicator for geochronological dating. A new  $^{53}\text{Mn}$  accelerator-mass-spectrometry (AMS) measurement method is developed based on the HI-13 Tandem Accelerator and  $\Delta E$ -Q3D detection system at China Institute of Atomic Energy. The performance of  $^{53}\text{Cr}$  isobar separation and suppression is tested by a series of  $^{53}\text{Mn}$  standards and commercial MnO samples. The results show that the  $\Delta E$ -Q3D detection system brought about an overall suppression factor of more than  $10^7$  for the interfering isobar  $^{53}\text{Cr}$ .

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Terrestrial cosmogenic nuclides (TCNs) have become indispensable tools in the earth sciences to quantitatively evaluate various geomorphological parameters, such as exposure ages, erosion rates and burial ages. The long-lived isotope  $^{53}\text{Mn}$  produced *in situ* in surface rocks by cosmic rays is a potentially useful tool for studying the evolution of the landscape. Its long half life of 3.7 Ma is well suited to the measurement of erosion rates for the exposure times of millions of years. In particular, with iron of the only primary target of producing  $^{53}\text{Mn}$ , the cosmogenic  $^{53}\text{Mn}$  method is potentially useful in studies of the history of iron-rich regolith covering the surface landscape, e.g., that of Tibet, China.

Most measurements of  $^{53}\text{Mn}$  have been conducted in meteorites with typical  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios being  $10^{-9}$  or higher, which can be accomplished by decay counting or neutron-activation techniques. In contrast, sensitivities of  $10^{-12}$  usually required in geochronological applications, such as exposure dating, can only be achieved by accelerator mass spectrometry (AMS). The chief technical problem encountered in AMS measurement of  $^{53}\text{Mn}$  is the presence of the stable isobar  $^{53}\text{Cr}$ , which is difficult to remove by chemical means to concentrations below 1 ppm in the finally purified samples. In other words, the typical content of  $^{53}\text{Cr}$  will be about six orders of magnitude higher than the content of  $^{53}\text{Mn}$  in geochronological samples. Therefore, it is crucial to the high sensitivity measurement of  $^{53}\text{Mn}$  to remove the interference of  $^{53}\text{Cr}$  by sophisticated AMS techniques.

A gas-filled magnet (GFM) combined with a multi-element gas-ionization detector has been developed for

AMS measurement of  $^{53}\text{Mn}$ ,<sup>[1,2]</sup> and the required sensitivity for exposure dating has recently been achieved by the Munich and ANU groups, respectively.<sup>[3,4]</sup> To further tap the potential of the China Institute of Atomic Energy (CIAE) AMS system in the measurements and applications of medium-heavy mass nuclides, a new beam line equipped with a  $\Delta E$ -Q3D detection system has been installed on the HI-13 tandem in recent years.<sup>[5]</sup> A method for AMS measurement of  $^{53}\text{Mn}$  has been developed at CIAE based on the  $\Delta E$ -Q3D detection system. Two beam lines are now usable for the AMS experiments (Fig. 1) at CIAE. Beam line 1 is dedicated to the AMS experiment.<sup>[6]</sup> Beam line 2 is a multi-user beam tube, and some beam time can now be used for AMS measurement. The AMS measurements of  $^{53}\text{Mn}$  reported here were conducted with this multi-user beam tube.

The basic principle of the  $\Delta E$ -Q3D detection method was described in detail in Ref. [5]. Briefly, a very homogeneous membrane of suitable thickness was used as an absorber placed at the entrance of the Q3D magnetic spectrometer with a maximal mass-energy product of  $193\text{ MeV}\cdot\text{a.u.}$ , an energy resolution of  $1.8\times 10^{-4}$  and a dispersion of  $11.37\text{ cm}$  (1% of  $\Delta P/P$  with  $P$  being the momentum).<sup>[7]</sup> When two isobars with the same energy pass through the absorber, their energy losses are different. The Q3D magnetic spectrometer can be used to separate isobars according to their different residual energies after passing through the absorber. A multi-anode ionization chamber was placed at the focal plane of the Q3D magnet spectrometer to collect events of the nuclides to be measured and to further reject the remanent interfering isobars.

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\*\*Correspondence author. Email: jiangs@ciae.ac.cn

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The combination of the Q3D magnetic spectrometer and multi-anode ionization chamber used in this work proves very effective for eliminating  $^{53}\text{Cr}$  isobaric interference problems in this work.

The sample form of  $\text{MnO}_2$  was adopted for the first AMS measurement of  $^{53}\text{Mn}$  at CIAE. The sample powder of  $\text{MnO}_2$  was mixed with a similar volume of pure (99.99%) silver powder for improving thermal and electric conductivity and pressed into the Al sample holders of a 40-sample NEC MC-SNICS ion source for AMS measurement.  $\text{MnO}$  ions were selected for injection into the HI-13 Tandem Accelerator, and the typical output current at the lower-energy Faraday cup (FC) was about 200 nA for  $^{55}\text{MnO}^-$  ions. The negative manganese molecular ions are accelerated by the tandem terminal voltage, typically set at 11.5 MV. Foil ( $3 \mu\text{g}/\text{cm}^2$ ) stripping was employed to break up the molecular ions and to produce atomic ions with high charge states. The resulting positively charged ions are further accelerated by the same terminal voltage. A  $90^\circ$  double focusing high energy analyzing magnet (HEAM) with a maximal mass-energy product of  $200 \text{ MeV}\cdot\text{a.u.}$  selects  $^{53}\text{Mn}^{11+}$  (and  $^{53}\text{Cr}^{11+}$ ) with an energy of 135 MeV, allowing further suppression of fragments from the molecular and isotopic background. None of these processes can achieve the

separation of  $^{53}\text{Mn}$  from the stable isobar  $^{53}\text{Cr}$ . By means of the switching magnet, the particles were transported further to the  $\Delta E$ -Q3D detection system. The experimental setup and the procedure are briefly described as follows. (1) A very homogeneous silicon nitride ( $\text{Si}_3\text{N}_4$ ) membrane (from Silicon Ltd./UK) with optimal thickness of  $4.5 \mu\text{m}$  (four  $1 \mu\text{m}$  plus one  $500 \text{ nm}$  lapped over) was mounted at the entrance of the Q3D as the absorber to produce different energy losses for  $^{53}\text{Mn}$  and  $^{53}\text{Cr}$ . (2) A movable position-sensitive detector (PSD) was placed on the focal plane of the Q3D to scan the beam spots (without absorber mounted in this step), and approximately located at the position for nuclides with a mass number of 53. (3) With the absorber mounted, a movable surface barrier detector (SBD) was used to search for and was located at the beam spot on the Q3D focal plane for recording the nuclide of  $^{53}\text{Mn}$ , and the magnet rigidity was optimized for transferring the nuclide of  $^{53}\text{Mn}$ . (4) A four anode gas ionization chamber with an entrance window of  $100 \text{ mm}\times 40 \text{ mm}$  was mounted at the accurately located position of the Q3D focal plane to replace the SBD, so as to further suppress the scattering interference and the remaining isobar interference of  $^{53}\text{Cr}$ , and identify  $^{53}\text{Mn}$ .

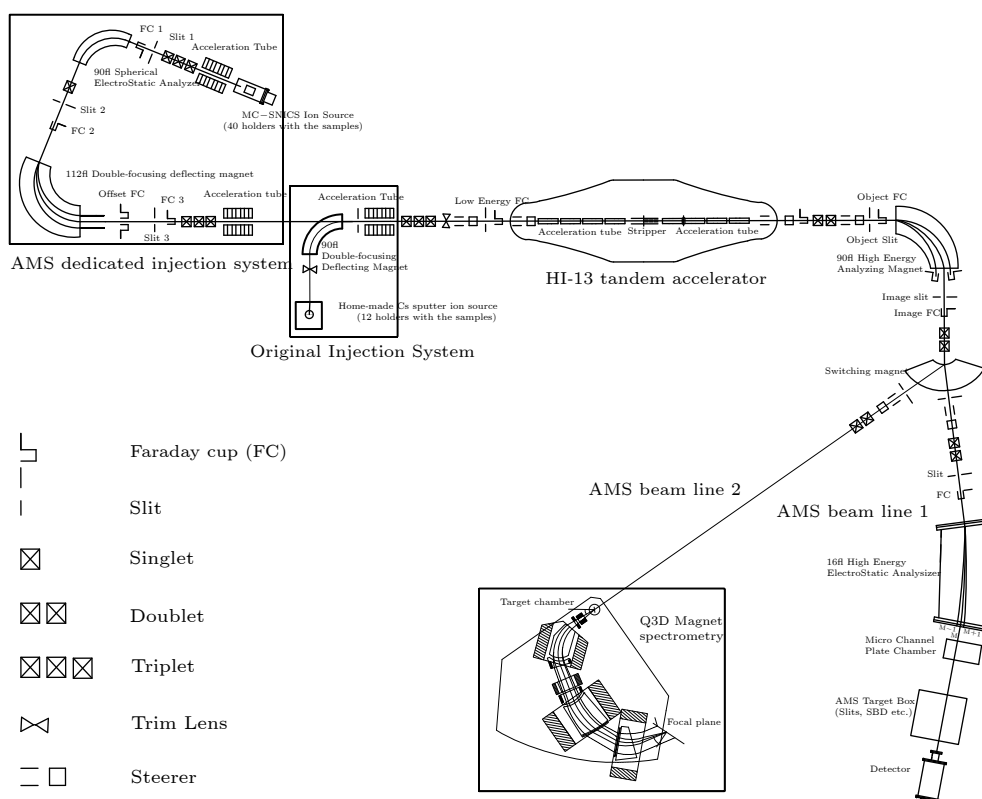
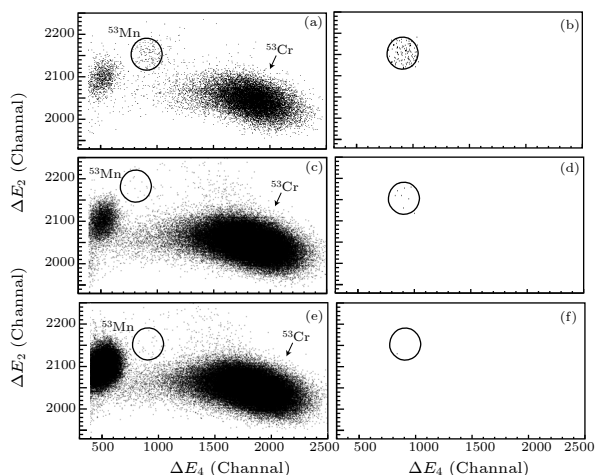


Fig. 1. Schematic diagram of the CIAE-AMS system.

After  $^{53}\text{Mn}^{11+}$  (and  $^{53}\text{Cr}^{11+}$ ) ions pass through the  $\text{Si}_3\text{N}_4$  membrane, ions with the charge state of  $17^+$ , which have an absorber stripping yield of 29%, were analyzed by the Q3D magnetic spectrometer. The peaks of  $^{53}\text{Mn}$  and  $^{53}\text{Cr}$  distributions were separated by about 10 cm on the focal plane and each had a width (FWHM) of 4 cm. By suitable choice of magnetic field, a suppression factor of more than  $10^4$  could be achieved for  $^{53}\text{Cr}$  ions, while 90% of the  $^{53}\text{Mn}$  ions were recorded by the detector.



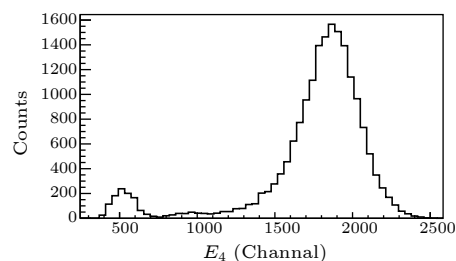
**Fig. 2.** Two-dimensional spectra of  $\Delta E_2$  vs  $\Delta E_4$  for two  $^{53}\text{Mn}$  standard and one blank samples ( $\Delta E_2$  and  $\Delta E_4$  are the energy loss signals from anodes 2 and 4, respectively): (a) for a sample with  $^{53}\text{Mn}/^{55}\text{Mn}=4.34 \times 10^{-10}$  with counting time 300 s, (c) for a sample with  $^{53}\text{Mn}/^{55}\text{Mn}=4.83 \times 10^{-12}$  with counting time 1800 s, (e) for a commercial blank with counting time 600 s. Here (b), (d) and (f) are for the same samples as (a), (c), (e), respectively, taken with coincidence gated at  $^{53}\text{Mn}$ . All samples used were as received without chemical treatment for the removal of Cr.

Commercial manganese dioxide ( $^{55}\text{MnO}_2$ ) was used for the test samples. Laboratory standards with  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios of  $4.34 \times 10^{-10}$  (CIAE ST1) and  $4.83 \times 10^{-12}$  (CIAE ST2) were produced by chemical dilution of Munich ST, [8]  $^{53}\text{Mn}/^{55}\text{Mn}=2.83 \times 10^{-9}$ , provided by the Munich group. All samples and standards used were as received without chemical treatment for the removal of chromium. Preliminary results for these samples are presented in Table 1. The results of the  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios were obtained by absolute measurements, based on the currents of  $^{55}\text{Mn}^{11+}$  ions measured in the offset Faraday cup upstream of the FC3 (Fig. 1) and the count rate of  $^{53}\text{Mn}$  recorded by the detector after software gate coincidence and background subtraction. The measured  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios for standards of  $10^{-10}$  and  $10^{-12}$  levels are 10% and 28% lower than their nominal ratios, respectively, after being normalized by the Munich ST. These discrepancies could be due to a number of factors: (1) uncertainties introduced in the preparation of CIAE standards ST1 and ST2, (2) unidentified losses of  $^{53}\text{Mn}$  ions for the low concentration

standards in the beam transport, (3) uncertainties in stripping yields (two times of stripping by the stripper in accelerator and the entrance window of  $\Delta E$ -Q3D, respectively), (4) improper  $^{53}\text{Cr}$  background subtraction, (5) insufficient counting statistics due to limited measurement time, especially for CIAE ST2 and blank samples.

In the  $\Delta E$ -Q3D system, the combination of the Q3D magnet and the ionization chamber brought about a very efficient suppression of interfering  $^{53}\text{Cr}$  ions. Figure 2 shows a plot of the energy loss of  $\Delta E_2$ , versus  $\Delta E_4$  for the CIAE ST1, ST2 standards and a commercial blank. For the standard CIAE ST1 ( $^{53}\text{Mn}/^{55}\text{Mn}=4.34 \times 10^{-10}$ ), the number of  $^{53}\text{Mn}$  counts can be reliably extracted with appropriate gates on various anode signals from the detector.

The suppression of  $^{53}\text{Cr}$  in the ionization chamber may also contribute to proper setting of software windows, which were optimized for the relatively high  $^{53}\text{Mn}$  content CIAE ST1 sample first, and then applied to the CIAE ST2 and commercial blank sample, as shown in Figs. 2(a) and 2(f). Nearly all  $^{53}\text{Cr}$  counts accumulated during the blank run can be discriminated with the software windows. Figure 2(f) shows that there is only one  $^{53}\text{Cr}$  event in the window, corresponding to a  $^{53}\text{Cr}$  suppression factor of more than  $10^4$  in the ionization chamber, according to the spectrum of  $\Delta E_4$  fractional energy loss of the CIAE ST1 sample shown in Fig. 3.



**Fig. 3.**  $\Delta E_4$  fractional energy loss spectrum of the CIAE ST1 sample.

In general, the total suppression factor of more than  $10^7$  for  $^{53}\text{Cr}$  can be obtained by using the  $\Delta E$ -Q3D detection system.

A procedure for AMS measurement of  $^{53}\text{Mn}$  was developed on the CIAE-AMS facility using a new  $\Delta E$ -Q3D detection method and encouraging results were obtained. The following aspects are identified for further improvement in the near future. (1) Further reduction of  $^{53}\text{Cr}$  interference is the key to the improvement in AMS measurement of  $^{53}\text{Mn}$ . Chromium may exist in the samples, sample holders, and ion source as an impurity or contaminant. Measures are being planned ranging from new chemical separation schemes to procedures in various stages of AMS measurements with the aim of further reducing  $^{53}\text{Cr}$  interference from the above-mentioned origins by at least two orders of magnitude. (2) Considering the forma-

tion of CrF being much more difficult than that of MnF, the use of MnF<sub>2</sub>, instead of MnO, as target material will bring about a reduction in <sup>53</sup>Cr interference by a factor of 3 in the process of ion extraction in the ion source.<sup>[8]</sup> Therefore, the sample form of MnF<sub>2</sub> will

be tried. (3) With the use of a new NEC cesium sputter ion source (spheroid ionizer), a higher yield of the extracted negative molecules and a better mass resolution will be achieved. The beam current MnO (or MnF) will be 3 times higher than the present one.

Table 1. Results of <sup>53</sup>Mn/<sup>55</sup>Mn ratios for CIAE standards and a commercial blank, normalized to the Munich standard. The background is estimated from the blank commercial MnO<sub>2</sub> sample.

Sample	Measured Ratio ( <sup>53</sup> Mn/ <sup>55</sup> Mn)	Normalized Ratio ( <sup>53</sup> Mn/ <sup>55</sup> Mn)	Nominal Ratio ( <sup>53</sup> Mn/ <sup>55</sup> Mn)	Measurement Time (s)	<sup>53</sup> Mn Counts
Munich ST	$2.49 \times 10^{-9}$	$2.83 \times 10^{-9}$	$2.83 \times 10^{-9}$	1380	1431
CIAE ST1	$3.47 \times 10^{-10}$	$3.94 \times 10^{-10}$	$4.34 \times 10^{-10}$	300	107
CIAE ST2	$3.33 \times 10^{-12}$	$3.78 \times 10^{-12}$	$4.83 \times 10^{-12}$	1800	6
Blank	$2.71 \times 10^{-12}$	\	≥ 10 ppm	600	1

Based on the above improvements, the detection limit of  $10^{-15}$  for the <sup>53</sup>Mn/<sup>55</sup>Mn ratio can be achieved with the ΔE-Q3D method in the near future.

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