In situ cosmogenic ^{53}Mn production rate from ancient low-denudation surface in tropic Brazil

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ABSTRACT

Preliminary results of ^{53}Mn measurements for seven Brazilian haematites are presented. The production rate of ^{53}Mn due to cosmic-ray induced disintegration of iron is estimated to be 103 ± 19 atoms $\text{g}(\text{Fe})^{-1} \text{yr}^{-1}$ at sea level and high latitude. This is consistent with the only previously published measurement. The muon contribution to the total ^{53}Mn production at the surface is estimated to be $\sim 7\%$. Cosmogenic-isotope dating employing ^{53}Mn is applicable to any rock/mineral type that contains iron as a major constituent, such as haematite, goethite, pyroxene and olivine. The method has the potential to extend the time scale of cosmogenic exposure dating to >10 Ma.

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1. Introduction

Terrestrial *in situ* cosmogenic nuclides have been invaluable tools in earth sciences to evaluate quantitatively various geomorphological parameters, such as exposure ages, erosion rates and burial ages [1]. Manganese-53, with its long half-life of 3.7 Ma (million years) [2], has the potential to extend the dating range to >10 Ma, and is an attractive choice as a partner of ^{10}Be in the study of long-term landscape evolution. In particular, with iron being the only primary target, the cosmogenic ^{53}Mn method is potentially useful in studies of desert landscape history, e.g., in Australia, where iron-rich regolith covers the surface and most other components, including quartz, are absent.

The cosmogenic ^{53}Mn method is yet to be fully explored, however, and to date only one paper has been published [3]. Technically, the challenge is to suppress sufficiently the stable isobar ^{53}Cr . Chromium is ubiquitous in rocks and suppression of this isobar requires careful sample chemistry and a sophisticated AMS detection system. Following the lead of the Munich group [4,5], a gas-filled magnet and associated gas-ionisation detector has been developed for ^{53}Mn detection at the Australian National University [6–8]. Effective separation of ^{53}Mn from ^{53}Cr is further enhanced by the high energies available from the 14UD accelerator. In paral-

lel, the sample preparation chemistry has been developed and refined.

In this paper we present results of our first measurements of terrestrial *in situ* cosmogenic ^{53}Mn concentrations in Brazilian haematites. The results are used to estimate the ^{53}Mn production rate that can be compared with the only previous measurement [3].

2. Method

2.1. Samples

Seven haematite samples were collected from undisturbed surfaces at three mining sites in Brazil (Table 1). All but UCM-65 were collected from the surface. Sample UCM-65 came from a depth ~ 1.5 m (equivalent to $\sim 400 \text{ g cm}^{-2}$) below UCM-62. The sites appear to have barely eroded since mid Tertiary. In particular, the erosion rate at the Urucum site is estimated to be $\leq 0.1 \text{ m Ma}^{-1}$, based on the $^{26}\text{Al}/^{10}\text{Be}$ ratio of samples from a coexisting quartz vein (J. Stone, unpublished data). Erosion rates for the Serra Pelada and Carajas sites are not independently known, but cosmogenic ^3He measurements of goethite (FeOOH) samples from nearby sites suggest that erosion rates are also $\leq 0.1 \text{ m Ma}^{-1}$.

Since all three sites are considered to have been constantly eroded for many millions of years, the ^{53}Mn concentrations in these samples have likely reached steady-state, which gives us

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Table 1

Sample locations, ICP-OES and AMS results for Brazilian haematites.

Sample	Location	Lat. (°S)	Alt. (m)	Sample weight (g)	Fe ^A (wt.%)	Mn ^A (ppm)	Mn carrier (mg)	⁵³ Mn/ ⁵⁵ Mn ^B (10 ⁻¹²)	⁵³ Mn (10 ⁶ atoms g(Fe) ⁻¹)
This study									
UCM-62 (250–500 μm)	Urucum mine, Brazil	19.1	850	17.2	70.5	17	1.992	216 ± 12	445 ± 25
UCM-62 (<250 μm)	Urucum mine, Brazil	19.1	850	39.1	72.5	17	2.000	651 ± 34	672 ± 36
UCM-65 (250–500 μm)	Urucum mine, Brazil	19.1	850	28.5	71.8	8.7	1.932	67.7 ± 4.6	78.9 ± 5.3
UCM-65 (500–850 μm)	Urucum mine, Brazil	19.1	850	26.2	74.3	8.6	2.068	62.9 ± 6.9	81.1 ± 8.9
SPEL-25	Serra Pelada, Brazil	6.0	680	5.8	71.2	331	-	53.4 ± 3.0	272 ± 15
SPEL-27a	Serra Pelada, Brazil	6.0	680	4.9	71.3	577	-	30.2 ± 3.4	267 ± 30
SPEL-27b	Serra Pelada, Brazil	6.0	680	4.9	71.3	577	-	29.3 ± 1.9	259 ± 17
N1-45-1	Carajas, Brazil	6.0	730	6.1	66.7	57	2.000	45.7 ± 2.7	288 ± 17
N1-45-2	Carajas, Brazil	6.0	730	19.7	73.4	65	2.038	80.3 ± 4.7	202 ± 12
N1-47	Carajas, Brazil	6.0	730	16.8	67.0	130	-	213 ± 11	453 ± 24
Gladkis [7]									
UCM-62	Urucum mine, Brazil	19.1	850	38.1	73.6	15	1.5	740 ± 50	643 ± 43

All samples were collected from the surface except UCM-65, which was collected at depth with shielding depth 401 g cm⁻². Letters “a” and “b” indicate duplicates. 1σ uncertainties, including counting statistics, blank corrections and 5% systematic uncertainties in quadrature, are shown.

^A Measured by ICP-OES. Typical uncertainties are <1% for Fe and <3% for Mn.

^B Measured by AMS. Ratios shown are corrected for blank and normalised relative to the standard.

opportunity to calibrate the ⁵³Mn production rate with independently-determined erosion rates. The Urucum samples are particularly suitable for this purpose; production rates are 25% higher than sea-level-high-latitude values, and high Fe (~70%) and low Mn (~10 ppm) contents guarantee high ⁵³Mn/⁵⁵Mn ratios, making AMS measurement relatively straightforward.

2.2. Chemistry

The chemical extraction of Mn from rock samples is similar to that established for meteorite samples [9] and has been described in our previous report [6]. In this study, however, extra procedures have been added to cope with the higher contents of Cr, Ti and Al that are found in geophysical samples. Briefly, crushed and sieved samples were dissolved in conc. HCl. Sufficient sample was dissolved to yield 2–3 mg of Mn. Where Mn concentrations were low, ⁵⁵Mn carrier was added. Iron was extracted into methyl-isobutyl ketone. The aqueous phase was dried, redissolved in 2 ml of 10 M HCl, and loaded on an anion exchange column (AG[®] 1-x8, 100–200#). The bulk Ti and Al were removed prior to this step with NaOH at pH = 4 and 12, respectively. The bulk of Cr and Ti and other metals such as Al, Na, K, Ca and Mg, were eluted with 18 ml of 10 M HCl. Manganese was then eluted with 40 ml of 7 M HCl. This column procedure was repeated three times, with high-purity distilled HCl produced in-house used in the final two passes. After repeated drying down and redissolution in HNO₃, manganese was precipitated as MnO(OH)₂ with NaClO₃. The precipitate was converted to MnO₂ by baking at 300 °C, and pressed into a copper holder with pure (99.99%) silver powder in a ratio of 1:2 (MnO₂:Ag) by weight.

Each pass through the column results in a factor of 100 reduction in Cr but an unavoidable Mn loss of ~10%. After three passes and the final precipitation step (further 15% loss) the yield is expected to be close to 60%, but in practice is 30–50% due to handling losses between steps. Chromium is suppressed by a factor of 10⁶, making residual ⁵³Cr contents <1 ng after the column chemistry. Some Cr is, however, added from the NaClO₃ (⁵³Cr ~1.1 ng), suprapur HNO₃ (~0.2 ng) and Ag (~0.7 ng), resulting in a residual ⁵³Cr content of ~2 ng, equivalent to 1 ppm in the final MnO₂. Assuming that the CrO⁻ and MnO⁻ ions are produced with similar efficiency, that the MnO⁻ current is 0.5 μA, and that transmission to the detector is 9%, the resulting ⁵³Cr¹¹⁺ flux would be 280,000 s⁻¹, which is in line with observation. For comparison, the highest ⁵³Mn/⁵⁵Mn ratio measured in the present work was 6 × 10⁻¹⁰ which corresponds to a ⁵³Mn flux of 170 s⁻¹.

2.3. AMS analysis

The ⁵³Mn measurements were performed using the 14UD Pelletron accelerator at the Australian National University [10]. Typical ⁵⁵MnO⁻ beam currents were 0.5–0.8 μA. Sequential gas and carbon-foil strippers in the high-voltage terminal gently dissociated the molecular ions before producing high-charge state atomic positive ions. Manganese ions with charge state 11+ were mass-energy-selected by the analysing magnet after the second acceleration. Switching between ⁵⁵Mn and ⁵³Mn was accomplished by changing the injection magnet, the accelerator voltage from 13.8 to 14.4 MV, and the electric field of the velocity (Wien) filter. Under these conditions, ⁵⁵Mn¹¹⁺ and ⁵³Mn¹¹⁺ ions have the same magnetic rigidity so that both can be transported to the detector station without change in magnetic components after acceleration. The ⁵⁵Mn¹¹⁺ beam current was measured by a retractable Faraday cup located immediately before the gas-filled magnet.

Separation and detection of the 170 MeV ⁵³Mn¹¹⁺ ions were performed with the gas-filled magnet and associated gas-ionisation detector that have been described previously [6,8]. Nitrogen gas at a pressure of 5 mbar filled the magnet. The magnetic field was set so as to suppress the ⁵³Cr beam by a factor of 200–400 while >90% of ⁵³Mn ions were accepted into the detector. The gas-ionisation detector provided four energy loss signals (ΔE_{1–4}) from the anode and a total energy signal from the cathode. Following Knie et al. [4,5], position and angle information are now obtained by splitting both the first and second anodes diagonally and taking separate signals from the left (L) and right (R) triangular sections rather than from proportional counter wires imbedded in the node plane as previously. Position is then (R – L)/(R + L) while ΔE = (R + L).

Counting times of 4 min were sufficient for all samples in this study. Measured ⁵³Mn/⁵⁵Mn ratios were normalised to a standard that had been prepared at Rutgers University from the Grant USNM 836 iron meteorite. The nominal ⁵³Mn/⁵⁵Mn ratio of 2.59 × 10⁻¹⁰ was measured by decay counting of the chromium X-ray line at 5 keV, following the electron-capture decay of ⁵³Mn. Note that the absolute ratio measured for the standard samples, i.e., the ratio of the ⁵³Mn count rate in the ionisation detector to the flux of ⁵⁵Mn¹¹⁺ ions as measured in the retractable Faraday cup, averaged 9.5 × 10⁻¹¹. This is only ~40% of the nominal ratio of 2.59 × 10⁻¹⁰. A similar shortfall was also observed in our previous study [6]. We checked for possible loss of ⁵³Mn events between the entrance of the gas-filled magnet and the detector using ⁵³Cr as a surrogate. Counting rates of ⁵³Cr were compared

with and without gas in the magnet. In the absence of gas, it was necessary to sum up the rates in the individual charge states. Any losses due to the presence of gas in the magnet were found to be minimal (<5%). At this stage, therefore, we do not have any clear explanation for this discrepancy between the measured and the nominal ratio of the standard samples. We will further investigate this through, e.g., interlaboratory measurements of the same standard samples.

Background contributions from ^{53}Cr ions were assessed using samples prepared from the ^{53}Mn -free carrier solution. These depended on the degree of gating during data analysis. Gates that accepted 95% or 70% of the ^{53}Mn events also accepted a background contribution from ^{53}Cr ions that corresponded to effective $^{53}\text{Mn}/^{55}\text{Mn}$ ratios of 2×10^{-11} and 5×10^{-12} , respectively (Fig. 1). For samples with $^{53}\text{Mn}/^{55}\text{Mn}$ ratios above 10^{-10} the generous (95%) gates could be used, but for lower level samples tighter (70%) gating was required in order to obtain a reliable estimate of the ^{53}Mn counts. A background contribution from ^{53}Cr ions was subtracted from the gated ^{53}Mn counts by scaling the background from the blank by the ratio between the sample and blank measurements of the total number of ^{53}Cr events detected in the ionisation chamber.

3. Results

3.1. ^{53}Mn results

The results of ^{53}Mn measurements for seven Brazilian haematites are shown in Table 1. The ^{53}Mn concentrations deduced from the duplicates of sample SPEL-27 and from the two grain-size fractions from UCM-65 are in excellent agreement. For the two grain-size fractions of UCM-62, however, one is only 2/3 of the other.

Since the higher value is consistent with our earlier measurement [7] (Table 1), we tentatively accept this value, but at present the reason for the discrepancy has not been ascertained.

3.2. ^{53}Mn production rate estimate

All samples measured in this study showed relatively high $^{53}\text{Mn}/^{55}\text{Mn}$ ratios ($\sim 10^{-11}$ – 10^{-10}), allowing ^{53}Mn concentrations to be determined with 5–7% precision, sufficient to permit an estimate of the production rate of ^{53}Mn produced *in situ* in iron at the earth's surface. A two-step approach was adopted. Since Urucum is the only site at which samples were obtained from both the surface and at depth, it was used to constrain both the fraction of production due to muons and the possible range of production rates. Data from all samples were then used to derive a better estimate of the production rate.

3.2.1. Urucum data analysis

The ratio of ^{53}Mn concentrations at depth and at the surface is independent of the production rate and depends only on the erosion rate and the fraction of muon production [11]. Based on the measured ratio, Fig. 2a shows that the muon fraction varies from 7% to 4% over the allowed range of erosion rates from 0 to 0.1 m Ma^{-1} . Despite the very low upper limit on the erosion rate, the ^{53}Mn production rate varies by a factor of two over the same range, from 98 to $205 \text{ atoms g(Fe)}^{-1} \text{ yr}^{-1}$, as shown in Fig. 2b.

3.2.2. Production rate estimate from all Brazilian samples

In the absence of a more precise measurement of the Urucum erosion rate, it is not possible to constrain further the production

Fig. 1. Plots of Position 1 (P1) vs ΔE_3 obtained for the standard (a–c) and blank samples (d–f). Four two-dimensional gates on different combinations of signals from the detector were applied to extract the ^{53}Mn counts from these spectra. Two sets of gates were used that accepted, respectively, 95% (red) and 70% (yellow) of the ^{53}Mn counts. Both ungated and gated spectra are shown, where the gated spectra are the results of applying three of the four gates. The fourth gate in the P1 vs ΔE_3 plane is shown. In this case, the background contribution for the standard is $\sim 5\%$ with the 95% gates (b), while it is $\sim 1\%$ with the 70% gates (c). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. The variations of (a) the fraction of muon production (f_{53}^{μ}) and (b) the production rate at sea level and high latitude (P_{53}^{slhl}) of *in situ* cosmogenic ^{53}Mn calculated from the Urucum sample data. The effects of $\pm 10\%$ changes to the ^{53}Mn half-life ($t_{1/2} = 3.7$ Ma) are also shown with dotted (3.3 Ma) and dashed (4.1 Ma) curves.

rate using the Urucum data alone. If, however, it is assumed that erosion rates at the Serra Pelada and Carajas sites are also $<0.1 \text{ m Ma}^{-1}$, as suggested by ^3He data from nearby sites, then the ^{53}Mn data from all three sites can be used to give a better estimate of the production rate and muon fraction. An optimisation procedure was employed that allowed the muon fraction and erosion rates at each site (within the range from 0 to 0.1 m Ma^{-1}) to vary so as to minimise the variation in the production rate from site to site. A ^{53}Mn half-life of 3.7 Ma, rock density of 3.5 g cm^{-3} , and attenuation lengths of 160 and 1500 g cm^{-2} for neutrons and

muons, respectively, were used in the calculation. Scaling factors were based on Stone [12].

The result of the optimisation procedure is shown in Fig. 3. The ^{53}Mn production rate at sea level and high latitude was determined to be $103 \pm 19 \text{ atoms g(Fe)}^{-1} \text{ yr}^{-1}$. Erosion rates of 0.01, 0.10 and 0.06 m Ma^{-1} for the Urucum, Serra Pelada and Carajas sites, respectively, were derived from the fit. The best-fit value of 6.8% for the muon fraction at sea level and high latitude falls between the values of 5% estimated by Schaefer et al. [3] and 10% proposed by Heisinger et al. [13,14].

4. Discussion

4.1. ^{53}Mn production rate estimate

The ^{53}Mn production rate obtained in this study is in excellent agreement with the only previous empirical value of $103 \pm 11 \text{ atoms g(Fe)}^{-1} \text{ yr}^{-1}$ determined from Antarctic dolerites [3]. It also agrees with a model value of $120 \pm 18 \text{ atoms g(Fe)}^{-1} \text{ yr}^{-1}$ [3], but differs by $\sim 70\%$ from another model estimate of $174 \text{ g(Fe)}^{-1} \text{ yr}^{-1}$ [13,14]. We believe, however, that the production rate derived here must be treated with caution. The derivation is crucially dependent on the assumption that the erosion rate at all three sites is less than 0.1 m Ma^{-1} . It is essential that this assumption be verified by measurements of cosmogenic ^3He at each site, and we have recently embarked on a program to carry this out.

4.1. Effect of ^{53}Mn half-life variation

The present uncertainty on the ^{53}Mn half-life is $\sim 10\%$ [2]. Fig. 2a and b shows that variations in the half-life of this magnitude do not have a dramatic effect on either the muon fraction or the production rate. A more precise value of the half-life would, however, be desirable.

5. Conclusion and outlook

The terrestrial *in situ* ^{53}Mn production rate has been estimated from ^{53}Mn measurements in seven haematite samples from tropical Brazil. A value of $103 \pm 19 \text{ atoms g(Fe)}^{-1} \text{ yr}^{-1}$ at sea level and high latitude and a muon contribution of $\sim 7\%$ were derived. The site-specific erosion rates derived by the optimisation were consistent with other cosmogenic nuclide data from the sites. The ^{53}Mn production rate obtained in this study is in good agreement with the previous measurement [3]. Both the production rate and the muon fraction depend crucially on erosion rates at the study sites, and better constraints from, for example, ^3He measurements are required.

In terms of methodology, a further reduction of the ^{53}Cr rate would be beneficial. There are two possibilities.

Since CrF^- formation is suppressed relative to MnF^- , a reduction by a factor of 10 in the ^{53}Cr rate should be achievable by using manganese fluoride (MnF_2) rather than MnO_2 in the ion source. (G. Korschinek, personal communication).

Use of high-purity NaClO_3 and Ag powder ($>99.99\%$), possibly combined with a modification of the column procedure using an organic-aqueous solvent [15], should further reduce Cr concentrations.

Finally, a series of iron- and silica-rich samples have been collected from the Pilbara region, Western Australia, for ^{53}Mn , ^{10}Be , ^{21}Ne and ^3He analyses, in order to extend previous studies of Australian aridity and landscape evolution [16–18]. Sample preparation for these samples is in progress.

Fig. 3. Optimisation result. The average ^{53}Mn production rate is shown as solid line with 1σ standard deviation (dotted line). Sample with asterisk (*) is from Gladkiss [7].

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