MANGANESE-CHROMIUM ISOTOPE SYSTEMATICS OF ORDINARY CHONDRITE FOREST VALE (H4) AND ENSTATITE CHONDRITE INDARCH (EH4).

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Introduction: The extinct short-lived radionuclide ^{53}Mn decays to ^{53}Cr with a half-life of 3.7 ± 0.4 Ma [1]. Variations in the abundance of ^{53}Cr recorded in meteorites indicate *in situ* decay of the once present ^{53}Mn [2]. Correlation of excess ^{53}Cr in different mineral phases of meteorites relative to the respective Mn/Cr ratio enables calculation of the ^{53}Mn/^{55}Mn ratio at the time of formation. This renders the Mn-Cr system a useful chronometer to date the formation of materials during the first ~20 Ma of Solar System history [3]. In this study, Mn and Cr concentrations and Cr isotope compositions were measured in whole rock and mineral separates of the ordinary chondrite Forest Vale (H4) and the enstatite chondrite Indarch (EH4) in order to facilitate the inter-calibration of the Mn-Cr and I-Xe system. Small aliquots of the separates will be analyzed for I-Xe within another study.

Samples and Preparation:

Forest Vale. An 8.639 g sample of Forest Vale was washed with ethanol, leached for 5 mins in 1N HNO$_3$ to remove potential surficial metal contamination, crushed, sieved and magnetically separated. From the non-magnetic fraction, a ~23 mg sub-sample was taken for whole rock analysis, whilst 90 mg from the magnetic fraction was processed. Density separation using methyl iodide was further performed on the non-magnetic fraction. Olivine, pyroxene and troilite were identified using a scanning electron microscope and ~10 mg sub-samples handpicked from the 40-80 μg fraction.

Indarch. Two fragments of Indarch (727 mg and 845 mg) were cleaned in ethanol, crushed and non-rusty chips separated for whole rock analysis. Using a differential dissolution procedure, the remaining material (867 mg) was treated with 0.5N and 9N acetic acid in order to ensure dissolution of sulfides [4]. Post leaching, the magnetic fraction was separated with a hand magnet from the silicate residue and further cleaned in ethanol. A 10 mg silicate sub-sample was handpicked from the residue.

Chemistry Separation. The fractions were digested on a hotplate using a 2:1 HF/HNO$_3$ mixture followed by 2-3 microwave procedures (ramp 15 mins, hold at 150 °C for 15 mins, 10 mins cool down). The method for chemical separation and purification of Cr was adapted from [5] and [6].

Mass Spectrometry: The Cr isotope measurements were carried out on a ThermoFinnigan Triton Thermal Ionization Mass Spectrometer using the procedure outlined in [6]. 1 uL of silica-gel was added sequentially in drops to single Re filaments, followed by 1-2 ug of sample in 1 uL of 3N HCl and then 1 uL of boric acid. Sample filaments were routinely heated at a rate of 150 mA min^{-1}. Each sample was loaded on 2 filaments and analyzed 2-3 times (see [6] for more details). The ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios were corrected for instrumental mass fractionation using the exponential law relative to ^{50}Cr/^{52}Cr = 0.051859 [7]. Reproducibilities of all individual (n=53) measurements of the NIST 3112a Cr standard for ε^{53}Cr and ε^{54}Cr (1ε = 1 part in 10,000) were 0.04 and 0.08 (2σ standard error), respectively. The external reproducibility (2σ standard error) of ε^{53}Cr and ε^{54}Cr for the mean of each analytical session is 0.10 and 0.12 respectively.

The ^{55}Mn/^{52}Cr ratios were determined using standard addition. Two mixed standards were prepared gravimetrically from 1000 ug ml^{-1} solutions in the ratios 0.5 (0.05 ppm Mn/0.1 ppm Cr) and 10 (0.1 ppm Mn/0.01 ppm Cr). Sample-standard mixtures were prepared gravimetrically to include 20 ppb of sample plus 0, 10, 20 or 40 ppb Cr standard. Mixtures were made up to 1 g with 0.4N HNO$_3$. The ^{52}Cr and ^{55}Mn intensities were measured and corrected for background using a Nu Plasma Multi Collector Inductively Coupled Plasma Mass Spectrometer.

Results and Discussion: The ^{55}Mn/^{52}Cr ratios versus ε^{53}Cr are shown for the ordinary chondrite Forest Vale (Fig. 1a) and the enstatite chondrite Indarch (Fig. 1b). The Mn-Cr data were obtained for olivine, troilite, metal and chondrules from Forest Vale. Analyses for whole rock and pyroxene separates are underway. Despite the relative long cosmic ray exposure age of Forest Vale (77 Ma [9]), the metal fraction shows the same ε^{54}Cr as olivine, troilite and chondrule separates that average to ε^{54}Cr = -0.23, typical of ordinary chondrites [5,6]. Because Fe is the main target for the production of cosmogenic Cr, this indicates that (i) the production of Cr isotopes due to cosmic ray irradiation is insignificant compared to the precision of the analyses and (ii) the analyzed Forest Vale sample was well shielded in the pre-atmospheric interior of the meteorite. This is similar for the preliminary

data of Indarch (exposure age ~12 Ma, [10]): metal, silicate and whole rock fractions all display identical ε^{54}Cr within analytical uncertainties, and therefore no correction for cosmogenic Cr was applied.

Forest Vale: Data for Forest Vale define a slope corresponding to a ^{53}Mn/^{55}Mn of 2.9 ($\pm$ 0.8) x 10^{-6} (Fig. 1a). This is identical within uncertainties to the initial ^{53}Mn/^{55}Mn of 2.42 ($\pm$0.31) x 10^{-6} obtained by [8]. However, our initial ε^{53}Cr (0.02 $\pm$ 0.06), is different to that reported by [8] (ε^{53}Cr = 0.35 $\pm$ 0.05). This is expected due to the second order mass bias correction that the latter authors used, which assumed ε^{54}Cr = 0. Ordinary chondrites, however, display an average ε^{54}Cr = -0.34 relative to the terrestrial standard [6]. Using the angrite D'Orbigny with a Pb-Pb age of 4564.42 ($\pm$0.12) Ma [11] and an initial ^{53}Mn/^{55}Mn ratio of 3.24 ($\pm$0.7) x 10^{-6} [12] as a time anchor results in a Mn-Cr age of 4563.9 (+2.5/-1.9) Ma. The choice of the angrite LEW 86010 [11] as a time anchor yields an age that is 0.8 Ma younger (4563.1 (+2.2/-1.5) Ma), but still overlaps within uncertainties. The obtained age is only marginally older than the Pb-Pb age from Forest Vale phosphates (4560.9 $\pm$ 0.7 Ma [13]). This suggests that the U-Pb and Mn-Cr systems reached their closure temperature almost simultaneously. The Forest Vale Mn-Cr age is concordant with that of the H4 chondrite Ste Marguerite reported by [5]. This emphasizes the ancient age and the close temporal relationship of the two H4 chondrites, which is also supported by other chronometers (e.g., Pb-Pb [13]).

Indarch: Figure 1b shows preliminary Mn-Cr data for the enstatite chondrite Indarch. Shown are data for the acetic acid leachate (9N), a handpicked silicate separate, a whole rock and metal fraction. The data defines a slope corresponding to an initial ^{53}Mn/^{55}Mn ratio of 5.7 ($\pm$ 1.2) x 10^{-6} and an intercept at ε^{53}Cr = -0.15 $\pm$ 0.10. This is a significantly steeper slope than reported elsewhere in the literature (2.8 x 10^{-6} [4] and 1.1 x 10^{-6} [14]). Taken at face value and using D'Orbigny as time anchor, the initial ^{53}Mn/^{55}Mn of 5.7 ($\pm$ 1.2) x 10^{-6} corresponds to the very old age of 4567.4 (+3.1/-2.2) Ma. The leachate of Indarch also displays a large negative anomaly in ^{54}Cr (ε^{54}Cr = -5.1 $\pm$ 2.4) suggesting the presence of nucleosynthetic anomalies in whatever phase was dissolved by this leaching. Similarly large negative anomalies in ^{54}Cr were seen in acetic acid leachates of Orgueil by [15]. A potential and at this stage speculative explanation for the different initial ^{53}Mn/^{55}Mn ratios is that our acetic acid leachate was dominated by an older generation of sulfides compared to those in previous studies. Wadhwa and co-worker [16] studied the Mn-Cr sys-

tem in single sulphide grains in Indarch. Their data showed a scatter that is consistent with varying degrees of re-equilibration and indicated initial ^{53}Mn/^{55}Mn ratios from 1.7 x 10^{-6} to 6.3 x 10^{-6}, consistent with the ^{53}Mn/^{55}Mn ratio of 5.7 ($\pm$ 1.2) x 10^{-6} obtained here. Overall this implies that the enstatite chondrite Indarch formed very early in our Solar System.
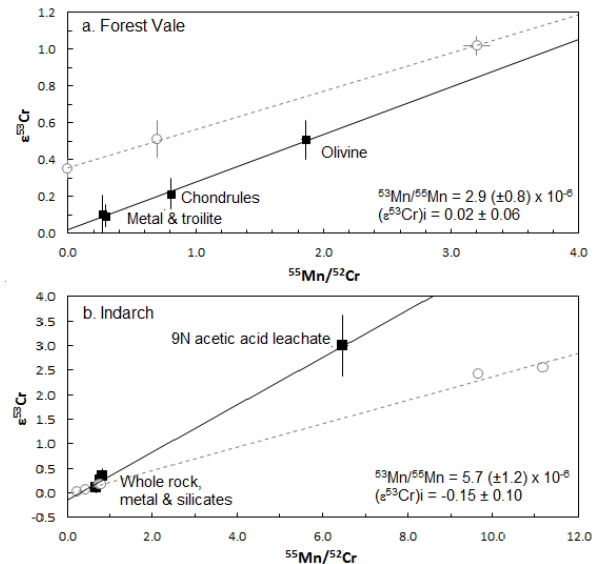

Figure 1. Manganese-chromium systematics (a) ordinary chondrite Forest Vale (H4). Closed squares = this study. Open circles = [8]. (b) enstatite chondrite Indarch (EH4). Closed squares = this study. Open circles = [4].

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