CHROMIUM ISOTOPE SYSTEMATICS OF MARTIAN METEORITES: IMPLICATIONS FOR THE DIFFERENTIATION HISTORY OF MARS. T.S. Kruijer[1], L.E. Borg, C.K. Sio and J. Wimpenny[2], [1]Lawrence Livermore National Laboratory, Nuclear and Chemical Sciences Division, 7000 East Avenue (L-231), Livermore, CA, 94550, USA (kruijer1@llnl.gov).

Introduction: Isotopic evidence suggests that Mars accreted and segregated its core very early, within only a few million years (Ma) after Solar System formation [*e.g.*, 1]. Although the early growth of Mars was followed by large-scale silicate differentiation, possibly involving a magma ocean, the exact timescales of these events remain uncertain [2,3]. For instance, Sm-Nd chronometry of martian meteorites indicates differentiation at ~60 Ma [2], whereas recent Hf-W chronometry suggests that large scale mantle differentiation may have occurred even earlier, possibly within ~20-30 Ma after Solar System formation [3]. The cause of this apparent discrepancy is currently not fully understood. Moreover, the Hf-W system only yields an upper time limit for the onset of silicate differentiation on Mars, making it unclear when these processes commenced.

Tighter bounds on the timescales of martian differentiation can potentially be inferred using the ^{53}Mn-^{53}Cr system (half-life: 3.7 Ma). This is because the relatively short half-life of ^{53}Mn limits the effective production of radiogenic ^{53}Cr variations to the first ~20 Ma of the Solar System. Thus, if Mars differentiated this early, and provided martian mantle sources had significantly fractionated Mn/Cr ratios, then ^{53}Cr variations may be detected in martian meteorites. In other words, finding such ^{53}Cr variations would provide unequivocal evidence for silicate differentiation on Mars within ~20 Ma. However, ^{53}Cr data have so far only been obtained for a few martian meteorites [4-6]. To more fully assess the differentiation history of Mars, we have initiated a Cr isotope study on a comprehensive suite of martian meteorites for which ^{182}W and ^{142}Nd were previously determined. Here we report our first results for several martian meteorites from distinct mantle sources, including four shergottites (Zagami, LAR 12095, NWA 7635, EET 79001) and Nakhla. These results do not only provide insights into the silicate differentiation history of Mars, but also into the volatile element budget and genetic heritage of the building blocks of Mars.

Methods: For the determination of Cr isotopic compositions, we used saved matrix aliquots of martian samples previously analyzed for Nd and W isotope systematics [3]. After chemical separation of Cr through several ion chromatography steps [5,6], Cr isotope compositions were determined on the Triton TIMS at LLNL largely following previously published methods [5,6]. Measured ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr were corrected for instrumental mass fractionation by internal normalization to ^{50}Cr/^{52}Cr = 0.00518, and are expressed as ε-unit (*i.e.* 0.01%) deviations relative to terrestrial reference materials (NIST NBS 979, BHVO-2).

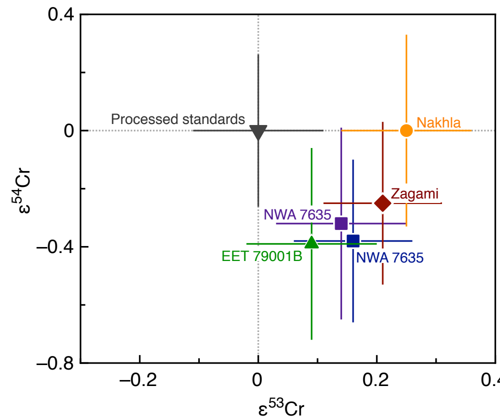

Fig. 1: Cr isotopic compositions of martian meteorites. Error bars denote external uncertainties (2s.d.).

Results: Consistent with prior work [4-6], we find that the shergottites and Nakhla exhibit small, but indistinguishable excesses in ε^{53}Cr (between *ca.* +0.1 and +0.3) relative to the terrestrial standards (Fig. 1), yielding a mean ε^{53}Cr of +0.16±0.04 (95% conf.) [+0.17±0.04 when Nakhla is also included]. Furthermore, small deficits in ε^{54}Cr are observed for the shergottites (mean ε^{54}Cr = –0.32±0.13), but not for Nakhla.

No evidence for ^{53}Cr heterogeneity in the martian mantle: The ε^{53}Cr of the martian meteorites investigated so far are indistinguishable, and our results therefore do not provide evidence for radiogenic ^{53}Cr variations within the martian mantle (Fig. 1). This may reflect (i) limited Mn/Cr variability amongst martian mantle sources resulting in unresolvable ^{53}Cr variations, and/or (ii) that silicate differentiation occurred after the effective lifetime of ^{53}Mn. Fully distinguishing between these possibilities is difficult given that the Mn/Cr of martian mantle sources are not *a priori* known. Nevertheless, martian meteorites exhibit varying Mn/Cr between *ca.* 0.5 and 4.5 [*e.g.*, 8]. Here we make the simple assumption that this range in Mn/Cr roughly reflects the variability within the martian mantle. Using the above range in Mn/Cr and an estimated bulk martian mantle Mn/Cr of ~0.74 [5], we calculated the expected ε^{53}Cr variations as a function of differentiation time (Fig. 2). This simple modelling illustrates that any Mn/Cr fractionation among martian mantle sources likely did not occur prior to ~10-20 Ma after CAI formation, otherwise the range in ε^{53}Cr would be larger than observed. Based on this, it seems likely that large-scale silicate differentiation on Mars only commenced after *ca.* 15 Ma post Solar System formation, in overall agreement with both Hf-W and Sm-Nd chronometry [2,3]. Although uncertainties are large, these results might also suggest that there was a time gap of several Ma between the end of Mars' accretion within ~10 Ma [1,3] and the onset of large scale silicate differentiation.

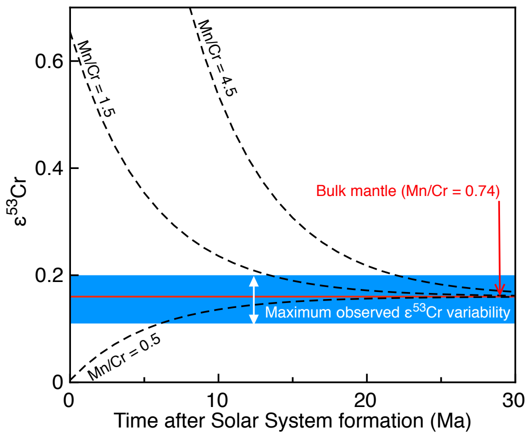

Fig. 2: Timescales of silicate differentiation on Mars inferred from Mn-Cr chronometry. Shaded area shows the maximum range in ε^{53}Cr observed for martian meteorites. Dashed lines denote the expected ε^{53}Cr of sources with variable Mn/Cr.

Origin of ε^{53}Cr excess in martian meteorites. Consistent with prior studies [4-6,9], our results demonstrate that martian meteorites have a well-resolved, uniform ε^{53}Cr excess of +0.17±0.04 relative to the Earth's mantle, that is likely representative of the bulk martian mantle. This ε^{53}Cr difference is very likely radiogenic in origin and thus reflects a Mn/Cr fractionation within the lifetime of ^{53}Mn, either induced during core formation or during volatility related processes.

As Cr is more siderophile than Mn [9], Mn/Cr fractionations can occur during core formation. Given that Mars' core probably formed within the lifetime of ^{53}Mn [1], core formation may thus in principle have left a ε^{53}Cr excess in the martian mantle relative to the bulk planet, as was also suggested for Earth [10]. However, unless entirely coincidental, the observation that the ε^{53}Cr and Mn/Cr inferred for the bulk martian mantle are very similar to those of ordinary and enstatite chondrites [5,6,9] suggests that any effect of core formation on the ε^{53}Cr of martian meteorites was likely minor.

The higher volatility of Mn (50% condensation temperature of 1158 K) relative to Cr (1298 K) may allow volatile-governed processes to fractionate Mn/Cr, thereby producing an excess of radiogenic ^{53}Cr in martian samples. Thus, ε^{53}Cr differences may provide a proxy for early volatile-element depletion in planetary bodies. In particular, previous Mn-Cr studies showed that, despite some scatter, bulk planets and chondrites define a Mn-Cr isochron with a slope corresponding to the age of the Solar System [5,6,8,10]. This points to a disk wide, volatility–induced Mn/Cr fractionation early in Solar System history. Both the Earth's mantle and martian meteorites plot on this isochron. Note that the bulk martian mantle plots together with ordinary and enstatite chondrites, at more elevated Mn/Cr than the Earth's mantle. This observation is consistent with the fact that bulk Mars is enriched in volatile elements relative to Earth [11]. It is therefore concluded that the ε^{53}Cr difference between Mars and the Earth is most readily explained by volatility-induced Mn/Cr fractionation in the beginning of Solar System history.

Nucleosynthetic ε^{54}Cr anomaly in Mars. Shergottites exhibit a uniform deficit in ε^{54}Cr (Fig. 1). Variations of ε^{54}Cr in Solar system materials are attributed to a heterogeneous distribution of presolar matter among Solar System bodies [*e.g.*, 12] and can be used to assess their genetic links. The shergottites analyzed here exhibit a mean ε^{54}Cr of –0.32±0.13 (95% conf.), nominally somewhat lower, but still indistinguishable from prior analyses [6,12]. These data indicate that Mars probably has a ε^{54}Cr deficit between that of enstatite and ordinary chondrites, consistent with isotope systematics observed for O and Mo, and possibly for Nd [3,12,13]. Overall, these findings imply that (i) the isotope composition of Mars can likely be reproduced using a mixture of enstatite and ordinary chondrite-like material, and (ii) that the feeding zone of Mars was on average genetically distinct from that of the Earth.

Finally, we point out that the ε^{54}Cr value of Nakhla of 0.00±0.33 overlaps with the terrestrial composition and appears slightly elevated compared to the shergottites (Fig. 1). Although this is currently not resolved, this observation might point to the existence of ^{54}Cr variations within the martian mantle. More Cr isotope analyses are underway to investigate this possibility.

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