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Chromium isotope systematics of martian meteorites: Implications for Mars' early differentiation

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CHROMIUM ISOTOPE SYSTEMATICS OF MARTIAN METEORITES: IMPLICATIONS FOR MARS' EARLY DIFFERENTATION. 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]. The early growth of Mars was followed by large-scale silicate differentiation, possibly involving a magma ocean, but the exact timescales of these events remain debated [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 less than ~20-30 Ma after Solar System formation [3]. The cause of this apparent discrepancy is currently not fully resolved. Moreover, the Hf-W system only yields an upper time limit for the onset of silicate differentiation on Mars, and it thus remains unclear when these processes commenced.

Tighter bounds on the timescales of Mars' early differentiation can potentially be inferred using the ^{53}Mn-^{53}Cr system (half-life: 3.7 Ma). This is because the relatively short held-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 large enough Mn/Cr variations exist amongst martian mantle sources, then ^{53}Cr variations may be detected in martian meteorites. Finding such ^{53}Cr variations would provide unequivocal evidence for silicate differentiation on Mars when ^{53}Mn was still alive. However, ^{53}Cr data have so far only been obtained for a few martian meteorites [4-6]. To more fully assess the extent and origin of ^{53}Cr variations on Mars, we therefore initiated a Cr isotope study on a comprehensive suite of martian meteorites. Here we report our first results for several martian meteorites form 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 volatile element budget and genetic heritage of Mars' building blocks.

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 previous studies [5,6]. Each sample was measured three times on individual filaments (~500 ng Cr each), and a single run consisted of 21 blocks of 20 cycles using amplifier rotation [7]. Measured ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr were corrected for instrumental mass fractionation by internal normalization to ^{50}Cr/^{52}Cr = 0.0051859, and are expressed as ε-unit (*i.e.* 0.01%) deviations relative to terrestrial reference materials (NIST NBS 979, BHVO-2). The precision of the Cr isotope measurements was assessed through measurements of terrestrial standards and a Monte Carlo approach.

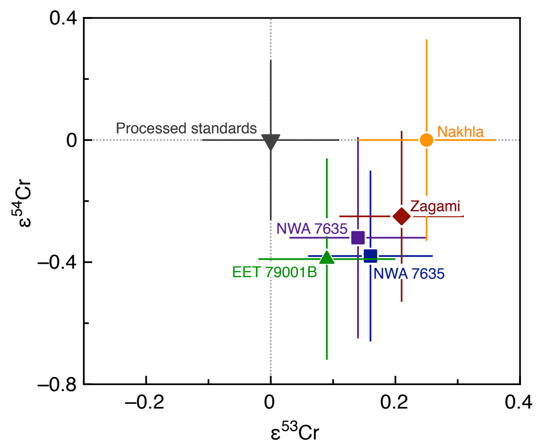

Fig. 1: Cr isotopic compositions of martian meteorites. Error bars denote external uncertainties (2s.d.).

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 that (i) Mn/Cr variability amongst martian mantle sources is too restricted to generate resolvable ^{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]. Making a simple assumption that this range in Mn/Cr roughly reflects the variability within the martian mantle, the expected ε^{53}Cr variations as a function of differentiation time were calculated (Fig. 2). This simple modelling illustrates that any Mn/Cr fractionation among martian mantle likely did not occur earlier than ~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 ~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 [1] and the onset of large scale silicate differentiation.

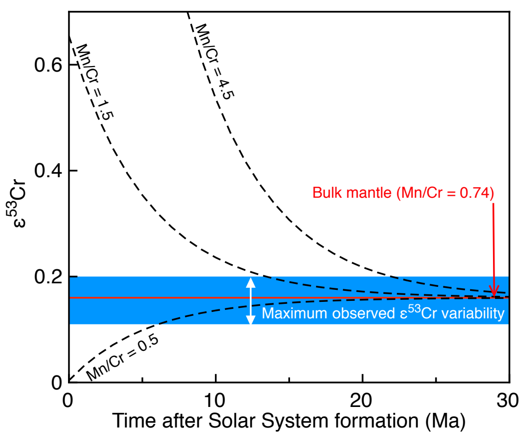

Fig. 2: Timescales of silicate differentiation on Mars inferred from Mn-Cr chronometry. Shaded area shows the maximum range in ε^{53}Cr observed for martian meteorites. Dashed lines denote the expected ε^{53}Cr of sources with variable Mn/Cr.

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. 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.

Because Cr is more siderophile than Mn [10], Mn/Cr fractionations can occur during planetary core formation. Given that Mars' core most likely 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 has also been suggested for Earth [11]. Nevertheless, given that the Mn/Cr and ε^{53}Cr of martian meteorites are very similar to chondrites [5,6,9], the effect of core formation on the ε^{53}Cr of martian meteorites was likely relatively small.

Due to the higher volatility of Mn (50% condensation temperature of 1158 K) relative to Cr (1298 K), volatile-governed processes lead to fractionated Mn/Cr, and following decay, radiogenic ^{53}Cr variations. Thus, ε^{53}Cr variations provide a proxy for early volatile 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 [5,6.9, 11], pointing 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, where martian meteorites on average plot 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 less depleted in volatile elements than the Earth [12]. The new ε^{53}Cr data presented here are fully consistent with these findings, and we conclude that the ε^{53}Cr difference between Mars and the Earth is most readily explained by a volatility-induced Mn/Cr fractionation right at the beginning of Solar System history.

Nucleosynthetic ε^{54}Cr anomaly in Mars. Besides ε^{53}Cr excesses, shergottites also exhibit a uniform deficit in ε^{54}Cr (Fig. 1). Variations in ε^{54}Cr are attributed to a heterogeneous distribution among meteorites and bulk planets [*e.g.*, 13] and can be used to assess genetic links between planetary bodies. 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 [6,13]. 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 [3,13,14]. 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 overlaps with the terrestrial composition and appears slightly elevated compared to the shergottites (Fig. 1). Although this is currently not fully 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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