COUPLED ^{142}Nd–^{182}W EVIDENCE FOR EARLY CRUST FORMATION ON MARS.

T.S. Kruijer[1], T. Kleine[1], L. Borg[2], G.A. Brennecka[1], M. Fischer-Gödde[1], A.J. Irving[3], A. Bischoff[1], C.B. Agee[4]. [1]Institut für Planetologie, University of Münster, Wilhelm-Klemm-Str. 10, 48149, Münster, Germany. [2]Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, Livermore CA, USA. [3]Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195, USA. [4]Institute of Meteoritics, University of New Mexico Albuquerque NM, USA. (thomas.kruijer@wwu.de).

Introduction: Mars likely represents one of the earliest-accreted larger planetary bodies of our solar system [e.g., 1,2], but the processes and timescales involved in the early differentiation of Mars remain debated [e.g., 2]. Insights into the nature of Martian mantle domains can be gained using the extinct ^{182}Hf-^{182}W ($t_{1/2}$ = 8.9 Myr) and ^{146}Sm-^{142}Nd ($t_{1/2}$ = 103 Myr) chronometers, and when combined, these chronometers may distinguish isotopic variations caused by (i) metal-silicate separation and (ii) silicate differentiation. For instance, the formation of the source regions of shergottites is thought to reflect large-scale differentiation associated with crystallisation of a Martian magma ocean [e.g., 2-4]. If this is the case, then coupled ^{142}Nd-^{143}Nd systematics of the shergottites would indicate that magma ocean crystallisation occurred at ~60 Ma after solar system formation [5] or, alternatively, between ~30 Ma and ~100 Ma [6]. Because core formation on Mars—based on Hf-W systematics—probably took place well within ~10 Ma after CAI formation [1,2], this would imply an extended period of magma ocean solidification. However, such a long time interval is inconsistent with recent thermal models suggesting mantle solidification in less than 5 Ma after accretion and core formation [e.g., 4]. If correct, then either core formation was later than currently thought or the isotopic signatures of the shergottites do not reflect primordial, large-scale differentiation on Mars.

To address these issues, we obtained high-precision ^{182}W and ^{142}Nd data for a suite of Martian meteorites, including different groups of shergottites, the orthopyroxenite ALH 84001 and polymict breccia NWA 7034. The last two samples are particularly important because they derive from strongly enriched and/or crustal sources and as such may provide insights into the earliest differentiation of Mars not recorded in the more common shergottites.

Analytical methods: Martian meteorite samples (~0.2-2.5 g) were digested in HF-HNO$_3$ (2:1) and W and Nd were then separated by ion exchange chromatography [5,7]. Tungsten isotope compositions were measured on a ThermoScientific® Neptune *Plus* MC-ICPMS at Münster, and Nd isotope compositions on a ThermoScientific® Triton TIMS at LLNL [5]. The data are reported in ε-units as the parts per 10^4 deviation from terrestrial standard values.

Results: Enriched shergottites define a uniform ε^{182}W excess of ~0.37, while depleted shergottites show larger ε^{182}W excesses between ~0.88 and ~1.46.

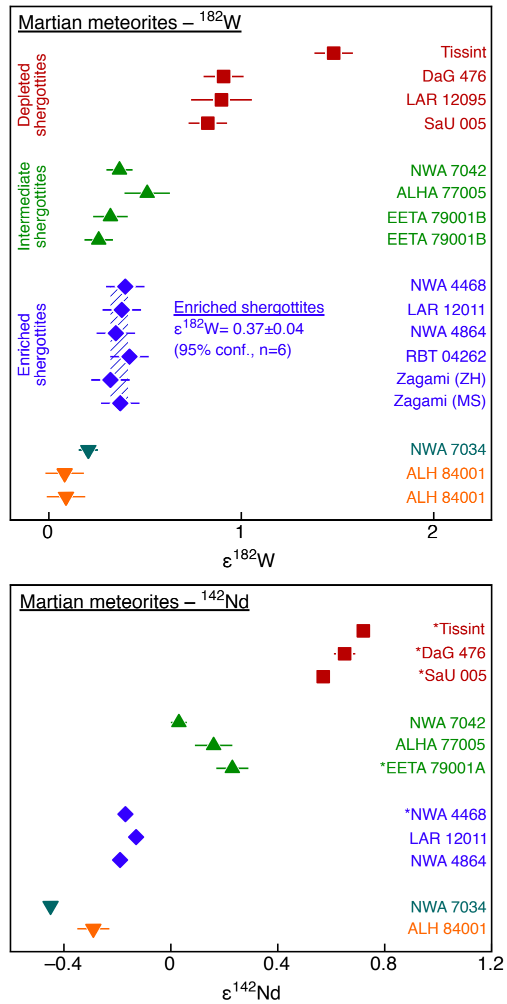

Fig. 1: ^{182}W and ^{142}Nd data for Martian meteorites from this study and from [5] (marked with *).

Different groups of shergottites also show distinct ε^{142}Nd, consistent with [5,6,8,9]. Notably, both ALH 84001 and NWA 7034 have distinctly lower ε^{182}W and ε^{142}Nd than any of the shergottites and both show the lowest ε^{182}W and ε^{142}Nd yet measured for any Martian material. Thus, compared to previous studies [5,6,8-11], our new high-precision isotope data greatly extend the ^{142}Nd and ^{182}W variations observed among Martian meteorites.

Discussion: The Martian samples exhibit a general correlation in ε^{182}W *vs.* ε^{142}Nd space (Fig. 2), indicating that silicate differentiation, and not core formation,

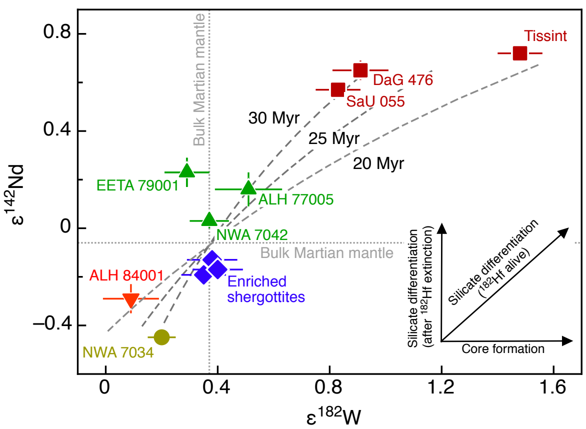

Fig. 2: ε^{142}Nd *vs.* ε^{182}W data of Martian meteorites. Dashed lines connect enriched and depleted mantle endmember compositions for mantle differentiation at 20, 25 and 30 Ma after CAI formation. Only EETA79001 plots off the trend, perhaps reflecting that ^{142}Nd and ^{182}W were measured on different lithologies (A *vs.* B) of this meteorite.

is the dominant cause of the observed ^{182}W variations. However, the ^{142}Nd–^{182}W systematics of all samples cannot be explained by a single differentiation event. Coupled ^{142}Nd-^{143}Nd systematics of shergottites indicate that their source regions formed relatively 'late' at ~60 Ma after CAI formation [5], but generating the observed ^{182}W variations at such a late time is difficult because ^{182}Hf was already almost extinct. For instance, the high ε^{182}W of the depleted shergottites would be difficult to explain by differentiation at ~60 Ma after CAI formation, unless an extreme Hf/W fractionation is invoked. Moreover, the low ε^{182}W of ALH 84001 and NWA 7034 indicates derivation from enriched sources with low Hf/W, but generating significant ^{182}W variations in such low Hf/W environments is not possible at ~60 Ma after CAI formation, when ^{182}Hf is nearly extinct. Also, models in which the shergottite source regions were established during magma ocean crystallisation imply that the ^{142}Nd and ^{182}W signature of the enriched shergottites represents that of late-stage liquids of the magma ocean. However, this is difficult to reconcile with the lower ε^{182}W (and ε^{142}Nd) of ALH 84001 and NWA 7034 compared to enriched shergottites (Fig. 1,2), because the residual liquid of a magma ocean likely has the lowest ε^{182}W (and ε^{142}Nd) of any Martian sample.

A possible scenario for the early evolution of Mars is that the Martian magma ocean crystallised earlier than previously thought [e.g., 4], and/or that an early crust formed after remelting of a then already crystallised mantle. Such a melting model has been proposed for NWA 7034 (NWA 7533) [12]. Using this melting model the isotopic signatures of both NWA 7034 and ALH 84001 are reproduced for differentiation between ~20 and ~30 Ma after CAI formation. Furthermore, the ^{182}W-^{142}Nd composition calculated for the corresponding depleted reservoir is similar to those measured for depleted shergottites. Similar results are obtained if the isotopic data are modelled as resulting from the crystallisation of a Martian magma ocean; the full range of observed ^{182}W and ^{142}Nd compositions of NWA 7034 and ALH84001 as well as depleted shergottites is again obtained for differentiation around ~20-30 Ma after CAI formation. It is noteworthy that a similar differentiation age is obtained from coupled ^{142}Nd-^{182}W systematics of the nakhlites, indicating that Mars underwent a major period of differentiation at ~20-30 Ma after solar system formation. Such an early time of crust formation and/or magma ocean crystallisation would be in very good agreement with Mars' early accretion and core formation age [1,2], and would alleviate the need for a long-lived magma ocean to explain the isotope systematics.

However, such early differentiation seems inconsistent with the ~60 Ma age for the formation of the shergottite sources [e.g., 5]. This implies that formation of the shergottite source regions cannot be attributed to the crystallisation of a global magma ocean but rather reflects a second, later differentiation event. The nature of this event and whether it had an endogenic (e.g., due to prolonged magmatic activity in the Martian mantle) or exogenic (e.g., due to an impact) origin is unclear at present. We note that this ~60 Ma event is not obvious in the ^{182}W data, perhaps because it occurred at a time when ^{182}Hf was already extinct in the Martian mantle. However, more work is needed to fully assess the significance of the combined ^{182}W-^{142}Nd data of the shergottites.

Conclusions: Coupled ε^{182}W–ε^{142}Nd systematics of Martian meteorites suggest that magma ocean crystallisation and crust formation on Mars occurred earlier than ~30 Ma after solar system formation. Such an early differentiation time is in better agreement with Mars' early accretion and core formation within 10 Ma after CAI formation. This implies that the ~60 Ma formation age inferred for the shergottite sources may not reflect the time of global differentiation on Mars.

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