HIGH-PRECISION $^{182}\text{W}$ MEASUREMENTS OF MARTIAN METEORITES FOR CONSTRAINING THE EARLY EVOLUTION OF MARS. T.S. Kruijer$^1$, T. Kleine$^1$, L. Borg$^2$, M. Fischer-Gödde$^3$, A.J. Irving$^3$, A. Bischoff$^4$, C.B. Agee$^5$. $^1$Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Kleffm-Strasse 10, D-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. (Correspondence: thomas.kruijer@wwu.de).

**Introduction:** The earliest evolution of Mars can be investigated through isotopic analyses of Martian meteorites. In particular, the short-lived Hf-W chronometer ($t_{1/2} = 8.9$ Myr) can place strong constraints on the core formation and early (silicate) mantle differentiation history of Mars [1-3]. Metal-silicate separation fractionates lithophile Hf from siderophile W, and provided that core formation on Mars occurred within the lifetime of $^{182}$Hf, may lead to a radiogenic $^{182}$W signature within its silicate mantle. Moreover, as a consequence of silicate differentiation processes, Hf/W fractionation may occur within the Martian mantle itself, potentially leading to $^{182}$W variability among Martian meteorites. Finally, the $^{182}$W signatures of Martian samples may in part reflect the addition of late-accreted material after core formation on Mars was complete [4]. Small, but resolved $^{182}$W anomalies relative to the modern terrestrial mantle in the Moon [5] as well as in some terrestrial rocks [6] have recently been interpreted to be the result of late accretion.

Many Martian meteorites indeed exhibit $^{182}$W excesses [1-3], demonstrating that Hf and W were fractionated in their source regions within the first ~60 Myr of solar system history (Fig. 1,2). Collectively, these anomalies likely reflect the combined effects of core formation and silicate differentiation processes within the Martian mantle. Although some Martian meteorites such as the nakshites, Chassigny, and NWA 8159 show large $^{182}$W excesses up to $+3.5$, analyzed shergottites show relatively smaller $^{182}$W anomalies of $+0.2$ to $+0.9$ (Fig. 1) ($e^{182}$W is the parts per 10$^3$ deviation from the $^{182}$W/$^{184}$W of the present-day bulk silicate Earth). The latter has been taken as evidence that (i) the shergottite source represents that of the bulk Martian mantle, and (ii) its slightly radiogenic $e^{182}$W is a signature of core formation on Mars [1-3,7,8]. Nevertheless, the available data for shergottites also hint at small $^{182}$W variability among different subgroups of shergottites (Fig. 1,2). However, the resolution of the available data is insufficient to fully resolve the anticipated small variations. Moreover, until now, the possible superimposed effects of late-accretion have not been assessed for most samples. Understanding the $^{182}$W variability in full detail is crucial for distinguishing among the processes highlighted above, and ultimately, for developing a chronology for the earliest differentiation history of Mars. We thus initiated a high-precision W isotope study of Martian meteorites with the aim to assess the full extent of $^{182}$W variability within Mars. Here we report preliminary results for Martian samples NWA 7034 and NWA 4468.

**Samples & analytical methods:** NWA 7034 (referred to as ‘Black Beauty’ by some) represents a geochemically enriched crustal rock with unique oxygen isotope values and an order-of-magnitude higher water content than in most other Martian meteorites [12]. It is also the only known polymict breccia from Mars [13]. NWA 4468 is a more typical, enriched, olivine-bearing shergottite. The analytical techniques for sample digestion, chemical separation of W, and W isotope ratio measurements by MC-ICPMS followed our previously developed procedures [14]. In brief, ~0.1-0.2 g sample powders were dissolved in HF-HNO$_3$ (130-150 °C, 2-3d). Tungsten was then separated from the sample matrix using a two-stage anion exchange chromatography in HCl–HF media. Tungsten isotope compositions were determined with a ThermoScientific® Neptune Plus MC-ICPMS at the Institut für Planetologie of the University of Münster. A single W isotope measurement comprised 200 cycles (4.2s each) and consumes as little as 30 ng W. Instrumental mass bias was corrected by internal normalization to $^{186}$W/$^{184}$W = 0.92767 (denoted ‘6/4’) using the exponential law. The accuracy and precision of our analytical routine were
assessed by repeated analyses of terrestrial rock standards (BHVO-2, BCR-2), separate digestions of which were processed through the full chemical separation procedure and analyzed alongside the Martian samples. The mean \(\varepsilon^{182}\text{W} (6/4)\) obtained for single analyses of terrestrial rock standards is \(\varepsilon^{182}\text{W} = 0.03\pm0.04\) (95% conf., \(N=10\)), demonstrating that our analyses are accurate (Fig. 2). The external reproducibility of a single W isotope measurement is \(10\varepsilon\) (2s.d.).

**Results:** The enriched shergottite NWA 4468 was analyzed three times and shows a positive \(\varepsilon^{182}\text{W}\) value of \(+0.42\pm0.10\) (2s.d., \(N=3\)). NWA 7034 exhibits a similar \(\varepsilon^{182}\text{W}\) excess of \(0.32\pm0.28\) (2s.e.). The poorer precision of the latter data point reflects that less W was available for analysis. The new \(\varepsilon^{182}\text{W}\) data obtained here are in good agreement with but more precise than most data previously obtained for shergottites (Fig. 2).

Fig. 2: \(\varepsilon^{182}\text{W}\) data from for shergottites and terrestrial standards from this study (filled symbols) and the literature [1-3] (open symbols).

**Discussion:** Tungsten isotope variations in the samples analyzed here may be caused by processes related to (i) metal-silicate separation, (ii) silicate mantle differentiation, or (iii) late-accretion. The magnitude of meteorite contamination can be assessed using HSE abundances of Martian samples. Using reported Ir and W concentrations for NWA 4468 and NWA 7034 [13,15], and assuming a composition of late-accreted material identical to that inferred for some lunar impact rocks [16], we infer by mass balance that late accretion would have lowered the \(\varepsilon^{182}\text{W}\) of both samples by <0.03. Thus, the effects of late-accretion are likely to be negligible. Nevertheless, late accretion-induced \(^{182}\text{W}\) shifts may become significant for samples with low W content, but high HSE abundances.

Coupled \(^{142}\text{Nd}-^{182}\text{W}\) systematics provide insights into the nature of Martian mantle domains, and may help to distinguish between isotopic variability caused by metal-silicate separation and silicate differentiation (Fig. 1). Despite large \(^{142}\text{Nd}\) variations—which must result from silicate differentiation—the shergottite sources seem relatively uniform in \(\varepsilon^{182}\text{W}\) [e.g., 7]. The new W data obtained here for NWA 4468 is in agreement with this observation. This is consistent with the \(^{142}\text{Nd}\) model age of 4504±5 Ma for the shergottites [11], indicating formation after \(^{182}\text{Hf}\) was almost extinct. Only poikilitic shergottite ALH87005 appears to have a slightly elevated \(\varepsilon^{182}\text{W}\) of \(<0.9\) [3]; we are currently re-analyzing its W isotope composition to assess whether it is distinct from other shergottites. Nevertheless, the \(\varepsilon^{182}\text{W}\) data for orthopyroxenite ALH84001 [3] and NWA 7034 (this study) seem consistent with the shergottite data, corroborating the interpretation that the mean \(\varepsilon^{182}\text{W}\) of \(0.42\pm0.11\) (95% conf., \(N=19\)) obtained for the shergottites may be representative of the bulk Martian mantle. It further suggests that silicate differentiation within the shergottite source regions that led to \(^{142}\text{Nd}\) heterogeneity did not introduce significant \(^{182}\text{W}\) variability. Thus, the uniform \(^{182}\text{W}\) excess defined by the shergottites likely is a signature of core formation alone.

**Conclusions and outlook:** New higher precision \(^{182}\text{W}\) data for two Martian samples are in agreement with earlier work on shergottites and suggest that the shergottite source regions have uniform \(^{182}\text{W}\) and may be representative of the bulk Martian mantle. However, more data on enriched, intermediate as well as depleted shergottites are needed to ascertain whether there is significant \(^{182}\text{W}\) variability among these subgroups, and if so, whether such variations are coupled with \(^{142}\text{Nd}\) variations. Such information will provide crucial new constraints on the accretion, core formation, and early differentiation history of Mars.

**References:**