**HOW RAPIDLY DID MARS ACCRETE? CONSTRAINTS FROM HF, TH, AND W IN CHONDRITES.** T. Kleine[1], S. Aciego[1], B. Bourdon[1], F. Nimmo[2] and J. Zipfel[3], [1]Institute for Isotope Geochemistry and Mineral Resources, Dept. of Earth Sciences, ETH Zurich, Clausiusstrasse 25, 8092 Zürich, Switzerland (kleine@erdw.ethz.ch), [2]Dept. of Earth and Planetary Sciences, University of California Santa Cruz, 1156 High St, Santa Cruz, CA 950645, USA, [3]Forschungsinstitut und Naturmuseum Senckenberg, Frankfurt am Main, Germany.

**Introduction:** Mars may have formed via runaway growth within ~1 Myr after the start of the solar system [1] or its accretion may have been more protracted and involved large impacts, similar to the histories of the larger terrestrial planets [2]. Determining which of these models is correct is critical for understanding the early evolution of Mars. For instance, if Mars accreted within the first Myr of the solar system, heating by decay of $^{26}$Al would have been a major heat source causing melting and early differentiaton. In contrast, if accretion of Mars was more protracted, then the energy brought in by large impacts would have been another important heat source.

The decay of $^{182}$Hf to $^{182}$W (half-life ~9 Myr) is well-suited to date core formation in planetary objects [3]. Application of Hf-W chronometry to Mars can therefore distinguish between the two aforementioned scenarios for the formation of Mars, provided Hf-W ages can be determined with sufficient precision. Reported Hf-W ages for Mars however range from <1 Myr up to ~12 Myr [4-7]. This range in ages is almost entirely due to different assumptions regarding the Hf/W ratio of the bulk Martian mantle. Here we present an improved determination of the Hf/W ratio of the bulk Martian mantle and use this to better constrain the Hf-W age of Mars.

**Methods:** *Determining the Hf/W ratio of the bulk Martian mantle.* Available trace element data for Martian meteorites suggest that Th and W have similar incompatibilities. The Th/W ratio of the Martian mantle (1.00±0.18, based on a compilation of Th and W abundances in Martian meteorites) can thus be used to infer its Hf/W ratio, provided its Hf/Th ratio is known. It is generally assumed that refractory lithophile elements (such as Th and Hf) occur in chondritic relative proportions in planetary mantles. The available Hf and Th data for chondrites however reveal variations in the Hf/Th ratios among carbonaceous chondrites [8]. Little data exist for ordinary chondrites. These variations translate to large uncertainties in the estimated Hf/W ratio of the bulk Martian mantle and hamper a reliable determination of Hf-W ages for Mars. To better constrain the Hf/Th ratios in chondrites and the Hf/W ratio of the bulk Martian mantle we developed analytical techniques for Hf and Th concentration measurements by isotope dilution.

*Precise determination of Hf and Th concentrations in chondrites.* About 1 g aliquots from 3-5 g whole-rock powders were dissolved in precleaned 60 mL Savillex vials at ~200°C on a hotplate using HF-$HNO_3$-$HClO_4$. After digestion the samples were dried and redissolved in 6 M HCl-0.06 M HF. At this step total sample dissolution was achieved. A ~10% aliquot of the sample was spiked with a mixed $^{180}$Hf-$^{183}$W-$^{229}$Th tracer that was calibrated against pure Hf, W, and Th metals. Total spike-sample equilibration was achieved in 6 M HCl-0.06 M HF on a hotplate over night. After drying the samples, Hf, W, and Th were separated using standard ion exchange techniques. All isotope dilution measurements were performed on a Nu Plasma MC-ICPMS at ETH Zurich.

**Results:** Our new Hf and Th concentration data for 9 ordinary chondrites (all falls) are shown in Fig. 1 and compared to previously published data for carbonaceous chondrites [8]. The Hf/Th ratios in the ordinary chondrites range from ~3.4 to ~4.5, similar to the range observed for carbonaceous chondrites. There are no systematic variation among the different groups of ordinary chondrites but there is variability in Hf/Th within each group of chondrites (Fig. 1). Most of the variability in Hf/Th ratios is caused by variations in Th contents. In contrast, Hf contents are rather constant within each group of ordinary chondrites.

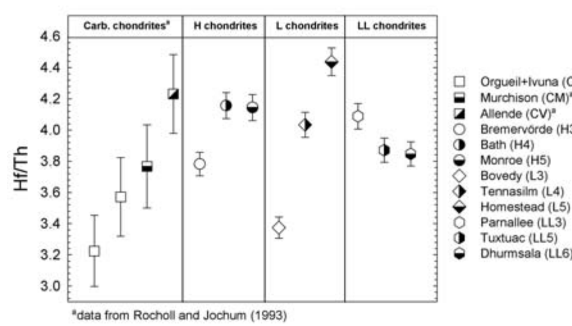


Fig. 1: Hf/Th ratio in chondrites measured by isotope dilution. The accuracy of our Hf/Th measurements for ordinary chondrites is estimated to be ±2% or better.

**Discussion:** There are at least two endmember interpretations for the origin of the observed variations in Hf/Th ratios among chondrite groups. They may reflect different proportions of solar nebula components accreted to the chondrite parent bodies, but they may also be due to open system behaviour of Hf and Th during parent body evolution (e.g., thermal metamorphism). The Hf/Th variations within each of the groups of ordinary chondrites provides evidence that redistributions have occurred. The variations within the ordinary chondrite groups do not allow precise Hf/Th ratios to be defined for each group. Bovedy and Bremervörde display the lowest Hf/Th ratio in our data set and excluding these two samples (which might be justified because they contain foreign clasts) results in a much narrower range of Hf/Th in the ordinary chondrites investigated here (average Hf/Th=4.1±0.4, 2$\sigma$). This value is identical to the Hf/Th ratios reported for CV but significantly higher than those of CI chondrites [8].

*The Hf/W ratio of the bulk Martian mantle*. There is evidence from O, N, and Cr isotopes that the composition of bulk Mars may be best represented (or dominated) by H chondrite-like material [9-12]. This is also consistent with Mg, Al, and Si abundance in Martian rocks [13]. Thus, to determine the Hf/W ratio of the bulk Martian mantle, the Hf/Th ratio of H chondrites may be most appropriate. Here we use Hf/Th=4.1±0.4 derived from our new Hf-Th data for ordinary chondrites as the currently best estimate for the Hf/Th ratio of the bulk Martian mantle. The Th/W ratio of 1.00±0.18 for the bulk Martian mantle then translates to a Hf/W ratio of 4.1±0.8.

*The $^{182}$W anomaly of the bulk Martian mantle.* To date core formation, the $^{182}$W anomaly of the Martian mantle relative to the W isotope composition of the bulk planet must be known. New W isotope data for ordinary chondrites reveal that there are variations in the W isotopic composition of different chondrite groups. The $\varepsilon_W$ values of H chondrites ($\varepsilon_W$ is the deviation of $^{182}W/^{184}W$ from the terrestrial standard value in parts per 10,000) are slightly more negative than those of carbonaceous chondrites ($\varepsilon_W$ = -1.9±0.1) and have an average $\varepsilon_W$ of ~-2.5 [14]. It is currently unclear however if these low $\varepsilon_W$ values could reflect open system behaviour of W isotopes during parent body evolution. The variations in $\varepsilon_W$ among chondrites therefore impose some uncertainty on the size of the $^{182}$W anomaly in the Martian mantle. We therefore calculated core formation ages relative to $\varepsilon_W$ values of both –1.9 and –2.5 (Fig. 2).

*Hf-W age for the accretion of Mars.* Fig. 2 shows Hf-W core formation ages as a function of the Hf/W ratio in the Martian mantle. Here we assumed that core formation occurred instantaneously although core formation in reality may be a protracted process. Thus, although the instantaneous core formation model age does not provide a realistic age of core formation, it corresponds to the earliest time core formation can have ceased. It thus provides a maximum age of accretion and as such important information to distinguish between the two aforementioned models for the formation of Mars. Fig. 2 shows that using our new estimate for the Hf/W ratio of the Martian mantle, the earliest time core formation in Mars could have ceased is >2 Myr, suggesting a protracted accretion history of Mars, similar to those of the larger terrestrial planets.

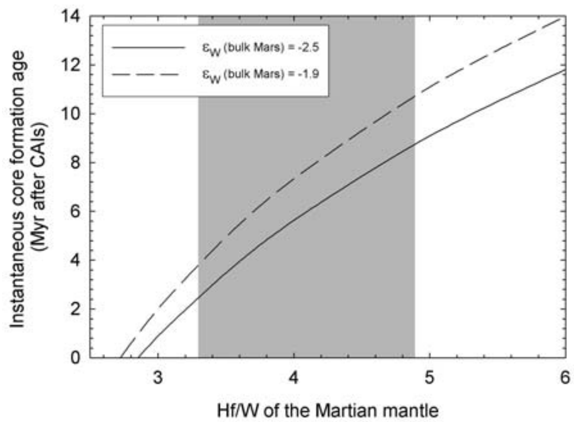


Fig. 2: Core formation timescale as a function of mantle Hf/W ratio. The grey area indicates our new estimate of the Hf/W ratio in the bulk Martian mantle. We used $\varepsilon_W$ ~2.3 for the bulk Martian mantle [4, 5].

**Conclusions and outlook:** Our study shows that with new high precision concentration data the uncertainties in the Hf-W age of Mars can significantly be reduced, such that Hf-W ages can be used to distinguish between the two contrasting models for the formation of Mars. More Hf-Th data for chondrites, however, are needed to better constrain the effects of parent body processes on Hf and Th abundances and to identify potential variations in Hf/Th among different chondrite groups. Once the Hf/Th systematics of chondrites are fully understood, these data will significantly improve our understanding of the formation and early evolution of Mars.

**References:** [1] Chambers J.E. and Wetherill G.W. (1998), *Icarus*, *136*, 304-327. [2] Agnor C.B. et al. (1999), *Icarus*, *142*, 219-237. [3] Harper C.L. et al. (1991), *LPSC*, *XXII*, 515-516. [4] Kleine T. et al. (2004), *GCA*, *68*, 2935-2946. [5] Foley C.N. et al. (2005), *GCA*, *69*, 4557-4571. [6] Halliday A.N. and Kleine T., in *Meteorites and the Early Solar System II*, D.S. Lauretta and H.Y. McSween (2006), p. 775-801. [7] Jacobsen S.B. (2005), *AREPS*, *33*, 531-570. [8] Rocholl A. and Jochum K.P. (1993), *EPSL*, *117*, 265-278. [9] Sanloup C. et al. (1999), *PEPI*, *112*, 43-54. [10] Mohapatra R.K. and Murthy S.V.S. (2003), *MAPS*, *38*, 225-241. [11] Burbine T.H. and O'Brien K.M. (2004), *MAPS*, *39*, 667-681. [12] Lodders K. and Fegley B. (1997), *Icarus*, *126*, 373-394. [13] Dreibus G. et al. (1998), *LPSC*, *XXIX*, #1348. [14] Kleine T. et al. (2007), *LPSC*, *XXXVIII*, this volume.