**AN INNER SOLAR SYSTEM ORIGIN OF VOLATILE ELEMENTS IN MARS.** T. Kleine<sup>1</sup>, T. Steller<sup>2</sup>, C. Burkhardt<sup>1</sup>, and F. Nimmo<sup>3</sup>, <sup>1</sup>Max Planck Institute for Solar System Research, Justus-von-Liebig-Weg 3, 37077 Göttingen, Germany (<u>kleine@mps.mpg.de</u>), <sup>2</sup>Institut für Planetologie, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany, <sup>3</sup>Dept. Earth and Planetary Sciences, University of California Santa Cruz, Santa Cruz, CA 95064, USA.

**Introduction:** Determining the origin of volatile elements in the terrestrial planets is important for understanding planet formation. Mars is a planetary embryo that accreted within the first ~5-10 million years (Ma) of solar system history [1] and as such provides a record of volatile element delivery to the inner solar system during the early stages of planet formation. Volatile elements on Mars may derive from its major building blocks or an exogenous source that otherwise contributed only little mass to Mars. Understanding volatile element accretion, therefore, requires identifying any genetic link between Mars' major building material and the source of its volatile elements. This in turn requires a genetic tracer that can link potential volatile element sources to a planet's building blocks.

The recent discovery of nucleosynthetic isotope anomalies in the moderately volatile element Zn [2,3] offers a new approach to this problem. Nucleosynthetic isotope anomalies reveal that the solar protoplanetary disk can be subdivided into the non-carbonaceous (NC) and carbonaceous (CC) reservoirs. This NC-CC dichotomy is well documented for several non-volatile elements [4]. The isotopic composition of a planet's mantle relative to the NC-CC dichotomy provides important information about the heritage of a planet's building material and how this material may have changed as accretion proceeded [5]. Whereas lithophile elements like Cr and Ti trace a planet's entire accretion history, volatile elements like Zn are depleted in Mars and, therefore, provide an isotopic record of only those objects that delivered volatile elements. Combining nucleosynthetic isotope anomalies for non-volatile and volatile elements, therefore, provides an efficient means for determining the source of volatile elements and for assessing whether they were delivered by a planet's major building blocks. To address these issues, we obtained Zn isotope data for five martian meteorites, including three shergottites (Tissint, Zagami, NWA 1195) and two nakhlites (Nakhla, MIL 03346).

**Methods:** The analytical methods for Zn isotope measurements by MC-ICPMS follow those described in [3]. The Zn isotopic data are normalized to  ${}^{67}$ Zn/ ${}^{64}$ Zn using the exponential law and are reported as  $\mu^{66}$ Zn and  $\mu^{68}$ Zn values (the parts-per-million deviation from the NIST SRM 683 standard).

**Results:** All five martian meteorites exhibit indistinguishable Zn isotope anomalies and plot well inside the NC field (Fig. 1). The mean Zn isotopic composi-



**Fig. 1:** Zinc isotope composition of Mars compared to meteorites and bulk silicate Earth (BSE).



Fig. 2: Relation of  $\mu^{66}$ Zn and  $\mu^{54}$ Cr among meteorites, Mars, and Earth.

tion of the five martian meteorites of this study plots on the  $\mu^{66}$ Zn- $\mu^{54}$ Cr correlation line defined by NC meteorites, between the compositions of enstatite and ordinary chondrites (Fig. 2). We, therefore, interpret the mean Zn isotope composition of the martian meteorites to provide a good estimate for the Zn isotopic composition of bulk silicate Mars (BSM).

**Discussion:** Building material of Mars. To quantify the contribution of NC and CC bodies to Mars' building blocks and its volatile element inventory, it is useful to assume a two-component mixing model, where the final planet's bulk composition is a mixture of NC and CC materials. The fraction of NC material accreted by Mars can then calculated by simple mass balance using concentrations of Zn in BSM and the CC end-member, and the Zn isotope compositions of BSM and the NC and CC end-members. If two different elements are considered, then any successful model must yield the same result for both elements, which allows determining the NC fraction in Mars quite precisely.

Using the  $\mu^{66}$ Zn and  $\mu^{54}$ Cr values for Mars and CI chondrites as the CC end-member, provides a precise estimate for the fraction of NC material in Mars of 99.5±3.4 % (2 $\sigma$ ), limiting the contribution of CI chondrite-like material to Mars to ~4% at most (assuming CV chondrites as the CC end-member yields ~10% CV chondrite-like material at most). Note that these are upper limits and that the contribution of these CC materials to Mars were likely smaller.

Origin of volatile elements in Mars. The low CC mass fraction in Mars combined with the observation that the BSM's Zn isotopic composition is intermediate between ordinary and enstatite chondrites provides two key insights into the origin of volatile elements on Mars. First, taking the upper limits from above together with the Zn concentrations in BSM and CI and CV chondrites reveals that at most  $\sim 20\%$  of the martian Zn derives from the CC reservoir. Second, for non-volatile lithophile elements such as Cr and Ti, which trace the isotopic composition of a planet's bulk building material, Mars' isotopic composition is consistently between those of ordinary and enstatite chondrites [6,7]. This is also the case for Mars' O isotope composition [8,9]. Importantly, the BSM's Zn isotopic composition is also intermediate between ordinary and enstatite chondrites, indicating that Zn was delivered to Mars together with its main building materials, whereas any contribution from exotic, outer solar system sources, were minor to absent.

Distinct accretion histories of Mars and Earth. Mars and Earth have distinct Zn isotopic composition, not only in terms of their Zn isotope anomalies, but also with respect to the NC-CC dichotomy: Whereas Mars plots within the NC field, Earth plots between the NC and CC fields. This is true not only for Zn isotopes (Fig. 1), but also for the  $\mu^{66}$ Zn– $\mu^{54}$ Cr diagram (Fig. 2). Applying the two-component mixing model of this study to Earth we find a larger CC contribution to Earth than to Mars (Fig. 3).

The higher CC fraction in Earth compared to Mars is unexpected, because Earth and Mars should have accreted roughly the same amount of CC material from roughly the same regions during the waning stages of accretion [10]. If this material consisted of small planetesimals, then one would expect a roughly equal fraction of CC material to have been delivered to both bodies. There are several possible solutions to this apparent paradox. One is that the nearly-complete Earth was



**Fig. 3:** PDFs for the fraction of NC material in Mars and Earth calculated using a two-component mixing model. For a given composition of the CC end-member, Mars accreted less CC material than Earth.

struck by one or a few large CC embryos-one of which may have been the Moon-forming impactor [11]-while Mars was not. However, because of the low probability of collision, this scenario would require the survival of hundreds or thousands of large, CC-like objects in the asteroid belt, which are not observed at present. A second possibility is that Mars was less able to retain volatile elements delivered during high-velocity impacts. Evaporative escape is a strong function of planetary mass [12], so this idea is qualitatively plausible, but it is not clear whether it works quantitatively. In short, the unexpected difference between the CC fraction of Mars and Earth will require further investigation with planetary accretion models, and will place constraints on how and when CC-type material was delivered to the inner solar system.

**Conclusions:** New Zn isotope data for Mars indicate that Mars accreted moderately volatile elements predominantly from its inner solar system building blocks, and that any contributions from exotic, outer solar system sources, were minor to absent.

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