

## The Great Mars Climate Paradox Redux

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We thank Shaw (2016) for his interest in the Research Focus piece by Hynek (2016) highlighting end-member climate scenarios for early Mars that range from warm and wet conditions supported by geological evidence to cold and icy conditions more consistent with climate models. In his Comment, Shaw promotes a hypothesis of a dense, reducing atmosphere derived from the reduction of carbon- and nitrogen-containing compounds by meteoritic metal to sustain water flow in Mars' distant past. Such an atmosphere, composed of the strong greenhouse gases methane and ammonia in abundance, would mitigate debate over whether there ever was a warm and wet early Mars. Yet there remain persistent unresolved issues with this idea, including (1) the nature of late accretion in the inner solar system in its first half billion years, (2) the geochemical evolution of magma oxygen fugacity of Earth and Mars, and (3) the predictions from physical-chemical climate models for early Mars (and early Earth).

The problem of water (and other volatile) delivery to the inner planets can be explained by physically plausible dynamical models that show that, at the tail-end of primary accretion of the planets, and before the time usually ascribed to the Moon-forming event, planets more than approximately half of Earth's mass ( $M_{\oplus}$ ) accrete a median value of  $\sim 1\%$   $M_{\oplus}$  of carbonaceous chondrite material (e.g., Rubie et al., 2011). Assuming  $\sim 10\%$  water by mass—consistent with carbonaceous chondrites—this yields about  $1 \times 10^{-3} M_{\oplus}$  of water (near the expected value). Instead, Shaw argues that Earth's volatiles were delivered after the Moon-forming event in a "Late Veneer" of approximately 1–2% of Earth's mass. Drake and Righter (2002) showed a water-rich late addition requires carbonaceous chondrite material, but the Os-isotopic compositions of these meteorites differ from that of the Earth's primitive upper mantle, and instead are consistent with anhydrous ordinary chondrites. New dynamical-geochemical-impact models of the early solar system show that if there was a "Late Veneer," the expected chondritic contribution to Mars was  $\sim 0.06$  wt% (Brasser et al., 2016). It appears water and other volatile elements were delivered in a heterogeneous manner, before the Moon-forming event, and not later in either a "Late Veneer" or "Late Heavy Bombardment."

Debate on the origin and reduced versus oxidized condition of the volatiles on Earth and Mars is justifiable given the uncertainties. Earth and Moon have indistinguishable oxygen isotope compositions (Young et al., 2016). If there was any significant delivery of water after Moon-formation, it would have made the Earth and Moon distinguishable in oxygen. As Shaw notes, the early planetary atmospheres were derived from magmatic outgassing and hydrothermal activity, thus the redox state of planetary mantles and early magmas provide clues. Experimental and theoretical work on silicate-metal partitioning during Earth's (very early) core formation demonstrate that the oxygen fugacity of the upper mantle evolved early and rapidly to within present-day levels (e.g., Frost and McCammon, 2008). Geological data support this notion. Analysis of the most ancient zircons—derived from mantle melts—show that Earth's mantle oxygen fugacity has not deviated much (if at all) from the fayalite-quartz-magnetite buffer value in the past 4.3 billion years (Trail et al., 2011). This result is also consistent with Archaean mantle residues and magmas exhibiting a redox state equivalent to present-day conditions (e.g., Canil, 2002). The resultant atmosphere from outgassing is correspondingly expected to have been at least mildly oxidizing from the

early days.

While we have far fewer data to assess the redox state of Mars' early mantle, Righter et al. (2016) showed that, while less oxidized than Earth's, it was still well above the iron-wüstite buffer and far more oxidized than metal-bearing meteorites. Data from direct analysis of martian meteorites show that martian magmas—in a record that spans over 4 billion years—were never so reducing as to stabilize methane or ammonia (e.g., Wadhwa, 2008). Should an ample source be found for these on Mars, a photochemically active gas mixture like this would nonetheless have to contend with rapid photolysis (Kasting et al., 1993) on the order of  $\sim 200$  days; the enhanced extreme ultraviolet flux of the young Sun should have been efficient in destroying  $\text{CH}_4$  and  $\text{NH}_3$ . Finally, if significant methane did build up in an early Mars atmosphere, the photolytic products create optically thick photochemical hazes that have a strong anti-greenhouse cooling effect (Haqq-Misra et al., 2008).

The Research Focus by Hynek was intended to challenge the community of planetary geologists to address the disparity between geological data and physical-chemical models of the ancient martian atmosphere. Data are inconsistent with the existence of a dense, ultra-greenhouse atmosphere on early Mars that was sustained by a buried and thermally processed reservoir of reduced organic compounds and meteoritic metal. We agree with Shaw that the evolution of Mars' atmosphere is an important and unresolved issue; available geochemical data have yet to resolve the paradox of warm and wet conditions on early Earth and Mars.

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