

## HOT AND STEAMY: ALTERATION OF THE PRIMORDIAL MARTIAN CRUST BY SUPERCRITICAL FLUIDS DURING MAGMA OCEAN COOLING.

K. M. Cannon<sup>1</sup>, S. W. Parman<sup>1</sup>, and J. F. Mustard<sup>1</sup>,  
<sup>1</sup>Department of Earth, Environmental and Planetary Sciences, Brown University, Providence RI 02906.  
 Email: kevin\_cannon@brown.edu

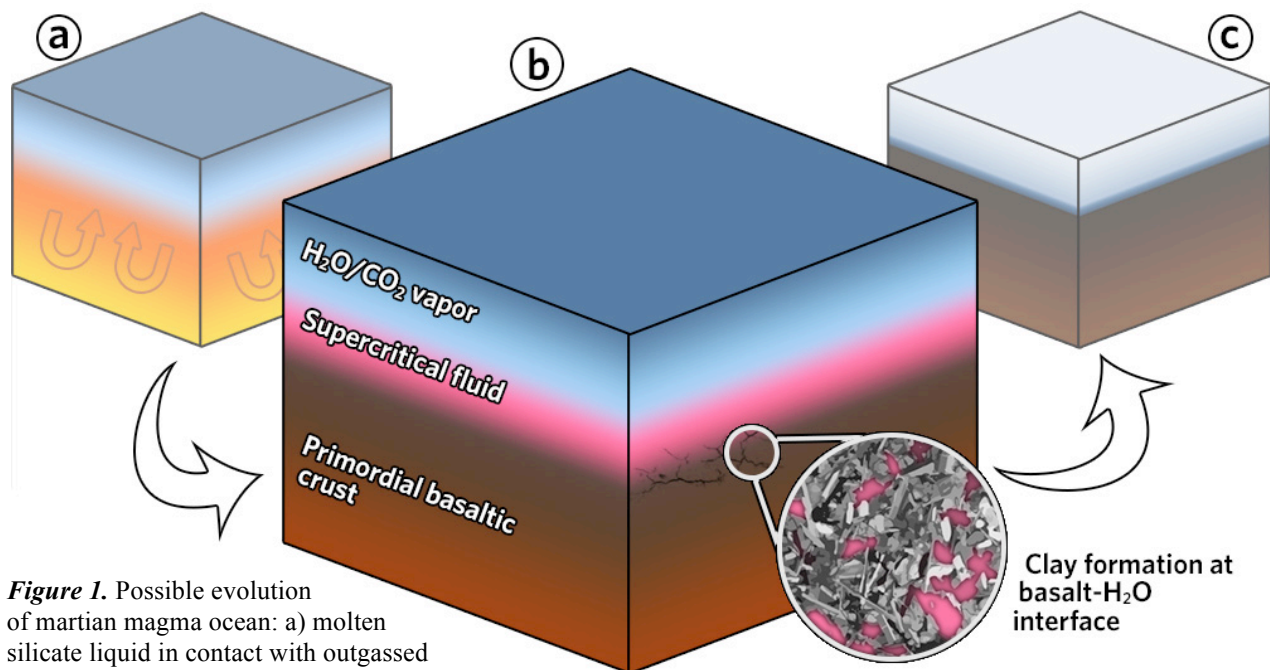
**Introduction:** Mars' basaltic crust has been altered by H<sub>2</sub>O to form hydrated silicates (mostly clays) that are distributed globally [1,2] and extend to great depth [3]. However, climate models for early Mars are challenged to generate warm and wet environments needed to form these minerals via weathering near or at the surface [4,5], and geomorphic evidence for surface hydrology seems to postdate most of this alteration: preexisting clays were simply moved around in the fluvial-lacustrine systems visible from orbit today [e.g., 6]. While some clays probably formed through low-grade metamorphism in an early, wet crust [7], the Pre-Noachian period has not been explored for possible clay formation. The Pre-Noachian was a time when Mars *had to have been warm and wet* because the planet was still cooling from a magma ocean [8,9]. What fraction of the secondary minerals observed today could have originally formed during this period? Here, we conduct a set of laboratory studies to determine if, and to what extent, a massive outgassed atmosphere could have altered the primordial martian crust during magma ocean cooling.

**Model:** As a martian magma ocean evolved, 10s to 100s of bars of outgassed H<sub>2</sub>O/CO<sub>2</sub> vapor likely sat emplaced on the silicate liquid surface [9] (Fig. 1a). As the magma ocean cooled further, this atmosphere may have entered the supercritical field [9], creating an

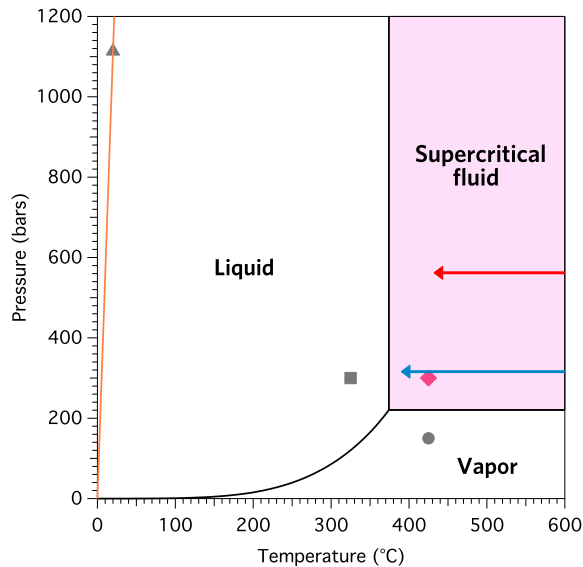
interface between supercritical fluid and the primordial basaltic crust, enhanced by seepage into fractures caused by impact bombardment (Fig. 1b). Further cooling should lead to hot water condensing and percolating through the fractured crust as Mars evolved toward clement conditions [10]. All three phases of water (vapor, supercritical fluid and liquid) can likely alter basalt, but engineering literature demonstrates the unique properties of supercritical fluids: they effuse through solids like gases and act as powerful solvents [e.g., 11]. However, few studies have investigated the rate and extent of basalt alteration by these fluids because the conditions imagined in Fig. 1b fall well outside typical P-T metamorphic pathways (Fig. 2) considered for Earth or Mars [12].

**Experimental:** We synthesized rock samples similar to the estimated composition of Mars' crust [13] (Fig. 3). Samples were created in a 1 atm furnace at QFM-1 and cooled from above the liquidus to 1000 °C at 5 °C/hr, then to room temperature at 250 °C/hr. The resulting material contains domains of both coarse (~200 μm) and fine (~30 μm) crystals with plagioclase (zoned) > clinopyroxene > olivine (zoned) > Ti-rich spinel > glass (with quench crystals). This material was then ground and sieved to a 500-1000 μm fraction, with clinging fines removed by washing under ethanol.

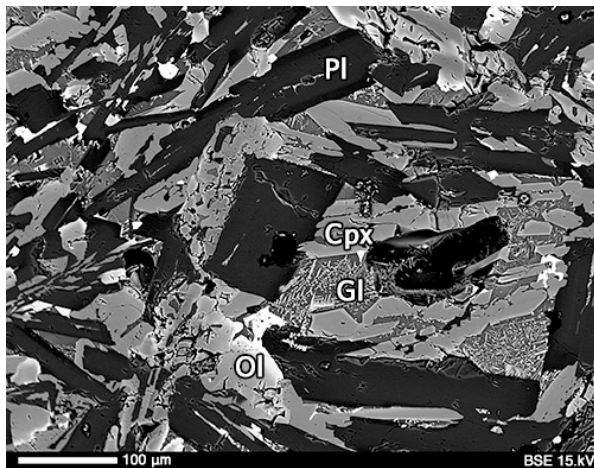
We will mix the basalt with water in a 1:1 ratio by



**Figure 1.** Possible evolution of martian magma ocean: a) molten silicate liquid in contact with outgassed H<sub>2</sub>O/CO<sub>2</sub> steam atmosphere; b) primordial crust with supercritical fluid at base of atmosphere; c) further cooling to clement conditions.



**Figure 2.** H<sub>2</sub>O phase boundaries (dark lines) with two possible cooling paths taken from [9] for martian magma oceans with initial depths of 2000 km (red arrow) and 500 km (blue arrow), both with 0.5 wt.% of initial H<sub>2</sub>O and 0.1 of wt.% CO<sub>2</sub> outgassed. Markers represent experimental conditions described above. Also shown is a 20 °C/km geotherm for Mars (orange line) assuming  $\rho=3000 \text{ kg/m}^3$ .



**Figure 3.** BSE image of our synthetic martian basaltic samples showing coarse crystals of plagioclase (Pl), clinopyroxene (Cpx), glass (Gl), and olivine (Ol).

weight, then seal the samples in Pt tubes. The tubes will be placed in hydrothermal cells pressurized by water, and reacted at four different conditions (Fig. 2): (1) Above the critical point, in the supercritical field ( $T = 425^\circ\text{C}$ ,  $P = 0.3 \text{ kbar}$ ); (2) Below the critical point, in the vapor field ( $T = 425^\circ\text{C}$ ,  $P = 0.15 \text{ kbar}$ ); (3) Below the critical point, in the liquid field ( $T = 325^\circ\text{C}$ ,  $P = 0.3 \text{ kbar}$ ); (4) Conditions corresponding to 1 km depth with a  $20^\circ\text{C/km}$  geotherm, a mid to high estimate for early Mars ( $T = 20^\circ\text{C}$ ,  $P = 1.11 \text{ kbar}$ ).

Reactions will be run for 2 weeks before breaking the samples out of the Pt tubes. For simplicity we do not consider the role of CO<sub>2</sub>, although true H<sub>2</sub>O-CO<sub>2</sub> fluids may exhibit more complicated behaviors including supercritical phase separation.

Samples will be analyzed by X-ray diffraction, visible/near-infrared spectroscopy, loss on ignition and electron probe micro-analysis. These techniques will be used synergistically to determine both the extent and nature of alteration at the four different conditions. Key questions to be addressed include: (1) Is there a sharp discontinuity in alteration extent past the critical point, i.e., do supercritical fluids have some special ability to strongly alter mafic rocks? (2) Is there a difference between hot vapors and hot water in terms of alteration style/extent? (3) How do the secondary minerals that form compare with those that have been discovered on Mars?

**Conclusions:** Hydrated silicates on Mars are commonly assumed to have formed during some vague “warm and wet” time in the Noachian. However, the role of the largest source of heat and water Mars ever had – a cooling magma ocean – has received little attention because of the gap in the geologic record between accretion and the late Noachian. We are testing the idea first proposed by Elkins-Tanton [9], that interactions between supercritical fluids and the primordial martian crust may be preserved to this day.

**References:** [1] Carter J. et al. (2013) *JGR*, 118, 831-858. [2] Ehlmann B. L. and Edwards C. S. (2015) *Ann. Rev. Earth Planet. Sci.*, 42, 291-315. [3] Sun V. Z. and Milliken R. E. (2015) *JGR*, accepted. [4] Forget F. et al. (2013) *Icarus*, 222, 81-99. [5] Mischna, M. A. et al. (2013) *JGR*, 118, 560-576. [6] Goudge T. A. et al. (2012) *Icarus*, 219, 211-229. [7] Ehlmann B. L. et al. (2011) *Nature*, 479, 53-60. [8] Abe Y. (1993) *Lithos*, 30, 223-235. [9] Elkins-Tanton L. T. (2008) *Earth Planet. Sci. Lett.*, 271, 181-191. [10] Parmentier E. M. et al. (2008) *LPSC XXXIX*, Abstract #1544. [11] Weingärtner H. and Franck E. U. (2005) *Angewandte Chemie Int.*, 44, 2672-2692. [12] McSween Jr. H. Y. (2015) *Meteorit. Planet. Sci.*, 50, 590-603. [13] Taylor S. R. and McLennan S. M. (2009) *Planetary Crusts*.