

**VOLATILE AND TRACE ELEMENT STORAGE IN A CRYSTALLIZING MARTIAN MAGMA OCEAN.** S. J. Sim<sup>1</sup>, M. M. Hirschmann<sup>2</sup>, and S. Hier-Majumder<sup>3,4</sup>, <sup>1</sup>School of Earth and Atmospheric Science, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332, USA (jssim@eas.gatech.edu), <sup>2</sup>Department of Earth Sciences, University of Minnesota, Twin Cities, MN 55455, USA, <sup>3</sup>Department of Earth Sciences, Royal Holloway University of London, Egham, Surrey, TW20 0EX, UK, <sup>4</sup>Now at: Advanced Scientific Computing Research, Office of Science, Department of Energy, Germantown, MD, USA.

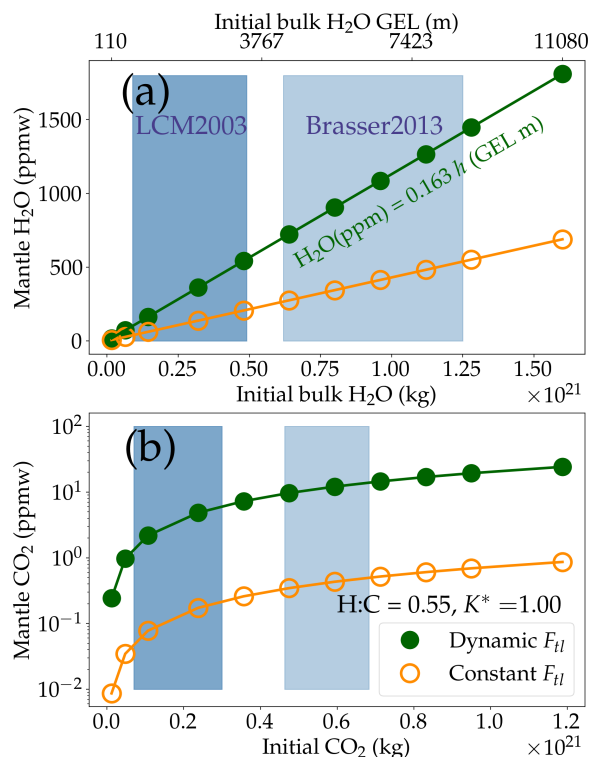
**Introduction:** Immediately following core formation on Mars, the planet underwent a transformative phase in which a magma ocean (MO) crystallized to form the primitive Martian mantle. Volatiles released from the MO formed a primitive atmosphere (PA), which modulated heat loss from the cooling planet through the greenhouse effect. The solidification and degassing of the MO were therefore coupled, as the release of volatiles during MO crystallization inhibited cooling and slowed solidification. Two important aspects of this coupled evolution are 1) the dynamics of melt trapping at the freezing front of the residual mantle (RM) and 2) the oxidation state of the Martian interior during crystallization. In this study, we investigate the influence of both in the evolution of the Martian MO.

**Methods:** *Thermal and chemical evolution.* We model the thermal evolution of the MO following [1]. As the MO crystallizes, secular cooling,  $dT/dt$ , is balanced by surface heat flux and latent heat of crystallization. The surface heat flux depends on the partial pressure of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the PA. The total mass of the volatile species remains constant while the species masses in the three reservoirs (MO, RM, PA) changes over time obeying conservation of mass.

*Dynamic melt trapping.* The fraction of melt trapped in the freezing front of the MO depends on the competition between the rates of crystallization and compaction following [1]. As the secular cooling rate,  $dT/dt$ , varies during the thermal evolution, so does the trapped melt fraction.

*Chemical reactions, redox factor and trace elements.* The thermal evolution depends on the atmospheric partial pressures which arises from the following reaction:  $\text{CO}_2(\text{vapor}) + \text{O}^{2-}(\text{melt}) \rightleftharpoons \text{CO}_3^{2-}(\text{melt})$ . To incorporate the effect of the redox condition, we also consider the graphite/diamond oxidation reaction,  $\text{C}(\text{s}) + \text{O}_2(\text{vapor}) \rightleftharpoons \text{CO}_2(\text{vapor})$ . The equilibrium constant of this reaction can be scaled such that the  $\text{CO}_2$  partial pressure of the reference condition [2] is related to the partial pressure under a more reducing condition through a redox factor:  $P_{\text{CO}_2}^{\text{ref}} = K^* P_{\text{CO}_2}$ . Trace elements are partitioned between the MO and RM only. We use the parameterization from previous work [3] to evaluate the abundance of minerals

with depths of crystallization and partition coefficients of each element.



**Figure 1.** Comparison between the effects of dynamic melt trapping (solid green circles) and a constant trapped melt volume fraction of 1% (open orange circles) on (a) the mantle  $\text{H}_2\text{O}$  and (b) total C concentrations at the completion of 99.5% crystallization of the MO, as a function of initial abundances of the volatiles. For all simulations, we used an initial H:C ratio of 0.55 and redox condition given by  $K^*=1$ .

**Results:** *Constant versus dynamic melt trapping.* For realistic values of compaction time, the freezing front of a solidifying magma ocean progresses faster than compaction, and so for Mars, trapped liquid fractions are near the disaggregation limit of 30%. In general, dynamic melt trapping greatly enhances the volatile and trace element content of the RM (Figure 1). The mass percent of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  trapped in the RM increases from 19.7% to 55.4% and from 0.07% to 1.7%

respectively with dynamic melt trapping.

The magnitude of trace element enrichments and depletions in the solidified martian mantle depends significantly on the efficiency of the crystal-melt segregation during the crystallization of the MO. Borg & Draper (2003) assumed perfect separation of cumulates, resulting in up to 6 orders of magnitude variations in trace element concentrations at 99.5% solidification (Figure 2). Constant melt trapping of 1% liquid leads to 4 orders of magnitude variations while dynamic melt trapping limits the variations to 2 orders of magnitude.

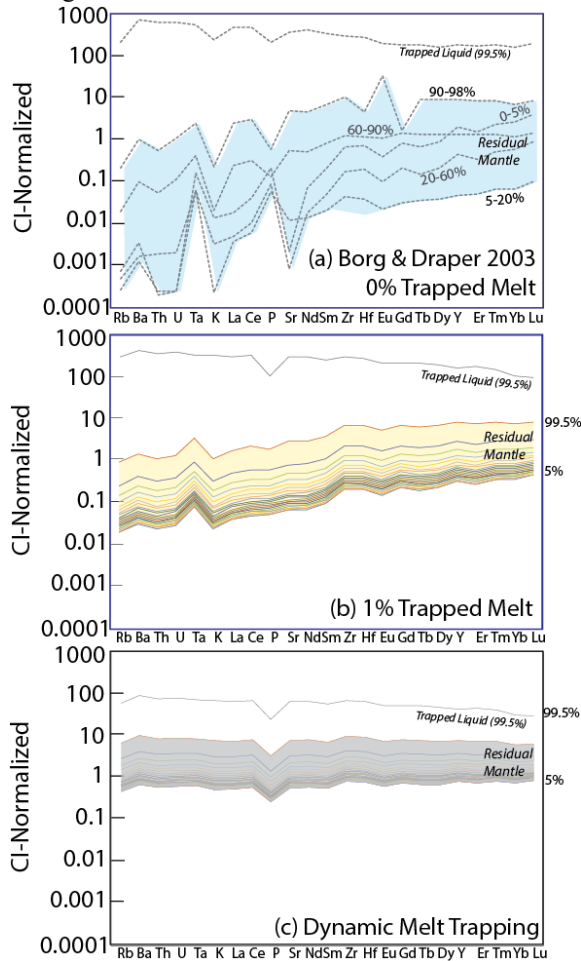


Figure 2. Variations in normalized trace element concentrations for different MO solidification scenarios: (a) compositions calculated from [1] for the residual mantle (RM) produced during mass solidification intervals of 0-5, 5-20, 20-60, 60-90, 90-98% and for the liquid remaining after 99.5% solidification. (b) and (c) are compositions calculated in this study assuming 1% melt trapping (b) and dynamic melt trapping (c) for mass solidification intervals in 5% increments to 95%, the 95-99.5% intervals and the liquid remaining after 99.5%.

**Redox factor.** Under more reducing conditions (higher values of  $K^*$ ), crystallization times are much shorter (Figure 3(a)). The diminished freezing time is caused by a significant decrease in greenhouse effect, as evidenced by a considerable decrease in the atmospheric partial pressure of  $CO_2$  from ~175 bars to 3-7 bars in Figure 3(b). The concentration of total carbon in the RM increases with reducing conditions. The mass percent of  $CO_2$  sequestered in the RM increases from 0.017% in the most oxidizing case to 80.4% in the most reducing case.

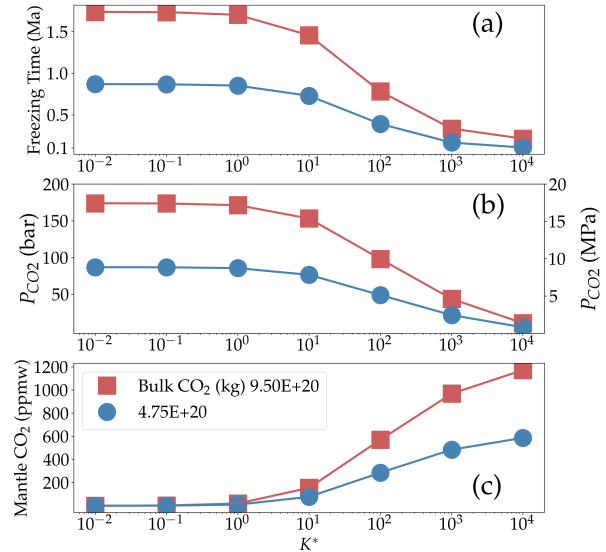


Figure 3. The effect of redox condition on (a) crystallization time, (b) partial pressure of  $CO_2$  in the PA, and (c) total mantle  $CO_2$  concentration (both as dissolved  $CO_2$  and solid), as a function of  $K^*$ , with larger values of  $K^*$  to the right corresponding to more reducing conditions.

**Discussion:** Compared to models that assume small or zero trapped melt in crystallizing RM solids, dynamic trapping limits variations in trace element concentrations and fractionations. Resulting variations in important isotopic parent/daughter ratios (Sm/Nd, Lu/Hf) cannot account for all of the isotopic diversity inferred for Martian basalt source regions. Additional elemental fractionations could have resulted from early partial melting of the mantle associated with formation of the primitive Martian crust. Alternatively, MO crystallization times could be much more protracted owing to processes not considered in this work.

**References:** [1] Hier-Majumder S. and Hirschmann M. M. (2017) *G<sup>3</sup>*, 18, 3078–3092. [2] Stanley B. D. et al. (2012) *Am. Min.*, 97,1841-1848. [3] Borg L. E. and Draper D. S. (2003) *Meteoritics & Planet. Sci.*, 38,1713-1731.