

**ASSESSING THE ACCURACY OF THERMODYNAMIC MODELING SOFTWARE FOR MARTIAN MAGMATISM.** J. B. Balta<sup>1-2</sup>, G. Garcia<sup>2-3</sup> and M. E. Holycross<sup>2</sup>, <sup>1</sup>Lunar and Planetary Institute/USRA, Houston TX 77058, jbalta@lpi.usra.edu, <sup>2</sup>Cornell University, Dept. of Earth and Atmospheric Science, Ithaca NY 14853, <sup>3</sup>Manhattan College, The Bronx, NY 10471.

**Introduction:** Tools for calculating the composition of minerals and co-existing magmas fall into two categories: empirical tools calibrated solely on observations and experiments and those which also take thermodynamic formulas into account. Each type of tool has its own advantages. For instance, it is expected that empirical tools will more accurately represent compositions with abundant experimental data because statistical minimization programs are not required to fit the observations to thermodynamic equations. However, thermodynamics-based programs offer added flexibility because they can be used on a broader range of compositions and can give useful context, even when there are misfits.

The most commonly used thermodynamics-based calculator for understanding planetary magmatism is the MELTS algorithm, which now is found in a number of different versions [1-4]. MELTS was originally calibrated based on thermodynamic parameters measured in mostly terrestrial compositions, and therefore any use of it on a planetary composition is inherently outside of its calibrated range. However, because of the thermodynamic basis of this calibration, it may be used to project outside of the range of its calibration, such as for martian compositions. It is then up to the user of the program to understand what misfits this may trigger and how to interpret the results. [5] conducted a detailed study of the accuracy of the original MELTS calibration when applied to martian magma crystallization and found that there are important errors in the calculated crystallization sequences – notably that the algorithm overestimates the stability of pyroxenes relative to olivine at pressures comparable to those in the shallow crust and below (>0.2 GPa). However, they recommended a set of steps that could be taken to either manage the misfit by either applying a correction factor to certain oxides, setting up the calculation to avoid the pressure conditions where there are issues, or by scaling the pressure to account for the offset in mineral stability.

The pMELTS version of the MELTS algorithm [2] was created to allow for calculation of melting at mantle pressures. It includes a broader range of compositions in its calibration database than the original MELTS calibration including lunar compositions. However, its calibrated range does not yet extend to martian compositions. Previous efforts have established that there are some errors in this calibration when applied to

martian compositions and suggested that offsets in various oxides (FeO, MgO, SiO<sub>2</sub>) could be used as a correction [6]. However, [7] showed that there are conditions where these errors are particularly large and difficult to manage. [7] then introduced Magmars, a calibrated simulation tool capable of more accurately calculating the compositions and melting conditions of martian samples based on the available experiments.

Although Magmars will be more accurate as it includes a better calibration for martian rocks, as with the study by [5], we believe that a detailed characterization of the accuracy and origin of misfits in pMELTS calculations continues to have value in understanding martian magmatism due to the thermodynamic nature of its calculations. The pMELTS algorithm includes the effects of water on melting and can also be used to compare with melts generated in Earth's mantle. Furthermore, noting areas where there are errors in pMELTS calculations can indicate interesting targets for future research [5].

In this study we will take two steps building on the work of [5]. As in that study and in the work of [7], we conducted a series of pMELTS calculations aimed at matching the conditions of experiments on martian compositions to characterize the calculation misfits. We will then evaluate the causes of such errors, including which phases are involved in misfits and over what conditions these misfits are largest. Finally, we present a preliminary experimental study to test an issue noted by [5]; that pMELTS unexpectedly predicts low liquidus temperatures for some martian basalts and show the value of additional experimental characterization of martian basalts.

#### **Methods:**

*Calculations.* We conducted a set of pMELTS calculations using the AlphaMELTS front end of [8]. Calculations were conducted in batch mode, with increasing melt fraction associated with increasing temperature. As done by [5] and [7], we compare the oxide abundances to those observed in experiments by [5, 7, 9, and 10].

*Experiments.* A set of piston-cylinder experiments was conducted in the experimental geochemistry laboratory at Cornell University. We generated a synthetic composition based on the meteorite Yamato 980459, following the experimental procedure of [11]. Experiments were then conducted in ½” diameter assemblies consisting of graphite capsules, BaCO<sub>3</sub>

pressure media, graphite heating elements, and alumina and MgO spacers. Samples were pressurized, heated to temperatures  $>1550^{\circ}\text{C}$  to ensure superliquidus conditions, and cooled to the experimental temperatures where they were allowed to dwell from 1-6 hours before rapid quenching by turning off the power. Samples were polished, observed using optical microscopy and then analyzed with a Zeiss Gemini 500 Scanning Electron Microscope to confirm the appropriate melt composition and to identify stable mineral phases.

### Results:

**Calculations.** Our results confirm the large offsets on FeO, SiO<sub>2</sub>, and Na<sub>2</sub>O suggested by [7]; we note here the exact conditions of these misfits. Na<sub>2</sub>O contents are found to be elevated particularly in low-degree melts; this is an issue that has been noted in the pMELTS calibration previously by [12]. Similarly, we show that pMELTS calculated magmas are elevated in FeO compared to experiments, as suggested again by [6-7]. We note here that this issue is particularly acute in the range of 1.5 to 2.0 GPa; at elevated pressures, the degree of misfit on each of these oxides decreases. The study of [10] included experiments conducted at 4 GPa; these experiments were low in SiO<sub>2</sub> and elevated in FeO as observed in the pMELTS calculations. Thus, we show that there is a range of pressures where pMELTS calculations are generally accurate, at pressures where garnet is stable, with misfits that are limited to 1-2 wt. % on SiO<sub>2</sub> and FeO. Other oxides, including CaO, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> are generally accurate to within small errors (e.g., 1-2 wt. % on Al<sub>2</sub>O<sub>3</sub> and CaO) across much of the tested pressure range.

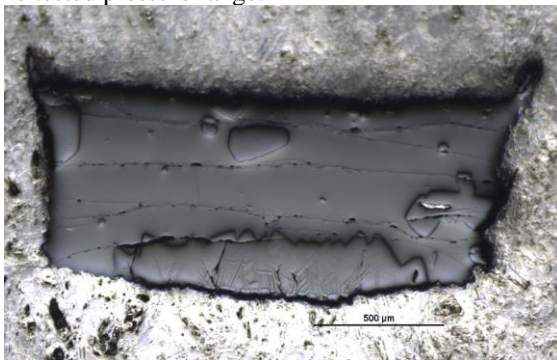


Fig 1: Piston cylinder charge containing synthetic Yamato 980459 melt. Olivine crystals are present at the capsule bottom.

**Experiments.** The Yamato 980459 composition was found to have a liquidus temperature between  $1490^{\circ}\text{C}$  and  $1520^{\circ}\text{C}$  based on the presence of equilibrium olivine in the lower-temperature experiment (Fig. 1). This temperature agreed with that in experiments of [10] and confirmed that pMELTS underestimates the Yamato 980459 liquidus temperature.

**Discussion:** In this work we verify some utility of pMELTS calculations in the pressure range of 2.5 to 4 GPa. As with the original MELTS calibration overestimating the stability of pyroxene at crustal pressures, the largest error is expressed as an issue with the behavior of this melting reaction with pressure. pMELTS projects the same type of high-FeO, low-SiO<sub>2</sub> magma generated at high pressures to be present in the range of 1.5-2.5 GPa, leading to errors on those oxides [13] used pMELTS to suggest the possibility of water contributing to the elevated CaO/Al<sub>2</sub>O<sub>3</sub> ratio of shergottite meteorites; the performance of pMELTS in this pressure range supports the use of this program to evaluate this hypothesis.

As shown by [5], pMELTS typically overestimates the liquidus temperatures for magmas, including martian compositions. However, this behavior is reversed in the high temperature compositions such as Yamato 980459. This suggests that the liquidus in high iron compositions is more sensitive to melt composition than has been predicted based on previous calculations and experiments. Further exploration of the liquidus relationships of the highest temperature martian primary melts is thus important for properly understanding martian melting behavior.

Recently a new thermodynamic minimization algorithm based on the Thermocalc database was made available. This program, Magemin, is more efficient at querying that database than previous applications of the Thermocalc database [14]. We plan to present additional calculations using this program upon their completion.

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