

**APPLICATION OF THE MELTS ALGORITHM TO THE COMPOSITION AND CRYSTALLIZATION OF MARTIAN (AND OTHER EXTRATERRESTRIAL) MAGMAS.** J. B. Balta<sup>1</sup> and H.Y. McSween<sup>1</sup>, Planetary Geoscience Institute and Department of Earth & Planetary Sciences, University of Tennessee, Knoxville, TN 37996-1410, jbalta@utk.edu.

**Introduction:** Since its formulation and publication [1], the MELTS algorithm has become the most commonly used tool for simulating the properties and crystallization paths of martian magmas. The MELTS algorithm calculates phase stabilities and compositions based on thermodynamic properties of phases and components calibrated using published experimental results. This thermodynamic basis allows projection to compositions beyond those in its calibration database, including extraterrestrial compositions. The original calibration includes some extraterrestrial compositions, but only a single study of martian compositions appears in the calibration database [2]. Martian basalts are elevated in Fe and CaO/Al<sub>2</sub>O<sub>3</sub>, depleted in CaO and Al<sub>2</sub>O<sub>3</sub>, and contain more sodic plagioclase than terrestrial basalts. Thus, the applicability of MELTS to martian and other extraterrestrial compositions relies upon the applicability of the underlying thermodynamics and calibrations to compositions with some differences from the majority of its calibration dataset. Previous authors have found both agreements and disagreements between MELTS-calculated results and observations, necessitating a more detailed analysis of the algorithm's applicability to planetary compositions.

Furthermore, since its introduction, the algorithm has been updated several times, including routines for calculating subsolidus compositions, the pMELTS calibration for calculating magma properties at pressures  $\geq 1$  GPa [3], routines for trace elements and water [4], the AlphasELTS front-end to enable rapid calculations [5], and the Rhyolite-MELTS revision with new calculation routines and calibrations for high-silica magma compositions [6]. In addition, a variety of new martian compositions have been discovered and melted experimentally since the original algorithm was introduced.

In order to better understand the strengths and weaknesses of the MELTS algorithm when applied to planetary compositions, we conducted a detailed analysis of the effectiveness of the various iterations of the MELTS algorithm when applied to recent martian magma compositions and experiments. We find that the algorithm is generally effective in fitting martian compositions but various deficiencies are noted and should be understood by users in future applications to martian or other extraterrestrial compositions.

**Methods:** We chose compositions of a series of proposed martian primary and near-primary magmas including Yamato 980459, LAR 06319, NWA 1068, and Gusev basalt compositions. These compositions

have been described in detail in the literature, giving petrologic details comparable with MELTS calculated results, and all data on them post-dates the original MELTS calibration. We also selected compositions that have been tested in experimental crystallization studies in addition to these near-primary magmas. We then performed a series of several hundred MELTS crystallization calculations using a variety of setups and the AlphasELTS and Rhyolite-MELTS front ends [5,6] to produce a large database of calculations that could be compared and contrasted with experimental and analytical results produced since the formation of the calibrations for the MELTS algorithm.

**Successes:** In general, we find that the MELTS algorithm in its various forms is able to fit the composition of the major crystallizing phases to within small variances which we can begin to characterize..

*Olivine:* the original MELTS calibration calculates olivine at the liquidus with a  $K_D$  of 0.25, outside the range of previously reported value of 0.34 for martian compositions [7]. However, the  $K_D$  increases with increasing crystallization and is within error of the published value of 0.34 after less than 10% crystallization. Calculations using the pMELTS calibration find olivine-liquid  $K_D$  values close to 0.34, indistinguishable from the experimental value. In fractional crystallization calculations, the variance in the original MELTS calibration would produce errors in the calculated liquid line of descent of less than 0.5 wt. % MgO or FeO.

*Pyroxenes:* The MELTS algorithm in both MELTS and pMELTS modes generally reproduces the compositions of observed pyroxenes. Calculated pyroxene compositions using the MELTS calibration resemble those found in the meteorite Shergotty and others reported in select experiments where pyroxene compositions have been measured. The algorithm predicts differences between fractional and equilibrium crystallization scenarios, with equilibrium crystallization producing end-member orthopyroxene, augite, and pigeonite as distinct phases and fractional crystallization producing a continuous trend in compositional changes. The calculated end-members generally bound the fields of measured pyroxene compositions and the continuous trend passes through the center. Consequently, differences in pyroxene compositions from those calculated will likely lead to errors in calculated liquid lines of descent of less than 1 wt. % on the major phases, a good general estimate for the overall error.

*Plagioclase:* Calculated plagioclase compositions differ between the two calibrations. Calculations using pMELTS are able to fit the compositions of plagioclase experimentally produced at pressures  $\geq 1$  GPa while calculations using the MELTS calibration are able to fit the compositions of plagioclase experimentally produced at low pressures to within small errors. However, if the pMELTS calibration is used outside its recommended pressure range, it calculates plagioclase compositions that differ substantially from experimental observations, leading to the possibility of large errors on liquid lines of descent ( $> 1$  wt. % for major oxides) if the calibration is used outside its recommended range.

#### Issues:

We find several specific issues with application of the MELTS algorithm, some of have been described previously for terrestrial compositions and one which has not been previously described that should be accounted for by users attempting to apply the algorithm to planetary compositions.

*Chromite:* Calculations in both the MELTS and pMELTS modes consistently place chromian spinel as the liquidus phase under virtually all conditions, including compositions for which there is evidence that olivine was the liquidus mineral. The mismatch is small ( $\sim 20^\circ\text{C}$ ) at low pressures and oxidized conditions, but the mismatch is large ( $> 100^\circ\text{C}$ ) at elevated pressures and reducing conditions. This issue has been discussed previously in the literature [8] and is likely due to a poor calibration for the stability of solid chromian spinel. This error causes early depletion of  $\text{Cr}_2\text{O}_3$  in calculated liquids but has a negligible ( $< 0.1$  wt. %) effect on other oxides in calculated liquid lines of descent.

*Temperatures:* Previous research has suggested that the MELTS calibration overestimates liquidus temperatures by  $50\text{--}100^\circ\text{C}$  and the pMELTS calibration does so by  $20\text{--}40^\circ\text{C}$  [9]. Generally similar temperature mismatches are observed when our calculations are compared to most available experimental results on martian compositions, although there are some experimental exceptions. We do not find a strong difference between the pMELTS and MELTS calibrations in their ability to reproduce liquidus temperatures, but instead both calibrations produce calculated temperatures that are  $\sim 50^\circ\text{C}$  above liquidus temperatures observed in most experimental studies of martian compositions. Little experimental data are available on the crystallization temperatures of phases that appear well below the liquidus like augite and plagioclase, but where available the data suggest similar variances on the crystallization temperatures of those phases.

*Multiple saturation pressures:* We used the pressure where olivine and orthopyroxene appear simulta-

neously on the liquidus for each composition as a fixed point in P-T space that could be compared with experiments. Using the pMELTS calibration, we calculated multiple saturation pressures typically just over 1.0 GPa. These calculations fit observed multiple saturation pressures from multiple studies to within 0.2 GPa, and predicted changes in multiple-saturation pressures between compositions are also similar to those observed in experiments. Thus, the pMELTS calibration accurately fits martian multiple saturation pressures. However, the MELTS calibration significantly misses these pressures. The MELTS calibration places multiple saturation pressures at 0.3 to 0.4 GPa; within the range for which the MELTS calibration is the appropriate choice. Thus, although the olivine/pyroxene relationship appears accurate at 1 atm. to within the temperature errors discussed previously, the MELTS calibration significantly overestimates the stability of pyroxene relative to olivine at low pressures and incorrectly simulates how the stabilities of these two minerals vary with pressure.

Thus, we expect pyroxene stability is overestimated at low pressures, possibly even at pressures as low as 0.1 GPa. As these pressures are outside the range for pMELTS, using either of these calibrations to calculate liquid lines of descent in the range between 0.1 and 1.0 GPa requires careful work and possibly manual correction. Based on the differences between calculated and observed multiple saturation pressures, a possible correction is to multiply pressures calculated using the MELTS algorithm by a factor of 4; however, we cannot verify that this correction applies successfully to phases other than olivine and orthopyroxene. To our knowledge, a similar comparison has not been performed between MELTS calculated crystallization and experimental results for terrestrial or other planetary compositions, and thus this mismatch may be likely in other compositions as well.

**Summary:** Thus, the MELTS algorithm is generally capable of fitting the crystallization paths of martian magmas to within small errors if the limitations of the currently-available calibrations are understood and possibly if corrections are applied where necessary.

**References:** [1] Ghiorso, M. and Sack, R. (1995) *CMP* 119, 197-212. Author A. B. and Author C. D. (1997) *JGR*, 90, 1151-1154. [2] Longhi, J. and Pan, V. (1989) *LPS XIX*, 451-464 [3] Ghiorso et al., (2001)  $G^3$ : 1030. [4] Asimow, P.D. et al. (2004)  $G^3$  5: Q01E16. [5] Smith, P. and Asimow, P.D. (2005)  $G^3$  6: Q02004. [6] Gualda, G.A.R. et al., (2012) *J. Petrol.* 53: 875-890. [7] Filiberto, J. and Dasgupta, R. (2011) *EPSL* 304: 527-537 [8] Hamecher et al. (2013) *CMP* 165: 25-43. [9] Asimow, P.D. and Longhi, J. (2004) *J. Petrol.* 45: 2349-2367.