

A PARAMETERIZED THERMODYNAMIC MODEL FOR ILMENITE SOLUBILITY IN SILICATE MELTS. C. Sun, Y. Liang, and P. C. Hess, Department of Geological Sciences, Brown University, Providence, RI 02912 (Chenguang_Sun@Brown.edu).

Introduction: The solubility of ilmenite in silicate melt is an important geochemical problem of broad lunar and planetary applications. In the standard lunar evolution model, ilmenite is the primary Fe-Ti oxide forming at the end stage solidification of a lunar magma ocean (LMO). Ilmenite may also present in the overturned lunar cumulate mantle that may serve as source regions for high-Ti magmas erupted on the lunar surface [1-4]. Alternatively, ilmenite or ilmenite-bearing cumulate may play an important role in the assimilation models for the origin of lunar high-Ti magmas [5-7]. Because ilmenite can preferentially incorporate high field strength elements (HFSE), the recycling of ilmenite-bearing cumulates to the lunar interior can significantly alter the HFSE inventory in the mantle and produce a HFSE-enriched reservoir within the lunar cumulate mantle. Thus, the fractionation of HFSE plays an important role in revealing mare basalt petrogenesis. A recent laboratory study of trace element partitioning between ilmenite and lunar basaltic melts demonstrates the strong dependence of HFSE partitioning in ilmenite on ilmenite solubility in the melts [8]. Hence, knowledge of ilmenite solubility in silicate melts would be invaluable to the petrogenesis of lunar basalts and picritic glass melts.

Although a number of ilmenite solubility models have been proposed in the literature [9-12], none of them are accurate enough for lunar magma genesis. Utilizing the MAGFOX program of John Longhi, the widely used LMO model of [4] suggested that ilmenite became a liquidus phase after 95% crystallization. However, the ilmenite solubility model implemented in MAGFOX [11] may have significant uncertainties. Figure 1a shows that MAGFOX significantly overestimates ilmenite solubility in low-Ti melts and underestimates ilmenite solubility in high-Ti melts for the compiled phase equilibria experiments reported in the literature. A more accurate model for ilmenite solubility in silicate melt is clearly needed for a better understanding of LMO crystallization and the thermal and chemical evolution of the Moon.

In this study, we present a parameterized thermodynamic model for ilmenite solubility in silicate melts obtained through multiple linear regression analyses of published phase equilibria experiments involving ilmenite. The new model allows us to critically reappraise ilmenite saturation in LMO crystallization and mare basalt petrogenesis.

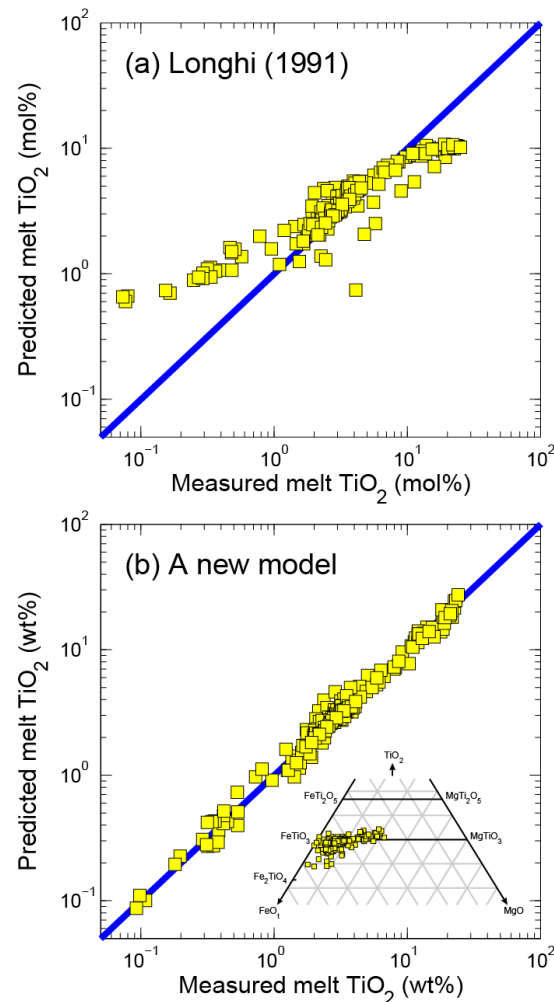


Figure 1. Predicted vs. measured TiO₂ abundances in ilmenite saturated melts from phase equilibria experiments. The predicted values using the model of [11] are shown in (a), and the predicted values using this new model are shown in (b). Insert to (b) shows the ilmenite compositions from the compiled experiments.

A new ilmenite solubility model: Because TiO₂ is a dominant component forming ilmenite, the chemical equilibrium of TiO₂ between ilmenite and silicate melts can be used to constrain ilmenite solubility in silicate melts. The distribution of TiO₂ between ilmenite and melts (D) can be described by the following thermodynamic expression

$$\ln D_{\text{TiO}_2} = a_0 + \frac{a_1}{T} + \frac{a_2 P}{T} + f(X, T)$$

where a_0 , a_1 and a_2 are constants to be determined by phase equilibria data, P is pressure, and f is a function of melt composition (X) and temperature (T).

We have analyzed the published phase equilibria experiments involving ilmenite, and obtained a predictive model for ilmenite solubility in silicate melts by constraining the coefficients and key parameters in the above equation through multiple linear regression analyses. We find that ilmenite solubility in silicate melts is positively correlated with T , and negatively correlated with P and SiO_2 , MgO and alkali abundances in the melt. Figure 1b shows the excellent agreement between the model-predicted and experimentally measured TiO_2 abundances in ilmenite-saturated melts from phase equilibria experiments reported in the literature, indicating significant improvement over the model implemented in MAGFOX. In addition, the new model can reproduce ilmenite solubility in two immiscible melts from phase equilibria experiments in [13] that are not included in the model calibration. This further validates the new ilmenite solubility model.

Implication for lunar magma ocean evolution: The fractionation sequence of ilmenite in the LMO has a strong influence on density and viscosity profiles in the stratified lunar cumulate mantle. In general, the model used in MAGFOX overestimates ilmenite solubility in low-Ti melts from phase equilibria experiments (Fig. 1a). The crystallization sequence of ilmenite in LMO may be considerably earlier than the 95% suggested by [4] using the MAGFOX program. Early crystallization of ilmenite can generate a thicker layer of ilmenite-bearing cumulate. A thicker layer of ilmenite-bearing cumulate may have a viscosity increasing with depth and a smaller density contrast with the underlying cumulate mantle. According to the analysis of Rayleigh–Taylor instability by ref. [14], a thick, dense layer of ilmenite-bearing cumulate with increasing viscosity with depth is feasible to create degree one downwelling that gives rise to the preferential distribution of mare basalts on the nearside of the Moon. With the new ilmenite solubility model, we will be able to reexamine the crystallization model of LMO, quantifying its effect on the thermal and chemical evolution of the Moon.

Implication for mare basalt petrogenesis: We apply the new model to lunar melts reported in multiple-saturation experiments [15–21] and estimate their TiO_2 abundances at ilmenite saturation. Figure 2 shows that the calculated melt TiO_2 abundances at around multiple-saturation points are all higher than those determined experimentally, indicating that ilmenite is under saturated with melts at multiple-saturation points. This is consistent with results from multiple-saturation experiments [15–21], and suggests that ilmenite is not a residual phase in the sources of lunar picritic glass melts. TiO_2 abundances in high-Ti picritic glasses may

be attributed to the preferentially assimilation of ilmenite during magma ascent in the lunar cumulate mantle. Combining the ilmenite solubility model with ilmenite HFSE partitioning models in [8] and a partitioning model for low-Ca pyroxene in [22], we will be able to model the fractionation of trace elements during partial melting of the cumulate lunar mantle and develop a more consistent model for mare basalt petrogenesis in the near future.

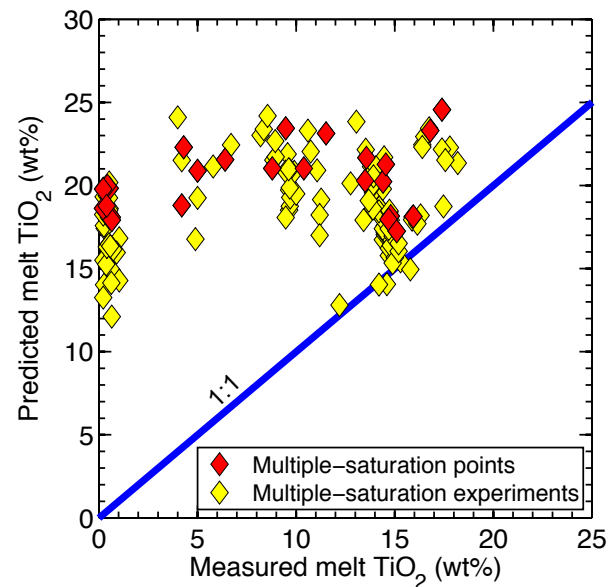


Figure 2. Comparison of predicted TiO_2 abundances at ilmenite saturation with measured values for melts from multiple-saturation experiments and those at around multiple-saturation points. Multiple-saturation experiments are from [15–21].

References: [1] Hess and Parmentier (1995) *EPSL*, 134, 501–514. [2] Shearer et al. (2006) *Rev. Mineral. Geochem.* 60, 365–518. [3] Wieczorek et al. (2006) *Rev. Mineral. Geochem.* 60, 221–364. [4] Snyder et al. (1992) *GCA*, 56, 3809–3823. [5] Papike et al. (1998) In: *Planetary Materials*. Chapter 5, pp1–234. [6] Beard et al. (1998) *GCA*, 62, 525–544. [7] Liu et al. (2010) *GCA*, 74, 6249–6262. [8] Dygert et al. (2013) *GCA*, doi: 10.1016/j.gca.2012.12.005. [9] Longhi (1980) *Proc. Lunar Planet. Sci. Conf.* 11, 289–315. [10] Nielsen and Dungan (1983) *CMP* 84, 310–326. [11] Longhi (1991) *Am. Mineral.* 76, 785–800. [12] Ariskin and Barmina (1999) *CMP* 134, 251–263. [13] Charlier and Grove (2012) *CMP* 164, 27–44. [14] Parmentier et al. (2002) *EPSL* 201, 473–480. [15] Delano (1980) *LPSC*, 11, 251–288. [16] Chen and Lindsley (1983) *JGR* 88, B335–B342. [17] Wagner and Grove (1997) *GCA*, 61, 1315–1327. [18] Elkins et al. (2000) *GCA*, 64, 2339–2350. [19] Elkins-Tanton et al. (2003) *Meteoritics & Planet. Sci.*, 38, 515–527. [20] Singletary and Grove (2008) *EPSL* 268, 182–189. [21] Krawczynski and Grove (2012) *GCA* 79, 1–19. [22] Sun and Liang (2013) *GCA*, in review.