Geophysical Research Abstracts, Vol. 7, 00771, 2005
SRef-ID: 1607-7962/gra/EGU05-A-00771

Orthorhombic Ti oxides and Planetary magmas

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Introduction: Orthorhombic Ti oxide solutions [1], hereafter Psd, were first recognized in lunar rocks and then identified as such on Earth. As inorganic materials they are constituents of ceramic materials or glass-ceramics and are of particular theoretical interest because of the strong order-disorder phenomena that affect their physical and thermal properties [2-4]. Even though they are less common than ilmenite and magnetite (s.l.), there is strong field, experimental, and theoretical evidence that they are not geological oddities [2], [5-8]. Besides, pseudobrookite oxide solutions may have had a critical role in the petrogenesis of the mare basalts and lunar picritic glasses as a source of TiO_2 and minor or incompatible elements (e.g., Cr, Hf, Zr, Nb, Ce). Finally, in general, it is a mineral that can have a strong effect on the speciation of elements important to isotope systems, e.g., Lu-Hf, W-Hf, Sm-Nd.

Discussion: Computations [2] predict the presence of primary Ilm+Ol+Opx, Rt+Ol+Opx, and Psd+Ol+Opx assemblages in terrestrial mantle rocks and xenoliths which in this order appear to mark nearly isothermal decreases in pressure conditions. Such predictions have field counterparts [6], [9]. Conceivably, near-solidus melting of such assemblages can produce Ti-enriched mantle melts in equilibrium with Ol+Opx or Ol+Ti oxide which, however, do not seem to be common on Earth.

However, we do find Ti-rich glasses among planetary samples; lunar glasses that are thought to represent lunar mantle material. Despite their Ti-rich composition, the conspicuous absence of a Ti oxide on the liquidus of the Ti-rich lunar glasses was noted and attributed to either ilmenite fractionation or consumption of ilmenite during melting or absence of ilmenite at the source [10-13]. From computations and chemography, it can be added that phase equilibrium constraints may prohibit either ilmenite or pseudobrookite oxide saturation in melts which are in equilibrium with orthopyroxene/low-Ca pyroxene, thus, enriching these melts in TiO_2. Alternatively, phase equilibrium constraints may prohibit the stable coexistence of Opx/low-Ca Px + Ti oxide + Olbearing assemblages at low to moderate bulk TiO_2 content and likely require extreme Ti-enrichment ($>$16 wt%) to stabilize Opx/low-Ca Px + Ti oxide + Ol on the liquidus [14].

The pristine lunar glasses are not constrained by compositions that are potentially multiply saturated with Ol, Opx, and Ti oxide or can be partial melts of model late-stage lunar magma ocean Cpx+Ilm cumulates [15]. It is such lack of compositional correspondence that necessitates mixing of Ti-poor deep mantle sources and Ti-rich materials in models of lunar mantle evolution. There are, however, model compositions for the lunar mantle and the source regions of the pristine glasses [16-19] that do project within such compositions, which in return, suggests that eutectic-like or small degree melting of such nominally Ol+Opx+Ti oxide-saturated mantle may produce primary melts enriched in TiO_2.

For instance, assuming equal amounts of olivine and orthopyroxene in the mode, 0.27 wt% TiO_2 in the bulk lunar mantle [16], [19], and appropriate mineral-melt partitioning coefficients [14], initial (F = 0) partial melts may have 4.7-8.2 wt% TiO_2. The variability in initial melt TiO_2 originates from the dependence of the Opx-Liq TiO_2 partition coefficient on the Al_2O_3 content of high-pressure Opx [14]. Increases in olivine augments the TiO_2 content of the initial partial melts up to 16.9 wt% at 100% Ol; in contrast, orthopyroxene will have the opposite effect with only 2.8-4.7 wt% Ti-enrichment at 100% Opx. Remelting of such Ti-enriched sources, and/or melting reactions between orthopyroxene and a Ti-rich oxide (Psd oxide, Ilm, or even Rt), if present, may further increase the amount of TiO_2 in the liquid. Polybaric pooled melts [20] in equilibrium with orthopyroxene may also become enriched in TiO_2 for the reasons outlined above. In general, mantle materials with bulk compositions that project on a Opx-Ti oxide tie line are capable of producing Ol-saturated, Ti-enriched liquids. Finally, the resulting silica activity variations in Ti-enriched lunar melts would impose additional controls on mineral equilibria among olivine, orthopyroxene, clinopyroxene, and plagioclase.

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