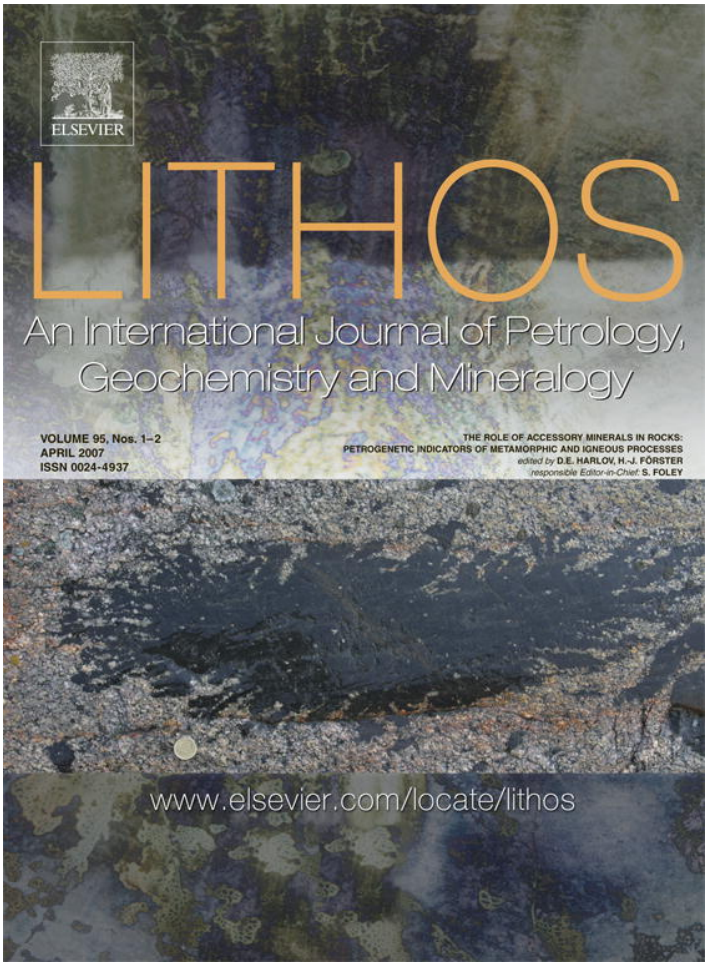
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Pseudobrookite-group oxide solutions and basaltic melts

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Abstract

Orthorhombic, (Bbmm), $R^{3+}_{2(1-x)}R^{2+}_{x}Ti_{1+x}O_5=[R^{3+},R^{2+},Ti]^{M1}\ [Ti,R^{2+},R^{3+}]^{M2}_{2}O_5$ solid solutions were first recognized in lunar rocks and then identified as such on Earth. 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. 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 may be present in other planetary bodies as well. As materials they are of particular theoretical and practical interest because of the cation order–disordering phenomena that affect their physical and mechanical properties, and participation in the TiO_2-slag smelting process.

X-ray crystallography and spectroscopy studies have shown that all the cations are in octahedral coordination occupying two nonequivalent sites with a 1:2 ratio. Evaluation of site fractions, configurational entropy in $R^{3+}_{2(1-x)}R^{2+}_{x}Ti_{1+x}O_5$ solutions, and of the known properties of pseudobrookite-group $MgTi_2O_5$ suggests that $R^{3+}_{2}TiO_5$ solutions may reach cation random distribution and thus entropy maxima at lower temperatures than $R^{2+}Ti_2O_5$-rich solid solutions. As a result, the entropy contribution to their thermodynamic stability may depend upon the $\frac{R^{2+}}{R^{3+}}$ ratio.

On the basis of computations, experiments, and chemography of mineral equilibria it is inferred that (1) assemblages of pseudobrookite-group Ti oxide, ilmenite, rutile, olivine, and pyroxene(s) should be expected under lower crust and upper mantle conditions in the Earth, and, conceivably, in other planetary bodies including the Earth's Moon; (2) reactions between pseudobrookite-group Ti oxide and olivine, orthopyroxene and pseudobrookite-group Ti oxide or ilmenite can produce ilmenite- or olivine-saturated Ti-enriched liquids; (3) lack of either ilmenite or pseudobrookite-group Ti oxide saturation in melts, which are in equilibrium with orthopyroxene and olivine enriches these melts in TiO_2; (4) the assemblage olivine+orthopyroxene+rutile has a large stability field and is probably replaced by olivine+orthopyroxene+ilmenite with increasing pressure and temperature, and olivine+orthopyroxene+pseudobrookite-group Ti oxide with decreasing pressure and increasing temperature; (5) lunar source regions, nominally saturated in olivine, orthopyroxene, and pseudobrookite-group Ti oxide or ilmenite may produce the range of TiO_2 content in the lunar pristine glasses which, apparently, cannot be derived by partial melting of model late-stage Lunar Magma Ocean oxide+silicate assemblages or equivalent bulk compositions.
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Keywords: Pseudobrookite-type Ti oxides; Armalcolite; Entropy stabilization; Basalts; Mantle

1. Introduction

Orthorhombic, (Bbmm/Cmcm), $R^{3+}_{2(1-x)}R^{2+}_{x}Ti_{1+x}O_5=[R^{3+},R^{2+},Ti]^{M1}\ [Ti,R^{2+},R^{3+}]^{M2}_{2}O_5$ solid solutions, hereafter pseudobrookite-group Ti oxide (Psd), are encountered either as an oxidation product of ilmenite (Ilm) and/or spinel (Spl) or a primary crystallizing phase in igneous and metamorphic rocks on Earth, and basaltic rocks on the Moon, e.g., basalt flows, crustal and mantle xenoliths, hornfels (MacGregor, 1969; Haggerty, 1991; Hayob and Essene, 1995; Ionov et al., 1999; Gregoire

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et al., 2000). Venusian surface processes may also involve Mg-rich pseudobrookite-group Ti oxide (Fegley et al., 1992). Lastly, the materials literature has a plethora of references covering the physical and mechanical properties of pseudobrookite-group Ti oxide glass-ceramics and by-products of TiO_2 slag smelting.

To fully exploit the petrological potential of pseudobrookite-group Ti oxide solutions we need to quantitatively understand the factors controlling their properties and stability, and thus, to extrapolate beyond any of the presently scanty calibration experiments. For that purpose, we need to combine thermochemistry, phase equilibria, and in situ P–V–T–cation disorder experimental data that, presently are either incomplete or lacking.

In this paper, I discuss cation disorder and entropy-stabilization in pseudobrookite-group Ti oxide solutions with respect to their R^{2+} and R^{3+} content, and oxide-silicate interaction in petrologically simple but fundamental chemical systems with an emphasis on pseudobrookite-group Ti oxide (Psd).

2. Discussion

2.1. Cation disorder and entropy

To a large extent, terrestrial and lunar pseudobrookite-group Ti oxide can be described as $MgTi_2O_5$–$FeTi_2O_5$–Fe_2TiO_5–Cr_2TiO_5–Al_2TiO_5–Ti_2TiO_5 solid solutions (Bowles, 1988). X-ray crystallography and spectroscopy studies have shown that all the cations are in octahedral coordination occupying two nonequivalent sites with a 1:2 ratio (Waychunas, 1991; Guo et al., 1999). Cation disorder between the two nonequivalent octahedral sites ($M1$ and $M2$, or A and B, or Wyckoff-positions 4c and 8f) depends upon temperature, composition, probably pressure, and it strongly affects the physical and chemical properties of end-members and solid solutions (e.g., Navrotsky, 1975; Wechsler et al., 1975; Brown and Navrotsky, 1989; Hazen and Yang, 1997; Yang and Hazen, 1998; Ghiorso et al., 1999; Xirouchakis et al., 2002).

Cation-disorder in $R^{3+}_{2(1-x)}R^{2+}_{x}Ti_{1+x}O_5=[R^{3+},R^{2+},Ti]^{M1}\ [Ti,R^{2+},R^{3+}]^{M2}_2O_5$ compounds can be described with the order parameters (Ghiorso and Sack, 1991; Ghiorso et al., 1999; Xirouchakis et al., 2002):

$$s_1 = s_{R^{2+}} = X^{M1}_{R^{2+}} - 2X^{M2}_{R^{2+}} \tag{1}$$

$$s_2 = s_{R^{3+}} = \frac{3}{2}X^{M1}_{R^{3+}} - X^{M2}_{R^{3+}} \tag{2}$$

and the following stoichiometry constraints,

$$X_{R^{2+}} = X^{M1}_{R^{2+}} + 2\cdot X^{M2}_{R^{2+}} = 1, \tag{3}$$

$$X_{R^{3+}} = X^{M1}_{R^{3+}} 2\cdot X^{M_2}_{R^{3+}} = 2, \tag{4}$$

and

$$\mathrm{Ti} = X^{M1}_{\mathrm{Ti}} + 2\cdot X^{M2}_{\mathrm{Ti}} = 2 \text{ or } 1. \tag{5}$$

The order parameters s_1 and s_2 are thus constrained to take values between 1 and −1 whereas R^{2+} and R^{3+} respectively represent major divalent and trivalent cations, e.g., Fe^{2+}, Mg, Ti^{3+}, Fe^{3+}, Al^{3+}, Cr^{3+}.

In $R^{2+}Ti_2O_5=[R^{2+},Ti]^{M1}[Ti,\ R^{2+}]^{M2}_2O_5$ pseudobrookite-group oxide solutions the algebraic expressions for site fractions as a function of s_1 are as follows:

$$X^{M1}_{R^{2+}} = \frac{(1+s_1)}{2} \tag{6}$$

$$X^{M2}_{R^{2+}} = \frac{(1-s_1)}{4} \tag{7}$$

$$X^{M1}_{\mathrm{Ti}^{4+}} = \frac{(1-s_1)}{2} \tag{7}$$

$$X^{M2}_{\mathrm{Ti}^{4+}} = \frac{(3+s_1)}{4}. \tag{8}$$

In $R^{3+}_2TiO_5=[Ti,R^{3+}]^{M1}[R^{3+},Ti]^{M2}_2O_5$ pseudobrookite-group oxide solutions, the site fractions as a function of s_2 can be described by the equations:

$$X^{M1}_{R^{3+}} = \frac{(1+s_2)}{2} \tag{9}$$

$$X^{M2}_{R^{3+}} = \frac{(3-s_2)}{4} \tag{10}$$

$$X^{M1}_{\mathrm{Ti}^{4+}} = \frac{(1-s_2)}{2} \tag{11}$$

$$X^{M2}_{\mathrm{Ti}^{4+}} = \frac{(1+s_2)}{4}. \tag{12}$$

For $R^{3+}_{2(1-x)}R^{2+}_{x}Ti_{1+x}O_5=[R^{3+},R^{2+},Ti]^{M1}\ [Ti,R^{2+},R^{3+}]^{M2}_2O_5$ oxide solutions, the site fractions change to:

$$X^{M1}_{R^{2+}} = \frac{(x+s_1)}{2} \tag{13}$$

$$X^{M2}_{R^{2+}} = \frac{(x-s_2)}{4} \tag{14}$$

$$X^{M1}_{R^{3+}} = \frac{(1-x+s_2)}{2} \tag{15}$$

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$$X_{R^{3+}}^{M2} = \frac{(3\cdot(1-x)-s_2)}{4} \quad (16)$$

$$X_{\mathrm{Ti}^{4+}}^{M1} = \frac{(1-s_1-s_2)}{2} \quad (17)$$

$$X_{\mathrm{Ti}^{4+}}^{M2} = \frac{(1+2\cdot x+s_1+s_2)}{4}. \quad (18)$$

Eqs. (6)–(8) require $x=1$ and $s_2=0$ whereas Eqs. (9)–(12) result from $x=0$ and $s_1=0$.

At $s_1=1$, $R^{2+}Ti_2O_2$ compounds are ordered with all of Ti^{4+} in the $M2$ site and the R^{2+} cations in the $M1$ site whereas random distribution of R^{2+} and Ti^{4+} cations is achieved at $s_1=-\frac{1}{3}$. In contrast, random distribution in $R_2^{3+}TiO_5$ pseudobrookite-group compounds is achieved at $s_2=\frac{1}{3}$ whereas $s_2=1$ accounts for full order with R^{3+} and Ti^{4+} cations in $M2$ site. The computed site fractions in both cases are depicted in Fig. 1.

The configurational entropy, $s_{\mathrm{config}}=-R\sum_i^n\sum_j^m X_i^j\cdot\ln X_i^j$, of $R_{2(1-x)}^{3+}R_x^{2+}Ti_{1+x}O_5=[R^{3+},R^{2+},Ti]^{M1}[Ti,R^{2+},R^{3+}]_2^{M2}O_5$ pseudobrookite-group oxide as a function of site fractions is shown in Fig. 2. The respective differences in the configurational entropy maxima of $R_2^{3+}TiO_5$ and $R^{2+}Ti_2O_5$ solutions result from differences in the parameters s_1 and s_2 and the different cation configurations.

In line with our knowledge of the configuration entropy variation in $MgTi_2O_5$ pseudobrookite as a function of cation disorder with temperature (Xirouchakis et al., 2002; Ghiorso et al., 1999), the depicted variations in Figs. 1 and 2) are interpreted to suggest that either $R_2^{3+}TiO_5$ solutions may reach entropy maxima at lower temperatures than $R^{2+}Ti_2O_5$ solutions or the configurational entropy of $R_2^{3+}TiO_5$ solutions is greater than that of $R^{2+}Ti_2O_5$ solutions at the same temperature. For example, the calculated order parameter for a Sc_2TiO_5 crystal with a nominal synthesis temperature of 1123 K (Kolitsch and Tillmans, 2003) is equal to 0.6 whereas

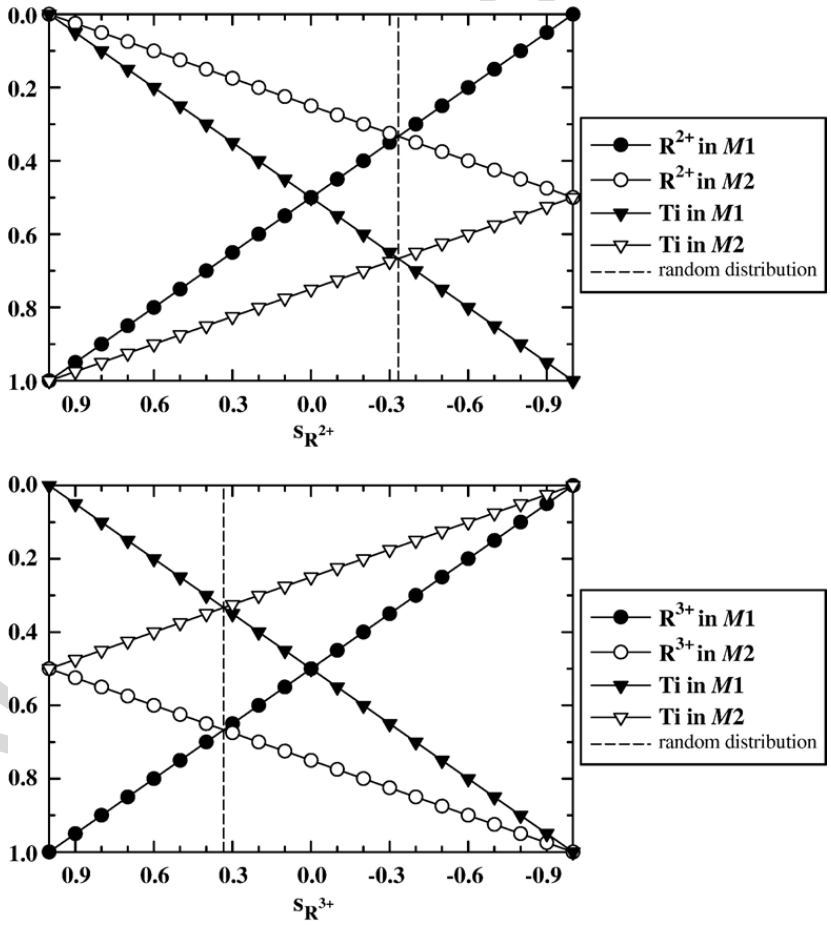


Fig. 1. Calculated $M1$ and $M2$ site occupancies in (a) R_2TiO_5 and (b) RTi_2O_5 pseudobrookite oxide end-members as a function of the respective order parameters, $s_1=X_{R2+}^{M1}-2X_{R2+}^{M2}$ and $s_2=\frac{3}{2}X_{R^{3+}}^{M1}-X_{R^{3+}}^{M2}$ that take values between −1 and 1. R^{2+} and R^{3+} represent major and minor divalent and trivalent cation that can be present in pseudobrookite-group Ti oxide.

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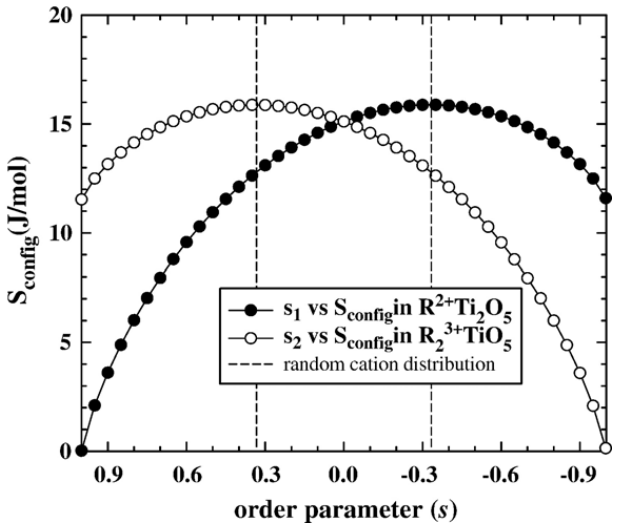


Fig. 2. Configurational entropy (J/mol) variations in R_2TiO_5 and RTi_2O_5 end-members as a function of the respective order parameters s_1 and s_2. End-member R_2TiO_5 pseudobrookite oxides achieve random cation distribution (maximum entropy) at positive order parameter values ($s_2 \simeq 0.3$) and probably at lower temperatures than end-member RTi_2O_5 pseudobrookite ($s_1 \simeq -0.3$). Such observations strongly suggest that entropy may enhance the stability of R_2TiO_5-rich solid solutions relative to RTi_2O_5-rich ones in general and either high or low fO_2 conditions at low to moderate temperatures in particular, depending on the major and minor trivalent cations (e.g., Fe^{3+}, Ti^{3+}, Cr^{3+}, REE).

the experimentally deduced order parameter value for $MgTi_2O_5$ is approximately equal to 0.4 at the same temperature (Wechsler and Navrotsky 1984; Brown and Navrotsky, 1989; Yang and Hazen, 1998). Therefore at 1123 K, from Figs. 1 and 2, it is predicted that the configurational entropy for $Sc_2Ti_2O_5$ is equal to 15 J/mol whereas that for $MgTi_2O_5$ is 12 J/mol. Conceivably, entropy stabilization (Navrotsky, 1975) may favor pseudobrookite-group oxide solutions at either high or low temperatures and either high or low oxygen fugacity conditions depending upon their chemical constituents. Moreover, maximum or nearly maximum configurational entropy in $R^{3+}_{2-x}R^{2+}_{x}Ti_{1+x}O_5$ compounds is apparently achieved for s_1 and s_2 values between 1/3 and −1/3, and possibly near 0 where Ti, R^{2+}, and R^{3+} occupation of $M1$ is nearly equal or close to 0.5. Interestingly, but not neces sarily fortuitous, lunar armalcolite ($Fe^{2+}_{0.5}Mg_{0.5}Ti_2O_5$) an nealed at 1700 K had 0.400 Ti^{4+} in $M1$ (Wechsler and Von Dreele, 1989), presumably with some reordering during quench.

3. Pseudobrookite-group Ti oxide and oxide–silicate interaction

There is little that we know of the stability of pseudobrookite-group Ti oxide solutions with respect to common rock-forming silicate minerals. Most of the past experiments and theoretical considerations concentrated primarily to relations with other Ti oxides in lunar basalts and since the last major review of the literature, little has been added (Lindsley, 1991).

The computed phase relations and experiments in Fig. 3 (Xirouchakis et al., 2002; MacGregor, 1969) offer the opportunity to look at reactions among pseudobrookite-group Ti oxide (Psd), ilmenite (Ilm), rutile (Rt), olivine (Ol), orthopyroxene (Opx), silica, and liquid in a simple but petrologically important chemical system.

The depicted phase relations indicate that $MgTi_2O_5$ pseudobrookite (Kar) can coexist with forsterite (Fo) and enstatite (En). Moreover, $MgTi_2O_5$ pseudobrookite is part of the mineralogy near and above the solidus. In this system, and in the range 0 to 4 GPa, eutectic melting takes place between 1390 and 1650 °C via the reactions:

$$Fo + En + Rt = Liq, \text{ between 4 and 1.5 GPa}$$

$$Fo + En + Kar + Rt = Liq, \text{ at 1.5 GPa}$$

$$En + Kar + Rt = Liq, \text{ between 1.5 and 0.5 GPa}$$

$$En + Kar + SiO_2 = Liq, \text{ below 0.5 GPa.}$$

In Fig. 3, the TiO_2 (wt.%) content of the product melts increases with pressure (MacGregor, 1969) while remaining in equilibrium with Fo and/or En and a Ti oxide other than $MgTiO_3$ ilmenite (Gk), probably up to 6 GPa where $MgTiO_3$ ilmenite becomes a liquidus mineral. A temperature increase of 30 to 50 °C changes the melting style from eutectic to peritectic (or from even to odd) while above and below 1.5 GPa the peritectic reactions (not shown) are Fo + Rt = Kar + Liq and En + Kar = Fo + L, respectively.

The phase relations in Fig. 3 may be incomplete, because they do not include Mg_2TiO_4 spinel (plots between $MgTiO_3$ and MgO on the ternary diagrams) due to insufficient thermodynamic data to properly account for the behavior of this crystalline solid (e.g., O'Neill et al., 2003). But also Mg_2TiO_4 spinel is likely not stable with respect to the other three Ti oxides for nominally olivine + orthopyroxene-saturated compositions in this P–T range (Fig. 3; MacGregor, 1969; Pelton et al., 1998). Nonetheless, the inferences based on the depicted phase relations are valid, and may serve as a template for the more complex lunar and terrestrial systems.

Calculations in the $CaO–MgO–TiO_2–SiO_2$ system involving end-member diopside and titanite as well as the rest of the phases shown in Fig. 3 suggest that reactions involving end-member diopside and titanite

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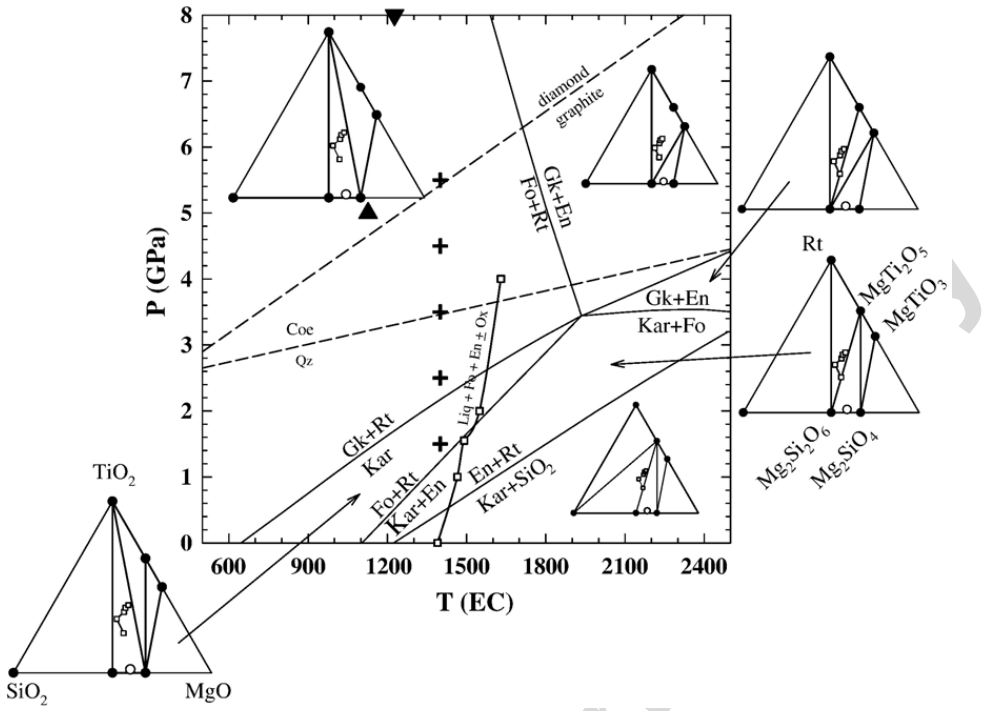


Fig. 3. Computed (Xirouchakis et al., 2002) and experimental (MacGregor, 1969) stable and metastable with respect to liquid phase relations among pseudobrookite oxide, ilmenite, rutile, orthopyroxene, olivine, silica, and liquid in the $MgO–TiO_2–SiO_2$ system. The Coesite↔Quartz and Graphite↔Diamond transition curves were taken from Liu (2002). Open squares represent eutectic or nearly eutectic melt compositions (mol%), (MacGregor, 1969). Filled circles represent the compositions of the crystalline solids (mol%). The open circle represents a Ti-poor but also nominally Fo+En+Ti oxide-saturated bulk composition. Mg_2TiO_4 spinel (not shown) plots between $MgTiO_3$ and MgO. The crosses (+) mark the Herman et al. (2005) equilibration conditions for the assemblage Fo+En+Rt whereas the upward-looking triangle. (▲) marks the Dobrzhinetskaya et al. (2000) data for the likely stable assemblage Fo_{90}+rutile and the downward-looking triangle (▼) the Dobrzhinetskaya et al. (2000) data for the likely stable assemblage Ol+Orthopyroxene+ Ilm in Ilm-seeded lherzolite.

are likely not stable with respect to liquid. Computations involving Mg–Ti spinel, ilmenite, pseudobrookite-group oxide and Ca–Mg olivine, pyroxene, and garnet are in progress.

Addition of elements such as Fe, Ca, and Al in this system will introduce clinopyroxene and expand the olivine stability field to pressures lower than 0.5 GPa. Concomitantly, the rutile stability field will shrink relative to pseudobrookite-group Ti oxide and ilmenite sta bility fields but also neither rutile nor pseudobrookite will have to disappear. The latter assertion and the computed phase relations in Fig. 3 are supported by the high-pressure experiments of Dobrzhinetskaya et al. (2000) who report olivine (~Fo_{90})+rutile at 5 GPa and 1127 °C, and olivine+ilmenite+orthopyroxene at 1227 °C and 8, 10, and 12 GPa in Ilm-seeded lherzolite, as well as Herman et al. (2005) who report stable forsterite+enstatite+rutile at 1400 °C from 1.5 and up to 5.5 GPa. Note that the Dobrzhinetskaya et al. (2000) data imply that in nature or near-natural chemical systems the reaction Opx+Ilm=Ol+Rt is displaced to temperatures lower than the ones shown in Fig. 3 for En+Gk=Fo+Rt. Lastly, the predicted change in Fig. 3 from Ol+Opx+Rt to Ol+Opx+Ilm, with increasing pressure is also in good agreement with the experimental results of Iizuka and Nakamura (1995) in eclogites.

Fig. 4 shows the $MgO–TiO_2–SiO_2$ (Per-Rt-Qz) ternary onto which are projected (mol%): (1) glass compositions (Delano, 1986; Jin and Taylor, 1990; Wagner and Grove, 1997; Elkins et al., 2000; Xirouchakis et al., 2001), and (2) Ti-oxide, olivine and pyroxene compositions from a lunar harzburgite (Morris et al., 1990) and high-pressure experiments (Delano, 1980; Wagner and Grove, 1997; Elkins et al., 2000; Xirouchakis et al., 2001). The data were taken from the much larger experimental data base for Ti oxides and silicates in lunar or lunar-like compositions. In Fig. 4, the spinel-ilminite-pseudobrookite-oxide sequence in the $MgO–TiO_2–SiO_2$ and $FeO–TiO_2–SiO_2$ systems is replaced by spinel–pseudobrookite–ilmenite because of the projected Fe- and Ti-poor spinel and Mg-poor ilmenite compositions. The reader can check this change by projecting oxide compositions with variable Fe/Mg ratios on the ternary $FeO–MgO–TiO_2$. Nonetheless, the inferred reactions (see below) are also maintained in projections onto the $FeO–MgO–TiO_2$, $FeO–MgO–SiO_2$, $FeO–TiO_2–SiO_2$ and $FeO–MgO–TiO_2$ ternaries.

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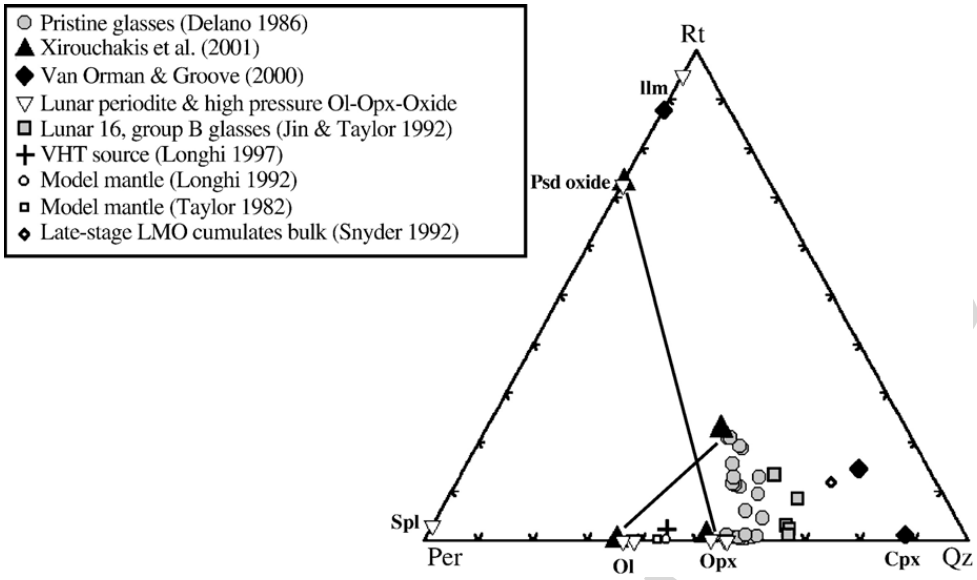


Fig. 4. Projections onto the Per-Rt-Qz ternary (mol%) from $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$, $CaO{\cdot}SiO_2$, and FeO of pristine lunar glass compositions (Delano, 1986), and mineral compositions from lunar harzburgite (Morris et al., 1990) and high-pressure experiments using VLT and VHT glass compositions (Delano, 1980; Wagner and Grove, 1997; Elkins et al., 2000). The Jin and Taylor (1990) data for the Luna 16, group B glasses, and the high-pressure experimental data of Xirouchakis et al. (2001) for coexisting Ol, Orthopyroxene, Psd oxide, and Ti-rich liquid are also shown for comparison. The Snyder et al. (1992) bulk composition, used by Van Orman and Grove (2000), represents the composition of a late-stage, ilmenite-bearing, crystalline assemblage after ~95% Lunar Magma Ocean (LMO) crystallization.

The projected mineral and melt compositions imply that melting of orthopyroxene+Ti oxide-bearing mineral assemblages may lead or add to melt enrichment in TiO_2 via the reactions:

$$Opx + Psd = Ol + Liq$$

$$Opx + Ilm = Ol + Liq.$$

Either olivine+ilmenite- or orthopyroxene+ilmenite-bearing assemblages may react to produce pseudobrookite-group Ti oxide and silicate melt:

$$Ol + Ilm = Psd + Liq$$

$$Opx + Ilm = Psd + Liq.$$

Spinel phase and clinopyroxene add to the complexity of oxide–silicate interaction with the following possible reactions:

$$Cpx + Ol/Opx + Spl = Opx/Ol + Psd/Ilm \pm Liq$$

$$Cpx + Spl = Opx/Ol + Psd/Ilm \pm Liq$$

$$Spl + Liq = Ol/Opx + Psd/Ilm$$

$$Spl + Opx = Ol + Psd/Ilm \pm Liq.$$

The computed phase relations and chemographies (Figs. 3 and 4) can explain the occurrence of oxide–silicate assemblages in mantle xenoliths that are thought enigmatic or atypical (e.g., Haggerty, 1991; Ionov et al., 1999; Wang et al., 1999; Gregoire et al., 2000): pseudobrookite-group Ti oxide (armalcolite) overgrowths on orthopyroxene or clinopyroxene and olivine; pseudobrookite-group Ti oxide (armalcolite) and olivine replacing orthopyroxene and/or clinopyroxene in the presence of feldspars that presumably represent the melt fraction; graphic rutile+olivine and rarer rutile+orthopyroxene intergrowths; and ilmenite+orthopyroxene intergrowths. Even though the exact conditions favoring these reactions remain elusive, it is apparent from the computed phase relations in Fig. 3 that the assemblage olivine+orthopyroxene+rutile has likely a large stability field and it is replaced by olivine+ orthopyroxene+ilmenite with increasing pressure or temperature, and olivine+orthopyroxene+pseudobrookite Ti oxide with decreasing pressure or increasing temperature. Conceivably, the sequence olivine+orthopyroxene+ilmenite → olivine+orthopyroxene+rutile → olivine+orthopyroxene+pseudobrookite Ti oxide, when observed in mantle rocks, may mark nearly isothermal decompression paths.

The inferred reactions and phase stabilities also agree with reports on extraterrestrial compositions (Grove et al., 2006; Monders et al., 2006), and may be relevant to the formation of lunar Ti-rich basalts and glasses, which are presently unique among terrestrial and extraterrestrial samples for their extraordinary TiO_2-variability and enrichment (0.3–16.4 wt.%). With a few

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exceptions (Jones and Delano, 1991; Cazzaniga and Hess, 1995; Hess, 1991, 2000; Hess and Finnila, 1997; Beck and Hess, 2001), the role of pseudobrookite-group Ti oxide, a titanium oxide that is at least 10–15 wt.% richer in TiO_2 than ilmenite or spinel, in the petrogenesis of the lunar volcanics is largely neglected, perhaps, because it is incorrectly thought to lack a high-pressure stability field relative to ilmenite and rutile or spinel.

Ilmenite is typically considered the chief source of TiO_2, and the TiO_2-enrichment and variability in mare glasses and basalts has been attributed to partial melting of mixed mantle sources or assimilation of either shallow level ilmenite-bearing cumulates or ilmenite by low Ti melts. According to these models, hybridization of the deep lunar mantle must have occurred after originally shallow, late-stage lunar magma ocean ilmenite-bearing cumulates sunk and mechanically mixed with early-stage lunar magma ocean olivine+orthopyroxene-dominated cumulates, or when shallow Ti-rich melts sunk and mixed with deep mantle source regions. However, these models have physical and chemical limitations. First, trace element and isotope systematics in lunar volcanics are more compatible with small degree partial melting of mineralogically inhomogeneous sources than low-pressure assimilation of Ti-rich materials by Ti-poor liquids (Shearer et al., 1996; Beard et al., 1998; Shearer et al., 2000). Second, sinking of shallow level solid ilmenite-bearing cumulates may be difficult due to viscosity limitations (Elkins Tanton et al., 2002). And, third, melting of mantle sources that are enriched by percolating downwards Ti-rich melts, produced by melting of model Cpx-Ilm cumulates (Elkins Tanton et al., 2002), do not result in partial melt compositions that resemble the actual lunar samples (Beck et al., 2003).

An alternative explanation is that neither Fe-rich ilmenite is the sole Ti oxide nor the Ti oxides are introduced into the deep lunar mantle, but rather have crystallized there along [or in equilibrium] with mantle silicate minerals. In this case mineralogically distinct and inhomogeneous mantle regions would behave differently during deep-seated melting. This is because the mineral phases, mineral proportions, and melting reactions would differ. Such critical parameters in geochemical models of lunar mantle melting remain unconstrained (e.g., Beard et al., 1998).

Melt compositions that project either within the limiting olivine–orthopyroxene–Ti oxide tielines or at the intersection of the olivine–liquid and orthopyroxene–Ti oxide tielines (Fig. 4) have the potential to be Ti-enriched and coprecipitate olivine, orthopyroxene, and a Ti oxide. The intersections apparently represent the multiply-saturated "points" in P–T space often reported in the lunar literature. Alternatively, the stable coexistence of orthopyroxene+Ti oxide+olivine on the liquidus likely requires significant Ti-enrichment (>16 wt.%) at near constant pressure and temperature conditions, (e.g., Xirouchakis et al., 2001). The pristine lunar glasses do not fall within compositions delimited by olivine–orthopyroxene–Ti oxide tielines (Fig. 4). Thus, they cannot be partial melting products of model late-stage lunar magma ocean clinopyroxene +ilmenite cumulates (Van Orman and Grove, 2000) that also have model bulk compositions (Snyder et al., 1992) far removed from that of the pristine glasses (Fig. 4). This is an inference that is in agreement with the Van Orman and Grove (2000) melting experiments. It is such lack of compositional correspondence that apparently necessitates mixing models for a Ti-poor deep mantle sources and Ti-rich materials.

There are, however, model compositions for the lunar mantle and the source regions of the pristine glasses (Taylor, 1982; Longhi, 1987, 1992a,b, 1996) that apparently project within the olivine–orthopyroxene–Ti oxide tielines, which in return, suggests that eutectic-like or small degree melting of such nominally olivine+orthopyroxene+Ti oxide-saturated sources may produce primary melts enriched in TiO_2. Remelting of such Ti-enriched sources, and/or melting reactions between orthopyroxene and a Ti-rich oxide (pseudobrookite-type oxide, ilmenite, or even rutile), if present, may further increase the amount of TiO_2 in the liquid. Polybaric pooled melts (e.g., Longhi, 1992a,b) in equilibrium with orthopyroxene may also become enriched in TiO_2 for the reasons outlined above.

4. Summary

Cation disorder and entropy-stabilization is anticipated to affect differently R^{2+}-rich and R^{3+}-rich pseudobrookite-group Ti oxide solutions. A prediction that needs to be verified by X-ray crystallography and thermochemistry experiments. Moreover, it is apparent that such data are critically needed to formulate thermodynamic models of pseudobrookite-group Ti oxide solutions, i.e., standard state properties (G, H, S, V, C_p), P–V–T equations of state, and activity–composition relationships as a function of P, T, and composition.

Computed oxide–silicate equilibria and chemography are consistent with field observations and experiments in terrestrial and lunar rocks, and either anticipate or can account for:

Assemblages of pseudobrookite-group Ti oxide, ilmenite, rutile, olivine, and pyroxene(s) at lower crust and upper mantle conditions in the Earth, and, conceivably, in other planetary bodies including the Earth's Moon.

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Reactions between pseudobrookite-group Ti oxide and olivine, orthopyroxene and pseudobrookite-group Ti oxide or ilmenite that produce ilmenite- or olivine-saturated Ti-enriched liquids.

The lack of either ilmenite or pseudobrookite-group Ti oxide saturation in melts that are in equilibrium with orthopyroxene and olivine which, in return, may enrich these melts in TiO_2.

A large stability field for the assemblage olivine + orthopyroxene + rutile that is replaced by olivine + orthopyroxene + ilmenite with increasing pressure or temperature, and olivine + orthopyroxene + pseudobrookite Ti oxide with decreasing pressure or increasing temperature.

The lack of compositional correspondence between pristine lunar glasses and melting products of model Lunar Magma Ocean clinopyroxene and ilmenite cumulates or equivalent bulk compositions.

Lunar compositions, nominally saturated in olivine, orthopyroxene, and pseudobrookite-group Ti oxide or ilmenite may produce the range of TiO_2 content in the pristine lunar glass via either eutectic or peritectic small-degree melting reactions.

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