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Stability of Pseudobrookite-type Titanium Oxides

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Orthorhombic, (Bbmm), $(Al, Fe, Cr, Ti)_{2}TiO_{5}$ -(Mg, Fe) $Ti_{2}O_{5}$ solid solutions (pseudobrookites, s.l.) are found either as an oxidation product of ilmenite or a primary crystallizing phase in igneous and metamorphic rocks on Earth (e.g., basalt flows, crustal and mantle xenoliths, hornfels), and basaltic rocks on the Moon. Moreover, orthorhombic oxides are often part of the crystalline matrix in glass/ceramics with useful applications, and play a major role in the industrial production of TiO_{2} . To fully exploit the potential of these compounds as petrogenetic indicators and/or useful materials we need to quantitatively understand the factors controlling their properties and stability, and thus, to extrapolate beyond the calibrating experiments. For that purpose, we need to combine thermochemistry, phase equilibrium, and in situ P-V-T-cation disorder experimental data that presently either are incomplete or lacking. Perhaps, the most complete data set is that for $MgTi_{2}SO_{5}$ (karroite) which allows the calibration of models for the Gibbs free energy of the $MgTi_{2}SO_{5}$ as a function of pressure, temperature, and the Mg^{2+} - Ti^{4+} distribution between the two nonequivalent octahedral sites. Consequently, the effect of cation disorder on $MgTi_{2}SO_{5}$ stability, and the phase relations among $MgTi_{2}SO_{5}$, other titanium oxides, and silicate minerals can be examined. Calculated phase relations in the Mg-Ti-Si-O system and phase equilibrium experiments in Fe-bearing compositions suggest that pseudobrookite-type oxides may be a more common in rocks than previously realized. However, homogeneous and heterogeneous equilibria, and crystallization paths likely affect their stability. For example, isobaric increases in temperature favor disordering and thus entropy-stabilization, in contrast, isothermal increases in pressure have the opposite effect. Although, currently, the potential effect of composition to cation disorder cannot be fully explored, it appears that enrichment in trivalent cations probably enhances entropy-stabilization and thus may increase the stability of (Al, Fe, Cr, Ti)-rich pseudobrookites relative to that of (Mg, Fe)-rich ones. In addition, high-temperature, nearly isothermal, decompression paths of olivine+orthopyroxene+oxide assemblages may favor pseudobrookites (s.l.) over rutile and/or ilmenite, in contrast, cooling at low pressures seems to favor ilmenite and/or rutile. In the case of crustal and mantle xenoliths, the presence or absence of orthorhombic oxides is probably controlled by reactions with olivine, orthopyroxene, ilmenite, and rutile. In oceanic mantle xenoliths such reactions may also involve a TiO_{2} -enriched but not SiO_{2} -enriched melt/fluid, because pseudobrookites (s.l.) would react with the SiO_{2} -enriched melt/fluid to form orthopyroxene and rutile. Parenthetically, experiments and model calculations in the Mg-Ti-Si-O system suggest that low degree partial melting of low- TiO_{2} bulk compositions may produce Ti-enriched liquids in equilibrium with olivine, orthopyroxene, and $MgTi_{2}SO_{5}$, rutile, or ilmenite.

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