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Effects of chemical composition on variation in thermal expansion for minerals in the garnet, olivine, pyroxene, amphibole, and tourmaline systems

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An area of interest by this laboratory has been the extent to which chemical composition within isostructural mineral groups affects the degree to which minerals thermally expand. Our past studies on framework silicates (Hovis and coauthors, 1999, 2003, 2006, 2008, 2010) have found chemical effects on thermal expansion to be substantial and clearly defined in the $AlSi_3$ feldspar, plagioclase feldspar, and silicic/subsilicic nepheline - kalsilite systems, yet not in Al_2Si_2 feldspars. In present work we have investigated additional silicate mineral groups through the calculation of unit-cell dimensions on members (numbers per group given in parentheses) of the garnet (6), olivine/monticellite (6), orthopyroxene (5), clinopyroxene (9), orthoamphibole (4), clinoamphibole (9), and tourmaline (13) systems based on X-ray powder diffraction data collected between room temperature and 900 ˚C. We have employed NIST 640a silicon as an internal standard for all unit-cell calculations and (in separate experiments) calibrated instrument temperatures utilizing known second-order phase transitions of various compounds over the temperature range of our experiments. Chemical differences among six near-end-member garnets produce little variation in the coefficients of thermal expansion for volume [α_V = 29.1 ($\pm 2\sigma$) ±3.4 x 10^{-6} deg^{-1}]. Because of the similar size of substituting cations, the same is true of α_V in Fe-Mg olivines (31.2 ±4.6 x 10^{-6} deg^{-1}) and Fe-Mg orthopyroxenes (32.9 ±4.9 x 10^{-6} deg^{-1}); in both cases, however, the smaller Mg^{2+}-bearing unit cell undergoes greater expansion than the larger Fe^{2+} analog. On the other hand, greater chemical variation in the clinopyroxene mineral group produces higher variability in α_V (28.7 ±6.9 x 10^{-6} deg^{-1}); moreover, the presence of Ca^{2+} in the M2 crystallographic site is associated with slightly greater expansion than is occupancy of M2 by Na^+ or Li^+. Orthoamphiboles exhibit relatively high variability in α_V (30.4 ±8.9 x 10^{-6} deg^{-1}) owing largely to the inclusion of holmquistite in that group. Clinoamphiboles display values of α_V (27.6 ±5.2 x 10^{-6} deg^{-1}) similar to those of clinopyroxenes. Collectively, thirteen members of the tourmaline group undergo less expansion than the other groups (α_V =23.3 ±4.6 x 10^{-6} deg^{-1}). Although chemical substitution does indeed have demonstrable and significant effects on thermal expansion in four of the five new silicate systems we have studied, there is generally less variation in α_V in these systems than those observed in the alkali (Li^+, Na^+, K^+, Rb^+) feldspar (α_V = 25.2 ±18.6 x 10^{-6}deg^{-1}; Hovis and coworkers, 2008, American Mineralogist), plagioclase feldspar (α_V = 22.5 ±12.1 x 10^{-6}deg^{-1}; Hovis and coworkers, 2010, American Mineralogist), and silicic/subsilicic nepheline - kalsilite systems (Hovis and coworkers, 2003 and 2006, Mineralogical Magazine), where size range of the substituting cations is relatively large and Al-for-Si substitution in tetrahedra has a profound effect on thermal expansion.