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The compression mechanism of garnets based on in situ observations

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Previously it was showed that the bulk modulus of garnet is strongly affected by the bulk modulus of the dodecahedra, while compressibility of other individual polyhedra displays no correlation with the compressibility of the structure as a whole (Milman et al., 2001). If so, Na-majorite (Na-maj) would have the smallest bulk modulus of all silicate garnets, as a phase with a predicted dodecahedral bulk modulus of approximately 70 GPa (Hazen et al., 1994). In fact Na-maj has the largest bulk modulus among the silicate garnets. This behavior must reflect the all-mineral framework of Na-maj with very small cell volume and silicon in the octahedral position. Thus, we conclude that not only the dodecahedral sites, but also the behavior of the garnet framework and relative sizes of the 8- and 6-coordinated cations, control garnet compression. The octahedral site in Na-maj is quite small (1.79 Å) and contains only silicon in comparison to the pyrope (1.85 Å) or majorite (1.88 Å). The small and highly charged octahedra shares four edges with the dodecahedra and thus restrict the volume of the large and low charged dodecahedra. In spite Na-maj has a large average X-cation radius (RNa = 1.07 Å) its dodecahedral volume is relatively small (V = 21.23 and 21.26 Å3).
Pacalo et al. (1992) suggested that XO8 polyhedra act as braces and controls the amount of rotation between tetrahedra and octahedra within the corner-linked chains. In case of pyrope XO8 cite is not filled up and polyhedra within the corner-linked chains can rotate freely to accommodate applied stress. In case of Na-maj the dodecahedral site is filled up and rotational freedom is minimized. The dodecahedral site in knorringite (Knr) contains cation with a small radius (Mg-O = 2.22 and 2.34 Å), so XO8 polyhedra is not filled up and can rotate freely to accommodate applied stress. In case of uvarovite not only octahedral but the dodecahedral site is also large (Ca-O = 2.35 and 2.51 Å), so the rotational freedom is minimized and such relations between the XO8 and YO6 sites provide evidence for comparatively more rigid structure. In case of uvarovite the bulk modulus is 162 GPa (Leger et al., 1990), while for Knr we obtain 154 GPa. Such relations between the XO8 and YO6 sites provide evidence for comparatively more rigid structure. As a result, Na-maj with all octahedral sites occupied by silicon has the largest value of the bulk modulus among garnets. It would be interesting to study compressibility of Li-majorite expressed by Yang et al. (2009). That phase has smaller cell volume (1430 Å3) and X-O distance (2.26 Å) but the same YO6 polyhedra fully occupied by silicon.

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