

Vránaite, ideally $\text{Al}_{16}\text{B}_4\text{Si}_4\text{O}_{38}$, a new mineral related to boralsilite, $\text{Al}_{16}\text{B}_6\text{Si}_2\text{O}_{37}$, from the Manjaka pegmatite, Sahatany Valley, Madagascar

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ABSTRACT

The system B_2O_3 - Al_2O_3 - SiO_2 (BAS) includes two ternary phases occurring naturally, boromullite, $\text{Al}_9\text{BSi}_2\text{O}_{19}$, and boralsilite, $\text{Al}_{16}\text{B}_6\text{Si}_2\text{O}_{37}$, as well as synthetic compounds structurally related to mullite. The new mineral vránaite, a third naturally occurring anhydrous ternary BAS phase, is found with albite and K-feldspar as a breakdown product of spodumene in the elbaite-subtype Manjaka granitic pegmatite, Sahatany Valley, Madagascar. Boralsilite also occurs in this association, although separately from vránaite; both minerals form rare aggregates of subparallel prisms up to 100 μm long. Optically, vránaite is biaxial (–), $n_\alpha = 1.607(1)$, $n_\beta = 1.634(1)$, $n_\gamma = 1.637(1)$ (white light), $2V_c(\text{calc}) = 36.4^\circ$, $X \approx \mathbf{c}$; $Y \approx \mathbf{a}$; $Z = \mathbf{b}$. An averaged analysis by EMP and LA-ICP-MS (Li, Be) gives (wt%) SiO_2 20.24, B_2O_3 11.73, Al_2O_3 64.77, BeO 1.03, MnO 0.01, FeO 0.13, Li_2O 1.40, Sum 99.31. Raman spectroscopy in the 3000–4000 cm^{-1} region rules out the presence of significant OH or H_2O . Vránaite is monoclinic, space group $I2/m$, $a = 10.3832(12)$, $b = 5.6682(7)$, $c = 10.8228(12)$ Å, $\beta = 90.106(11)^\circ$; $V = 636.97(13)$ Å³, $Z = 1$. In the structure [$R_1 = 0.0416$ for 550 $F_o > 4\sigma F_o$], chains of AlO_6 octahedra run parallel to [010] and are cross-linked by Si_2O_7 disilicate groups, BO_3 triangles, and clusters of AlO_4 and two AlO_5 polyhedra. Two Al positions with fivefold coordination, Al4 and Al5, are too close to one another to be occupied simultaneously; their refined site-occupancy factors are 54% and 20% occupancy, respectively. Al5 is fivefold-coordinated Al when the Al9 site and both O9 sites are occupied, a situation giving a reasonable structure model as it explains why occupancies of the Al5 and O9 sites are almost equal. Bond valence calculations for the Al4 site suggest Li is likely to be sited here, whereas Be is most probably at the Al5 site. One of the nine O sites is only 20% occupied; this O9 site completes the coordination of the Al5 site and is located at the fourth corner of what could be a partially occupied BO_4 tetrahedron, in which case the B site is shifted out of the plane of the BO_3 triangle. However, this shift remains an inference as we have no evidence for a split position of the B atom. If all sites were filled (Al4 and Al5 to 50%), the formula becomes $\text{Al}_{16}\text{B}_4\text{Si}_4\text{O}_{38}$, close to $\text{Li}_{1.08}\text{Be}_{0.47}\text{Fe}_{0.02}\text{Al}_{14.65}\text{B}_{3.89}\text{Si}_{3.88}\text{O}_{36.62}$ calculated from the analyses assuming cations sum to 24. The compatibility index based on the Gladstone-Dale relationship is 0.001 (“superior”). Assemblages with vránaite and boralsilite are inferred to represent initial reaction products of a residual liquid rich in Li, Be, Na, K, and B during a pressure and chemical quench, but at low H_2O activities due to early melt contamination by carbonate in the host rocks. The two BAS phases are interpreted to have crystallized metastably in lieu of dumortierite in accordance with Ostwald Step Rule, possibly first as “boron mullite,” then as monoclinic phases. The presence of such metastable phases is suggestive that pegmatites crystallize, at least partially, by disequilibrium processes, with significant undercooling, and at high viscosities, which limit diffusion rates.

Keywords: Vránaite, boralsilite, Madagascar, pegmatite, new mineral, structural complexity, Ostwald step rule, borosilicate minerals