

zincostaurolite formed during the M1-event and is associated with gahnite ( $X_{Zn} = 0.91$ ), chloritoid, diaspore, calcite, hematite, rutile, tourmaline, muscovite and omphacite. During the M2-event, the staurolite was replaced to variable degrees by Na-Ca-Li mica, bluish gahnite ( $X_{Zn} > 0.82; X_{Co} = < 0.05$ ), Ni-rich chlorite ( $X_{Zn} = 0.42-0.59; X_{Co} < 0.02$ ), zincohögbomite ( $X_{Zn} = 0.68-0.80$ ), diaspore and Fe-(Mn)-oxides. This decompression-related breakdown of staurolite was investigated by EMP and SIMS studies, including detailed element distribution mapping by both methods. With regard to major elements (Al, Si, K, Ca) both imaging techniques provided consistent results. Li and H analysis by SIMS, calibrated with natural staurolite reference samples, indicate an essentially homogeneous distribution of Li and H in the central parts of staurolite grains, whereas in the outer parts of grains, Li is increasing and H decreasing in the outer parts of grains, where staurolite has reacted to form white Na-Ca-Li mica plus gahnite. The rims are also characterized by a higher Fe/Zn ratio than the central parts of the grains. The overall results indicate a systematic Zn-Fe-Mg-Ni-Co partitioning between staurolite and decomposition products, implying local scale chemical equilibrium and isochemical staurolite replacement. The observed chemical zoning of staurolite is thought to be related to the flexibility of its structure and sensitivity to changing physico-chemical conditions. It is most likely that H- and Zn-rich M1-formed staurolite marginally adapted its composition during M2 greenschist-grade decompression.

**B21-3: The crystal chemistry of holtite**

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Holtite [c. (□,Ta,Al)Al<sub>6</sub>(BO<sub>3</sub>)<sub>2</sub>(Si,Sb,As)<sub>3</sub>O<sub>12</sub>(O,OH,□)<sub>3</sub>], which is isostructural with dumortierite, has been found in pegmatites from only three localities worldwide. Voloshin *et al.* (1987) recognized two types of holtite from the Kola Peninsula: the low-Sb holtite I, an early-formed phase, and the high-Sb holtite II, a late-formed phase. The two types plot in distinct fields in terms of Sb and Si, whereas Ta contents are similar. Our electron microprobe analyses of holtite confirm this chemical distinction, not only in a Kola sample, but also in the holotype and one other sample from the type locality, Greenbushes, Australia. Pieczka and Marszałek's (1996) electron microprobe data on a sample from Szklary, Poland also fit the pattern. Considering only our analyses and that of Pieczka and Marszałek (1996), the clustering in terms of <sup>14</sup>Si<sup>4+</sup> and <sup>13</sup>(Sb,As)<sup>3+</sup> is even more evident. Electron-microprobe analyses give Si + Sb + As ≈ 3 and Al ≈ 6 per formula unit, consistent with negligible Al at the A11 site as indicated in our X-ray refinements. Sb and As replace Si with a concomitant loss of O at the O2 and O7 sites linking the Si tetrahedron to the partially occupied A11 octahedron. Nonetheless, there is little evidence for a relationship between the amount of Ta at the A11 site and the amount of As + Sb at the Si site.

That holtite I and II occur together at both the type locality and at Kola, with no obvious intermediate compositions, suggests that these are two different minerals. However, the two holtites do not qualify as distinct species using the standard definition that at least one site must be occupied by a different cation. In both holtites, > Sb on the two Si and A11 is dominantly Ta (cf. Hoskins *et al.*, 1989). Hoskins *et al.* (1989) cited diffuse layers on X-ray films as evidence for ordering of Si and Sb in a given tunnel, but that there is little correlation from one tunnel to another, so that the crystal as a whole is disordered. This would be analogous to disordered stacking of sheets each of which is ordered in a layer silicate. In the case of holtite II, the Si:(Sb + As) ratio is 7:3 compared to 8.5:1.5 in holtite I, i.e., holtite I is midway between holtite II and dumortierite in terms of tetrahedral composition.

**B21-4: Stability of the alluaudite + triphylite paragenesis in granitic pegmatites**

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The petrographic relations between alluaudite and triphylite indicate that these phosphate minerals have crystallized simultaneously in the Li-rich granitic pegmatites of Buranga, Kibingo (Rwanda), and Hagendorf-Süd (Germany). Starting from chemical compositions corresponding to the idealized compositions of these two phosphates, an experimental investigation was initiated in order to constrain the conditions under which the alluaudite + triphylite paragenesis crystallizes in granitic pegmatites.

The hydrothermal syntheses were carried out between 400 and 800°C at 0.1 GPa, using vertically arranged Tuttle-type cold-seal bombs. The oxygen fugacity was controlled by the Ni-NiO buffer. Below 600°C, alluaudite is associated with triphylite, whereas maricite appears between 600 and 700°C. At 800°C, an undetermined phase crystallizes together with triphylite.

Because maricite has never been observed in granitic pegmatites as far as we know, the upper stability limit of the alluaudite + triphylite paragenesis corresponds to 600°C. This temperature is in good agreement with the conditions generally considered to occur in granitic pegmatites.

The determination of the unit-cell parameters of alluaudite and triphylite serves to estimate semi-quantitatively the Fe/(Fe + Mn) ratios of these phosphates. The partitioning coefficients of Fe and Mn between alluaudite and triphylite are close to 1.00, whereas the values measured on the natural phosphates are comprised between 0.45 and 2.25. Because the Fe/(Fe + Mn) ratios of alluaudite and triphylite are very close in our experimental runs, the similarity of these ratios in some natural associations of these two phosphates can not be considered any more as an argument for a metasomatic replacement of triphylite by alluaudite.

**B21-5: Estimation of light element concentrations in tourmaline: How accurate can it be?**

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Electron microprobe analysis of tourmaline can be a somewhat daunting process, particularly with light elements (B, Li and H) comprising up to 18% of the total oxide wt.%, and with the possibility of transition elements having multiple oxidation states. Because of a greatly improved understanding of tourmaline's crystal structure and chemistry as well as the constraints imposed by geochemical settings of tourmaline, estimation techniques for unanalyzed light elements and oxidation states are possible. The general chemical formula of tourmaline is  $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$ ; with the most common site occupancies being X = Ca, Na, K, □ [vacancy]; Y = Li, Mg, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Al, Cr<sup>3+</sup>, Fe<sup>3+</sup>; Z = Al, Mg, Fe<sup>3+</sup>, Cr<sup>3+</sup>; T = Si, Al (B); B = B; V = OH, O; W = OH, F, O. Apparent lack of vacancies in the Y, Z and T sites enable several viable normalization and light element estimation procedures.

Light element and oxidation states estimation procedures are tested against high-quality, completely-characterized tourmaline analyses that were carried out with a variety of techniques (wet chemical, SIMS, Mössbauer spectroscopy, U-extraction line, SREF, ICP-AES). The results indicate that light element estimation can be reasonably accurate with the appropriate assumptions. [1] Estimation of B. The assumption that B fully occupies the triangular B site and can be calculated using stoichiometric constraints (i.e. B = 3) is generally valid. However, there are a few unusual instances involving high-pressure, Al-rich tourmaline in which some B may also be tetrahedral. [2] Estimation of Li. Li can be approximated by assuming that Li fills any cation deficiency in the Y site. However, this requires that the formula be calculated either on a fixed cation basis (e.g. Si = 6) or that Li be iteratively calculated using a fixed number of oxygens. The Si = 6 approach appears to work well for Li-rich tourmaline (Li > 0.7 a.p.f.u.). A lack of significant amounts of Li can also be inferred for those tourmalines that coexist with other mafic silicates due to preferential partitioning of Li into coexisting silicates relative to tourmaline. [3] Estimation of H. H contents can be determined by charge balance if oxidation states can be measured or inferred. Putative oxidation state evidence can be derived from tourmaline optical properties or by mineral assemblages,