

## The origin and composition of polyphase inclusions in tourmaline from the Greenbushes pegmatite

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The (2.527 Ga) Greenbushes rare-element pegmatite in Western Australia is an important source of lithium and tantalum. The pegmatite, which was emplaced syngenetically into the Donnybrook-Bridgetown shear zone within the Western Gneiss terrain of the Yilgarn Craton, consists of five distinct petrologic zones. Zoned tourmaline crystals in the Ta-rich albite zone of the pegmatite contain numerous solid-liquid-vapor inclusions. The inclusions occur within an inner brown-green pleochroic growth zone and are distributed as planar arrays in healed microcracks, oriented subnormal to the c-axis, and as isolated groups. The inclusion-bearing tourmaline is overgrown by an inclusion-free blue-green growth zone. Solid phases in the inclusions were identified using Raman spectroscopy and one representative polyphase inclusion was analysed using a dual beam focused ion beam-scanning electron microscope (FIB-SEM) for three-dimensional textural and chemical characterization. Fluid inclusion assemblages (FIA) show highly variable liquid-vapor-solid phase proportions. Measurements of phase ratios using a petrographic microscope and image analysis system show a direct relationship between inclusion size, percent volume solids and mineralogy. Large inclusions (>300 $\mu\text{m}^2$ ) containing >50% volume solids are dominated by a silicate assemblage, which may contain quartz, pollucite, lepidolite, zabuyelite and an arsenic-antimony rich phase (predominantly native arsenic, senarmontite, paakonite and/or arsenolite) and aqueous carbonic fluid. Intermediate sized inclusions ranging from 5-50% volume solids may contain zabuyelite, an arsenic-bearing phase and aqueous carbonic fluid. The smallest inclusions (<100 $\mu\text{m}^2$ ) have less than 5% volume solids and contain aqueous carbonic fluid and an arsenic-bearing solid phase. Rare nahcolite and lithiophosphate were also identified in some inclusions. The variability in inclusion size and phase proportions within a FIA is attributed to mineral precipitation prior to trapping and inclusion necking. The inclusions are interpreted to represent the products of a silicate-rich aqueous carbonic fluid that was entrapped during the growth and recrystallization of the early brown-green tourmaline.

## Extreme Fractionation of Rare Earth Elements in Volcanogenic Massive Sulfides of the Bathurst Mining Camp: Evidence from Europium Anomalies in Hydrothermal Apatite

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Rare earth element (REE) mobility in hydrothermal systems has been the focus of numerous studies [1,2], with the most direct evidence coming from active hydrothermal vents [3], which display prominent enrichments in Eu and LREE. Exhalative sedimentary rocks generally contain small quantities of REE when compared to volcanic and clastic sedimentary lithotypes; e.g., massive sulfides of the Bathurst Mining Camp (BMC) have  $\Sigma\text{REE}$  contents that average 36.8 ppm, and range from 0.93 to 249 ppm. Nevertheless, REE in massive sulfides of these exhalative horizons can exhibit considerable fractionation, with chondrite-normalized REE profiles [4] displaying prominent Eu anomalies. Values of  $\text{Eu}_N/\text{Eu}^*$  calculated for massive sulfides are consistently positive with values as high as 36.7 (ave., 6.26). A positive  $\text{Eu}_N/\text{Eu}^*$  correlation ( $n=286$ ) with Sn ( $r^2=0.55$ ) and In ( $r^2=0.40$ ) suggests enrichment in primary hydrothermal fluids associated with base-metal sulfide precipitation.

Petrography and micro-analytical data for massive sulfides have shown that exhalative gangue and accessory minerals, in particular phosphates control REE contents; this is supported by a strong correlation (bulk) between  $\Sigma\text{REE}$  and  $\text{P}_2\text{O}_5$  ( $r^2=0.53$ ). Fluorapatite is the most abundant phosphate in exhalates of the BMC, occurring as nodular to colloform masses and intimate mixtures with carbonate and sulfide minerals. Imaging of fluorapatite reveals a distinct cathodoluminescence consistent with the substitution of  $\text{Mn}^{2+}$  and  $\text{Eu}^{2+}$  in the fluorapatite mineral structure and suggests formation under reducing hydrothermal conditions.

*In situ* laser-ablation ICP-MS analyses ( $n=169$ ) reveal elevated  $\Sigma\text{REE}$  contents in fluorapatite, averaging 1,548 ppm, and ranging from 250 to 24,038 ppm. Europium accounts for approximately  $\frac{1}{4}$  of all REE substitution in apatite, with Eu contents as high as 1,554 ppm (ave., 295 ppm). Chondrite-normalized REE profiles display prominent enrichment in Eu, with  $\text{Eu}_N/\text{Eu}^*$  values as high as 222 (ave., 19.0). To date, these anomalies represent the largest reported fractionation of Eu in the solar system, exceeding values for mesosiderites, and both terrestrial and lunar anorthosites [5]. This extreme fractionation of Eu suggests protracted growth of apatite or some precursor phase (i.e., francolite) under reducing (low $f\text{O}_2$ ) and high temperature hydrothermal (>250°C) conditions, further corroborated by the prevailing pyrrhotite-pyrite-chalcopyrite stockwork assemblage. Apatite associated with lower temperature assemblages exhibits diminished Eu signatures, reflecting a more-distal hydrothermal environment and defining a vector for mineralization.

[1] Graf (1977) *Econ Geol* **72**, 527-548. [2] Campbell *et al.* (1984) *Chem Geol* **72**, 181-202. [3] Michard (1989) *Geochim Cosmochim Acta* **53**, 745-750. [4] McDonough and Sun (1995) *Chem Geol* **120**, 223-253. [5] Mittlefehldt *et al.* (1992) *Science* **257**, 1096-1099.