

The boron isotopic composition of tourmaline as a guide to fluid processes and boron source in the South-west England orefield: an ion microprobe study

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Recent work has shown the boron isotopic composition of tourmaline to be sensitive to a number of factors including boron source, water-rock interaction and temperature and pressure of formation (Palmer and Slack, 1989; Palmer *et al.*, 1992). The boron isotopic composition of hydrothermal fluids has also been shown to be sensitive to boiling (Leeman *et al.*, 1992). The boron isotopic composition of individual tourmalines from S.W. England has been determined in order to investigate both fluid source and fluid processes by attempting to detect isotopic differences within crystals and between samples.

Samples were analysed from three main rock types:- granites, quartz-tourmaline (tourmalinite) and quartz-topaz-tourmaline (QTT) rocks and greisen(Sn,W)-related veins. Three main sample areas were used - the St.Austell granite and its associated tourmalinites and QTT rocks at Roche

and St. Mewan's Beacon, the roof zone of the Land's End granite exposed at Porth Ledden and the Cligga Head granite and sheeted vein system. Tourmalinites and QTT rocks are important as they are considered to represent the transition from magmatic to hydrothermal conditions (Manning, 1981; Bottrell and Yardley, 1988).

Method

The samples were analysed for $\delta^{11}\text{B}$ and Li concentration using the Cameca IMS 4f ion microprobe at the University of Edinburgh. Back-scattered electron images of the individual tourmalines were acquired prior to analysis in order to identify chemical zoning and to allow accurate location of analyses. The analysis method was essentially the same as that outlined in Chaussidon and Albaredo (1992), except that 5s

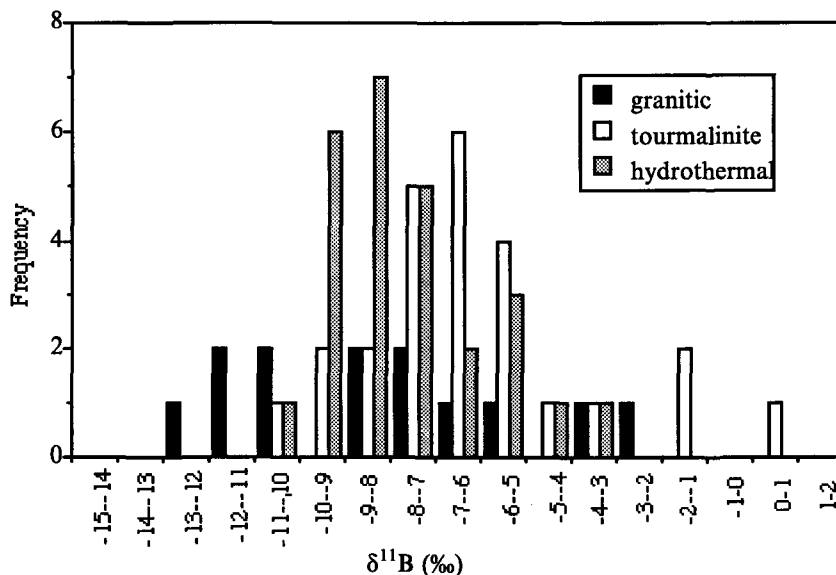


FIG. 1. Variation in $\delta^{11}\text{B}$ values in S.W. England tourmalines.

and 2s count times were used on the ^{10}B and ^{11}B peaks respectively, each measurement consisting of 4 blocks of 5 cycles. After correction for instrumental mass fractionation an overall analytical error of ~ 1 to 1.5% (1s) was obtained.

Results

The $\delta^{11}\text{B}$ values determined in this study are shown in figure 1. Values are means of analyses (generally $n = 2$ to 5) on individual crystals, or on separate chemical zones within a single crystal. The variation within each set of averaged analyses is usually about 1 to 1.5% (1s). The data show a relatively restricted range from ~ 0 to -15% . Within this range primary granite tourmalines show a bimodal distribution, with the ^{10}B enriched group representing late magmatic, fine grained tourmaline, while the heavier group represents early magmatic tourmaline phenocrysts.

There is a consistent relationship between the granites analysed and their associated tourmalinites, with the tourmalinites (-4 to -9%) being typically 2 to 3% lighter than the latest related granite tourmalines. (-10 to -13%) If tourmalinites are assumed to have formed from aqueous fluids the isotopic difference between such tourmalinite fluids and the granites would have been even larger, due to the fractionation between tourmaline and aqueous fluids (Palmer *et al.*, 1992).

The distribution of isotopic compositions from the Cligga Head hydrothermal system is exceptionally homogenous, with only slight ^{11}B enrichment occurring in some Li rich tourmalines.

Boron isotopic zonation in samples was rare despite the presence of strong chemical zoning in many tourmalines. Unequivocal zoning was found only in the fine grained fraction of the Cligga Head granite, and in the quartz/topaz/tourmaline rocks from St Mewan's Beacon and Porth Leven. Variations between individual crystals do occur in the tourmalinites, suggesting that zoning may occur to some extent within these samples.

Discussion

If tourmalinites and QTT rocks truly represent crystallisation from primary magmatic fluids, it is necessary to interpret the differences in boron isotope ratio observed between granites and their associated tourmalinites. It has been assumed that there is little fractionation of boron isotopes between tourmaline and melt. The principal control on boron isotopic fractionation is the co-ordination in any particular phase, with ^{10}B preferentially forming tetrahedral complexes and ^{11}B preferentially forming trigonal complexes (Palmer *et al.*, 1992).

Boron in granitic melts is likely to substitute for silicon in tetrahedral sites (Pichavant, 1983; Chakraborty *et al.*, 1993). Tourmalinites and QTT rocks may have crystallised from either alkali enriched borosilicate melts or hydrothermal fluids (Manning, 1981). In both of these cases boron is likely to have had a significant component in trigonal co-ordination. In alkali enriched borosilicate melts it occurs as Na or Li tetraborates which contain 2 trigonal and 2 tetrahedral units in their basic formula (London, 1986). In aqueous fluids at high pH it occurs as boric acid ($\text{B}(\text{OH})_3$) (Felmy and Weare, 1986). The fractionation between tourmalines in granites and associated tourmalinites can therefore be related to the co-ordination change between magma and a volatile enriched phase separating from it. The depletion in ^{11}B seen between early and late granite tourmalines may either be a result of extraction of this ^{11}B -enriched fluid, or conceivably of contamination with boron from a ^{10}B enriched source. Contamination with isotopically light boron is however unlikely, since almost all crustal boron reservoirs are isotopically heavier than the tourmalines analysed here. We conclude that primary magmatic hydrothermal fluids may have significantly heavier boron isotopic compositions than their parent magmas.

QTT rocks show isotopically heavier zones in some crystals. This may be due to the crystallisation of tourmaline from a vapour formed by boiling of aqueous fluids associated with QTT rock formation. Leeman *et al.* (1992) have shown that boron fractionations of approximately 2–3% can occur between liquid and vapour on boiling, with the vapour phase being enriched in ^{11}B . Fluid inclusion evidence for boiling of aqueous fluids occurs in all the QTT rocks and tourmalinites studied (D. Banks pers. comm.).

The boron isotopic ratios of hydrothermal vein tourmalines from Cligga Head are exceptionally homogenous. This can only be interpreted as a more or less constant boron source through out the evolution of the hydrothermal system. This source is not significantly different from that for the tourmalinites, even when the isotopic composition of aqueous fluids in equilibrium with the two tourmaline types is considered. The boron involved in the greisen forming hydrothermal system is therefore interpreted to be of magmatic origin. Although little fluid inclusion evidence for boiling has been found in greisen-related veins at Cligga Head it is suggested that the ^{11}B -enriched tourmalines may have formed by crystallisation from fluids representing the vapour phase produced by boiling of aqueous fluids.