Hydrogen zoning in zinc-bearing staurolite from a high-$P$, low-$T$ diasporite (Samos, Greece): A combined EMP-SIMS-FIB-FTIR study

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ABSTRACT

Li-rich zincostaurolite occurs as millimeter-long crystals at the marble footwall of a meta-karst-bauxite on eastern Samos. The Samos rocks have been metamorphosed during an early Alpine high-$P$, low-$T$ metamorphism (M1) followed by a late Alpine greenschist-grade overprint (M2). Textures and mineral chemistry indicate that staurolite formed from gahnite, cookeite, and pyrophyllite during the early M1 stage. Staurolite crystals show growth zoning with cores enriched in Zn. Concentrations of Fe, Mg, Co, and, to a minor extent, Li increase toward the rims.

Hydrogen concentrations were analyzed by SIMS. They are significantly higher in cores (up to 5.97 atoms H per 48 O) compared to rims (3.9 to 4.5 atoms H) and clearly negatively correlated with Al. Synchrotron-light polarized FTIR spectra on oriented FIB-prepared foils show the same zonation effect, the absolute hydrogen concentrations being systematically lower by about 25%. The discrepancy is caused by sub-micrometer scale hydrogen loss at the crystal surface during FIB-thinning. This staurolite is unique as from the three available hydrogen sites the H3 site has the highest occupation ever observed, whereas the H2 site is not occupied. This is probably due to the high Li content.

The zonation in hydrogen is interpreted as reflecting the two-stage growth. M1-staurolite that formed a low $T$ of about 400–450 °C and high $P$ of >1.5 GPa incorporated nearly the maximum amount of hydrogen allowed by the staurolite structure (6 H pfu) and was subsequently overgrown and marginally replaced during the M2 stage by less hydrous, Fe-Co richer staurolite. Hydrogen zoning in staurolite is facilitated by the sensitivity of its structure to changing $P$-$T$ conditions. Water in staurolite is maximized at high $P$ and low $T$. Cores of staurolite from Samos represent the most hydrous staurolite compositions reported to date.

Keywords: Staurolite, hydrogen zoning, SIMS, FTIR, Metabauxite

INTRODUCTION

Staurolite is an important index mineral for determining the metamorphic grade of Al-rich rocks. It has a flexible structure and the crystal chemistry is complex (Holdaway et al. 1986a, 1986b, 1991, 1995; Dutrow et al. 1986; Dyar et al. 1991; Hawthorne et al. 1993a, 1993b, 1993c; Koch-Müller 1997; Koch-Müller et al. 1997, 1998; Chopin et al. 2003). This is due to variably occupied lattice sites resulting in various coupled vacancy-cation and other complex intracrystalline cation substitutions, which may induce local ordering. Further complexity arises from the fact that staurolite may incorporate highly variable amounts of hydrogen (e.g., Lonker 1983; Holdaway et al. 1986a). A special feature is that staurolite in zinc- and lithium-rich bulk compositions may accommodate large amounts of Zn and Li into the structure (e.g., Feenstra et al. 2003; Chopin et al. 2003, and references therein). Because both Zn and Li strongly partition into staurolite compared to other common Fe-Mg-Al silicates, this leads to considerable expansion of the staurolite stability field, both toward lower and higher metamorphic grades (e.g., Feenstra et al. 2003).

The general formula of staurolite is $A_4B_4C_{16}D_4T_8O_{40}X_8$ (Hawthorne et al. 1993c). The structure can be considered as alternating oxide-hydroxide and kyanite-like layers. Three distinct octahedra (M) are present in each of these layers: M1A, M1B, and M2 in the kyanite layer, and M3A, M3B, and M4 in the oxide-hydroxide layer. The tetrahedral site of the kyanite layer is termed T1 and that of the oxide-hydroxide layer T2 (Hawthorne et al. 1993a). Preferential site occupations of the various cations and their relation to the general formula are given in Table 1 (Hawthorne et al. 1993c; see also Chopin et al. 2003). There is extensive work on the various coupled substitution mechanisms, both in natural and synthetic staurolites (cf. above). It has been shown, for example, that Zn-Fe substitution in staurolite is continuous (Griffen 1981) and that Li incorporation in T2 is restricted to a maximum of 1.5 apfu, calculated on the basis of 48 O (Dutrow 1991; Feenstra et al. 2003). However, correct formulation of the crystal chemistry and proper assignment of the cation sites are hampered by the fact that hydrogen

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