

## Application of accessory phase/trace element thermometry to blueschists from Syros and Sifnos, Greece

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Three new geothermometers involving accessory phases (Ti in quartz + rutile, Ti in zircon + rutile + quartz, and Zr in rutile + zircon + quartz) have been applied to blueschists from Syros and Sifnos, Greece, to determine their suitability to the study of subduction complexes.

Mafic and pelitic blueschists were imaged to determine the extent of CL zoning in quartz, which has been shown to correlate with Ti content. Most quartz grains are unzoned or only weakly zoned, and no obvious differences between CL intensity of quartz inclusions and quartz in the matrix was observed. Ti concentrations were determined on the IMS 3f at WHOI. Counting precision propagated to ca ± 5 C and replicate analyses on individual grains yielded ca ± 5 C (1 sigma s.e.). Values range from 0.25 ppm to ca 50 ppm corresponding to temperatures of ca 345 C to 680 C with schists recording the lower temperatures and eclogites recording the higher temperatures. The temperature disparity proves the eclogites are exotic blocks tectonically emplaced within the blueschists.

Ti concentrations of zircons performed on the IMS 3f at WHOI correspond to temperatures of ca 650 to 750 C. CL zoning in these zircons is oscillatory, which, coupled with the high temperatures, suggests that the ca 54-91 Ma U/Pb ages record crystallization from a melt. If so, then the onset of subduction must have been later than ca 55 Ma.

Zr concentrations in rutile measured on the electron microprobe are on the order of a few tens of ppm, and carry large uncertainties (±25-40 C). Nevertheless, calculated temperatures range from 450 to 550 C. Better precision (i.e. using the ion microprobe) is required before meaningful temperatures can be extracted.

These results indicate that with analyses done on the ion microprobe, the three new thermometers have precisions that permit temperatures to be calculated with uncertainties of ca ±5 C, enabling subtle differences between different tectonic blocks to be resolved. Coupled with an age determination, Ti in zircon provide the unique T-t point at which the zircon crystallized.

## Fluorine – X-site vacancy avoidance in natural tourmaline: internal vs. external control

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F can be a significant constituent in many varieties of tourmaline. F occurs at levels of up to 1 F atom per formula unit (apfu). However, the incorporation of F in tourmaline is a function of both F concentrations in the coexisting fluid and crystallographic factors, similar to many other silicate minerals. 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,  $X^{\square}$  [vacancy]; Y = Li, Mg,  $Fe^{2+}$ ,  $Mn^{2+}$ , Al,  $Cr^{3+}$ ,  $Fe^{3+}$ ; Z = Al, Mg,  $Fe^{3+}$ ,  $Cr^{3+}$ ; T = Si, Al (B); B = B; V = OH, O; W = OH, F, O. Of particular importance is that F only occurs on a single anion site, the W site. This site is located in the center of the tetrahedral ring, and is influenced by the cation in the X site.

Occupancy of the X-site appears to be a critical factor influencing incorporation of F in tourmaline. The X-site is generally occupied by cations of variable charge,  $Na^{1+}$  and/or  $Ca^{2+}$ , and/or is vacant (zero charge). Because of the local bonding of the W site anion to the three neighboring Y-site cations and the X-site cation, the charge of the X-site cation is likely to affect the F occupancy in the W site. For instance, the dominant W-site occupancy in Ca end-members is F e.g. the liddicoatite or uvite type material. Infrared spectroscopy measurements and local charge balance considerations establish that F should not be present where there is a 7+ -charge (or more) environment such as proximal to the three Y sites in an X-site vacant tourmaline.

Natural tourmaline data verifies the antipathetic relationship between the magnitude of the X-site vacancy and concentration of F in tourmaline. A summary of >560 tourmaline analyses from many different tourmaline varieties illustrates that in tourmalines not dominated by X-site vacancies, F concentrations range from 0-1.0 apfu. A large number of these tourmalines fall in the F-subgroup field. However, for those tourmalines with more than 0.5 X-site vacancies there is little or no F present in the tourmaline. In addition to the crystallographic factors, F concentrations are also a function of the F concentrations in the coexisting fluid phase. This influence can be illustrated from a study of fibrous tourmaline replacing preexisting tourmaline in a pegmatite pocket that apparently has undergone rupture. The change in the tourmaline fiber compositions reflect an infiltrating fluid that becomes progressively fractionated.