



## **Growth of huttonite ( $\text{ThSiO}_4$ ) on monazite-(Ce) from 300 - 900 °C and 200 - 1000 MPa**

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The monoclinic monazite group of minerals comprises three end-members: monazite  $[(\text{Ce}, \text{La}, \text{Nd})\text{PO}_4]$ , brabantite  $(\text{CaThPO}_4)$ , and huttonite  $(\text{ThSiO}_4)$  (e.g., Förster, 1998). Of these, huttonite has a lower-T tetragonal dimorph, thorite. The phase transition between thorite and huttonite at 1 atm has been experimentally located between 1210 and 1225 °C (Finch et al., 1964; Seydoux and Montel, 1997). At higher pressures, huttonite is apparently stable over a range of temperatures reminiscent of the mid to lower crust (Dachille and Roy, 1964). For example, Peiffert and Cuney (1999) have synthesized the complete solid-solution series between monazite-(La) and huttonite at 780 °C and 200 MPa. To date, huttonite has only been definitely described in three different localities: 1) its type-locality, Gillespie's Beach, South Island, New Zealand (Pabst and Hutton, 1951; Förster et al., 2000); 2) granitic pegmatites from Bogatynia, Poland (Kucha, 1980); and 3) nepheline syenites from Brevik, Norway (Meldrum et al., 1999).

In the peraluminous S-type Tribe granodiorite, Slovakia, secondary overgrowths of a  $\text{ThSiO}_4$  phase on monazite-(Ce) has been conjectured to be huttonite (Broska et al., 2000). Other unconfirmed occurrences of huttonite-monazite associations in granites and pegmatites include pegmatites from the Santa Maria de Itabity, Minas Gerais, Brazil (Bilal et al., 1998), and the Monte Capanne pluton, Elba Island, Italy (Dini et al., 2004). In order to establish whether or not huttonite, in relationship to monazite, could be stable over a range of metamorphic temperatures and pressures much wider than implied from the experimental data,  $\text{ThSiO}_4$  has been grown on natural monazite at pressures and temperatures ranging from 200 - 1000 MPa and 300 - 900 °C, respectively. BSE imaging, EMP analysis, TEM, and HRTEM are then used to characterize

the  $\text{ThSiO}_4$  phase in conjunction with the monazite.

The natural monazite-(Ce) used for all experiments consists of clear, bright olive green, inclusion free, 100 - 500  $\mu\text{m}$  size, euhedral - semi-euhedral crystals from a 'late stage' dolomitic carbonatite from the Kangankunde carbonatite complex in the Chilwa Alkaline Province, southern Malawi (Wall and Mariano, 1996). The monazite-(Ce) contains amounts of Th, U, and HREE below the microprobe detection limit, is strongly enriched in LREE, with a  $\text{La}_{\text{CN}}/\text{Y}_{\text{CN}}$  ratio of about 1500, and contains variable amounts of SrO averaging to around 1.8 wt%. All experiments consisted of 10 mg of monazite-(Ce) crystals, 5 mg of  $\text{Th}(\text{NO}_3)_4$ , 2.5 mg of  $\text{SiO}_2$ , and 5 mg of  $\text{H}_2\text{O}$  loaded into 3 mm wide, 1 cm long Pt capsules, which were then arc welded shut. Three sets of experiments were performed (300 °C, 200 MPa; 600 °C, 500 MPa; 900 °C, 1000 MPa). The experiment at (1000 MPa; 900 °C) was done using a  $\text{CaF}_2$  assembly in a two piston cylinder apparatus, left up for 8 days, and then quenched. The experiments at (300 °C, 200 MPa) and (600 °C, 500 MPa) were performed using a standard cold seal autoclave in conjunction with the hydrothermal apparatus and left up for 10 weeks and 4 weeks, respectively. After each experiment, the monazite grains were removed, mounted in epoxy grain mounts, and then polished.

BSE imaging indicates that a  $\text{ThSiO}_4$  phase grew on a selection of monazite grains as an apparent overgrowth sometimes on one face, though more commonly on all faces of the monazite crystal. The majority of monazite grains remained free of any overgrowth. Electron-microprobe analysis indicates that with increasing temperature, this phase becomes increasingly more endmember  $\text{ThSiO}_4$  in composition, i.e. at 300 and 600 °C, a small amount of P, La, Ce, Pr, Nd, and Sm (i.e. < 1.0 oxide wt%) still occur whereas at 900 °C, this phase is pure endmember  $\text{ThSiO}_4$ . Electron-diffraction analysis of a TEM foil from the (600°, 500 MPa) experiment cut perpendicular to the monazite- $\text{ThSiO}_4$  interface using FIB confirms that the  $\text{ThSiO}_4$  phase is indeed monoclinic in symmetry and therefore is huttonite. The huttonite overgrowth is characterized by both fluid inclusions and small solid inclusions heavily enriched in Th, some of which are associated with fluid inclusions. These Th-enriched inclusions are probably remnants of either  $\text{Th}(\text{NO}_3)_4$  or  $\text{ThO}_2$ , which were enclosed by the growing huttonite. The interface between the huttonite and monazite is also characterized by numerous fluid inclusions. High resolution TEM analysis also indicates that at the interface, the lattice fringes from the huttonite and monazite appear to be continuous with little or no mismatch indicating that the huttonite used the monazite structure as a substrate upon which to nucleate and grow.

The principle conclusion of this study is that if monazite is present to act as a substrate for nucleation and growth, huttonite appears to be a metastable phase or possibly even a stable phase over a wide range of temperatures and pressure and subsequently, might

be a more common accessory phase in both metamorphic and igneous rocks than previously realized.

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