

Thermodynamic forward modelling of main and REE-bearing phases linking in situ U-Th-Pb REE-epidote ages and pressure-temperature conditions

B. Huet¹, D.A. Schneider², G. Rantitsch³

¹*GeoSphere Austria, Vienna*

²*Department of Earth and Environmental Sciences, University of Ottawa*

³*Department of Applied Geosciences and Geophysics, Montanuniversität Leoben
e-mail: benjamin.huet@geosphere.at*

REE-epidote is a solid solution of epidote-group minerals with rare earth elements plus yttrium that is a common phase of greenschist facies metapelites and a popular target for geochronology. Linking the time information to metamorphic conditions is however complicated by the diversity of reactions leading to the formation of REE-epidote as these involve REE- and/or Ca-bearing phases (e.g., monazite, apatite, calcite and plagioclase). We compiled a thermodynamic dataset for the system NaKCaFeMgAlSiTiHCOCeYPF from several sources (Berman, 1988; Connolly, 1995; Franzolin et al., 2011; Gaboreau et al., 2005; Hoschek, 2016; Pourteau et al., 2014; Spear, 2010; Spear & Pyle, 2010) in order to model equilibrium assemblages and phase chemistry for both main and REE-bearing phases in metapelites, especially in the greenschist facies.

We tested the dataset on a graphitic micaschist of the Schwarzkopf Formation collected at the foot of the Hochgamsburg (Fusch valley, Tauern Window). The sample shows relatively simple phase relationships and exhibits evidence for only one metamorphic event. The metamorphic assemblage consists of porphyroblasts of chloritoid, kyanite, REE-epidote and apatite in a matrix of muscovite, paragonite, margarite and quartz. Small rutile, graphite, xenotime and zircon are present as inclusions or in matrix. REE-epidote occurs as euhedral to subhedral, 250-1000 μm long grains and displays a microstructural and chemical core-mantle-rim zonation. The core has a patchy or oscillatory BSE pattern and is rich in inclusions of amoeboid quartz and minute graphite, as well as subordinate muscovite, chloritoid, rutile, xenotime and thorite. The mantle is discontinuous ($< 60 \mu\text{m}$ thick), inclusion-free and shows a bright smoother BSE pattern. The rim corresponds to dark and thin discontinuous overgrowths ($< 20 \mu\text{m}$ thick). Core, mantle and rim contain decreasing contents of REE+Th+U in the range 0.5–0.6, 0.4–0.6 and 0.1–0.3 a.p.f.u., respectively. The core and mantle are LREE-rich whereas the rim is HREE+Y-rich. LA-ICPMS analyses of REE-epidote mantle were carried out using a 20 μm laser spot diameter. All thirty-one analyses define a 27.5 ± 1.3 Ma U-Th-Pb isochron date (MSWD: 0.69) that is consistent with the conventional Tera-Wasserburg U-Pb date of 27.0 ± 2.3 Ma (MSWD: 0.36).

Thermodynamic forward modelling indicates that the observed assemblage chloritoid+kyanite+REE-epidote+muscovite+paragonite+margarite+apatite+rutile+xenotime+quartz is stable together with a graphite buffered COH-fluid in a narrow field centred at 12 kbar – 500 $^{\circ}\text{C}$, in agreement with results of Raman spectroscopy on carbonaceous material (511 ± 26 $^{\circ}\text{C}$). This field corresponds to the innermost part of the REE-epidote stability domain, in which the Ce-concentration progressively decreases from the margin to the centre. Modelling helps with interpreting the zonation of REE-epidote. The core grew from U-Th-rich monazite and most likely lawsonite once REE-epidote became stable. Xenotime inclusions represent products of this reaction. The mantle formed during continued growth further inside the REE-

epidote stability domain under increasing temperature. The HREE+Y-rich rim finally grew in an environment depleted in LREE, where xenotime was the main REE-source. Additionally the modelled compositions of chloritoid, white micas and apatite is compatible with the measured ones. Tests on the effect of unknown inputs (e.g., the bulk rock concentration of F) or poorly constrained thermodynamic data (e.g., the standard enthalpy of endmember allanite) indicate that these parameters have little impact on the results.

We could therefore acquire estimates for pressure and temperature and timing as well as coupling them tightly through thermodynamic modelling. The U-Th-Pb isochron date 27.5 ± 1.3 Ma represents the timing of the REE-epidote mantle growth and therefore corresponds to conditions close to peak metamorphism at 12 kbar – 500 °C. These P-T-t constraints are entirely consistent with the Barrovian metamorphic event that is widespread in the Tauern Window (“Tauernkristallisation”).

- Berman RG (1988): Internally-consistent thermodynamic data for minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. - J Petrol 29, 445-522
- Connolly JAD (1995): Phase diagram methods for graphitic rocks and application to the system C-O-H-FeO-TiO₂-SiO₂. - Contr Miner Petrol 119, 94-116
- Franzolin E, Schmidt MW, Poli S (2011): Ternary Ca-Fe-Mg carbonates: subsolidus phase relations at 3.5 GPa and a thermodynamic solid solution model including order/disorder. - Contr Miner Petrol 161, 213-227
- Gaboreau S, Beaufort D, Vieillard P, Patrier P, Bruneton P (2005): Aluminum phosphate-sulfate minerals associated with Proterozoic unconformity-type uranium deposits in the East Alligator River Uranium Field, Northern Territories, Australia. - Canad Miner 43, 813-827
- Hoschek G (2016): Phase relations of the REE minerals florencite, allanite and monazite in quartzitic garnet-kyanite schist of the Eclogite Zone, Tauern Window, Austria. – Eur J Miner 28, 735-750
- Pourteau A, Bousquet R, Vidal O, Plunder A, Duisterhoeft E, Candan O, Oberhänsli R (2014): Multistage growth of Fe-Mg-carpholite and Fe-Mg-chloritoid, from field evidence to thermodynamic modelling. - Contr Miner Petrol 168, 25 pp
- Spear FS (2010): Monazite–allanite phase relations in metapelites. - Chem Geol 279, 55-62
- Spear FS, Pyle JM (2010): Theoretical modeling of monazite growth in a low-Ca metapelite. - Chem Geol 273, 111-119