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Sm–Nd isotope systematics of high-REE accessory minerals and major phases: ID-TIMS, LA-ICP-MS and EPMA data constrain multiple Permian–Triassic pegmatite emplacement in the Koralpe, Eastern Alps

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ABSTRACT

Detailed Sm–Nd mineral ID-TIMS, EMPA and LA-ICP-MS analysis of meta-pegmatite minerals from the Koralpe–Stubalpe area, Austria, involving single crystal separation, step-wise dissolution and acid leaching techniques, yielded (i) information about the partitioning of REE between accessory and major mineral phases in meta-pegmatites, and (ii) age constraints on the long-lasting "Permian–Triassic event" in the Austroalpine basement units of the Eastern Alps.

Internal Sm–Nd mineral isochrons performed on porphyroclast domains from the three localities Rostockbach, Kuppergrund and Wildbachgraben, including garnet, xenotime, apatite, monazite and feldspar indicate multiple emplacement of pegmatoid melts between 273±2 and 258±3 Ma. Other localities yielded younger ages, indicating that magmatic garnet crystallisation persisted from 251±7 to c. 230 Ma. Ages calculated between high-REE accessories (monazite, apatite, xenotime) and the low-REE major phases feldspar and garnet are largely consistent. Zircon, however, plots clearly off the internal regression line. H_2SO_4 leaching experiments on meta-pegmatite garnet rich in micron-sized xenotime and apatite inclusions, locally affected by dynamic recrystallisation, yielded information about the behaviour of the Sm–Nd system during strong tectono-metamorphic overprinting. The data suggest multiple injections of pegmatite melts, at distinctly different times, during protracted crustal thinning and heating in the Permian–Triassic. Ky-paramorphs after andalusite, and micro-inclusions of kyanite, staurolite and sillimanite in magmatic garnet indicate crystallisation of the garnet at moderately high, but variable pressure conditions. During subsequent eclogite-facies overprinting (peak PT c. 700 °C/2.2 GPa) and intense deformation in Cretaceous time, the magmatic chemical and isotopic signatures of porphyroclasts were largely preserved, except for localized within-grain micro-shear zones and outermost rim domains, whereas part of the feldspar-rich matrix recrystallised during pervasive mylonitisation along the eclogite- to amphibolite-facies-grade exhumation path.

1. Introduction

Accessory ("heavy") minerals play a key role in controlling the REE budget of most crustal rocks because of their high to very high REE (>1000 ppm) concentrations (e.g., Taylor and McLennan, 1985; Bea, 1996; Tomkins and Pattison, 2007; Watt and Harley, 1993). Therefore, high-REE accessories are crucial for the interpretation of Sm–Nd isotope data. However, up to the present time, very few studies have analysed the Sm–Nd isotope systematics of accessory phases using pure mineral separates in sufficient detail. Bea (1996) pointed out that the REE-budget of accessory phases is very important in granitic, especially peraluminous systems, and that concentrations of REE, Y, Th and U in accessory phases of partial melts are not determined by crystal-melt distribution coefficients, but rather by solubility relations and dissolution kinetics (see also Clarke et al., 2007). Therefore, reliable trace element data sets of different minerals in single samples are important for defining empirical trace element distributions in accessories, especially when combined with precise age information. Considering geochronology, monazite and zircon, and possibly also allanite, can be successfully dated by *in situ* U–Th–Pb methods (SHRIMP, ELA-ICP-MS or EPMA; e.g., Hermann and Rubatto, 2003; Foster et al., 2000; Foster and Parrish, 2003; Hinchey et al., 2007; Paquette and Tiepolo, 2007; Tomkins and Pattison, 2007; Gregory et al., 2007). Other straightforward conclusions concerning the REE group may be drawn from detailed Sm–Nd isotope analysis, based on

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the similar geochemical behaviour of Nd and Sm (Thöni et al., 2007). Quite a number of recent studies have addressed the importance of accessory high-REE phases, such as monazite, apatite, allanite, or xenotime, with respect to the "inclusion- problem" for garnet Sm–Nd dating (Zhou and Hensen, 1995; Prince et al., 2000; Anczkiewicz and Thirlwall, 2003; Thöni and Miller, 2004). These studies, however, have a qualitative character only, because micron- to submicron-sized inclusions could not be analysed, thus preventing accurate determination of trace element concentrations and Nd isotope compositions of pure high-REE phases.

Theoretically, different approaches are possible to study element distribution/concentrations and Sm–Nd isotope systematics/age correlation in trace minerals: (i) Leaching experiments eliminate REE-rich micro-inclusions, e.g. in garnet, by dissolving the inclusions via leaching with strong acids (e.g., concentrated H_2SO_4; Anczkiewicz and Thirlwall, 2003), leaving garnet as a more or less pure residual phase (R=residue). If the element concentrations and the Nd isotopic composition of the leachate (L) can also be reliably determined, element distribution and age relation in the solid mixture can be semi-quantitatively deduced. (ii) Analysing both, accessory and major phases is a far better approach, but this is rarely possible, since accessory phases in geological samples are often too small to be separated by conventional means and micron-/submicron-sized inclusions are not accessible to *in situ* analytical techniques. (iii) LA-ICP-MS analyses may provide important information on concentration and element zonation in both accessory and major phases, down to a scale of some tens of microns (crater width) and concentrations of c. 100 ppb at a precision of few %. However, precise Nd isotope analysis to identify within-crystal age domains is impossible even by high-resolution *in situ* analytical techniques, at least for low concentration materials. Here we present new Sm–Nd isotopic and LA-ICP-MS trace element data, mineral-chemical and petrological results, both for accessory (monazite, apatite, xenotime, zircon) and major (feldspar, garnet) minerals of meta-pegmatites from different outcrops in the Koralpe–Stubalpe region, Eastern Alps. The aim of this study is (i) to contribute new information on concentrations and internal variation of REE and the distribution between different pegmatite minerals, notably REE-rich accessories; (ii) to draw first-order information on Sm–Nd isotope systematics and age correlation of the pure accessory phases present in some samples, such as xenotime, apatite and monazite; (iii) to estimate the effect of REE-rich accessory phase micro-inclusions on Sm–Nd isotope systematics and the age of low-REE major minerals, especially garnet, by applying acid leaching experiments; and (iv) to discuss the new age results in the context of timing and evolution of the long-lived Permian–Triassic LP-HT event in the Austroalpine units of the Eastern Alps.

2. Regional geologic outline and sampling sites

The Koralpe–Stubalpe units are part of the polymetamorphic Austroalpine basement nappes, forming the easternmost, north–south striking mountain range of the central Eastern Alps (Fig. 1). They form a flat-lying, allochthonous nappe, or displaced terrane, overthrust onto other Austroalpine basement units ("Muriden nappe system" *sensu* Tollmann, 1971) that are exposed in the Wolfsberg window (Fig. 1; Frank, 1987; Krohe, 1987). Following recent tectonostratigraphic/paleogeographic considerations, the area is part of the "Koralpe–Wölz high-pressure nappe system" (Schmid et al., 2004; see Fig. 1), interpreted as former distal passive margin of Neo-Tethys, sandwiched between the southern and the northern margin of the Meliata embayment (a western outlier of Neo-Tethys) during Cretaceous subduction and "nappe stacking". At a later stage, the Koralpe was gently refolded into a series of open syn- and antiforms (Putz et al., 2006).

Lithologically, the Koralpe crystalline *sensu stricto* comprises paragneisses, mica schists, abundant meta-pegmatites, N-MORB-type meta-basites (metagabbros, eclogites), and few meta-carbonates (*e.g.*, Beck-Mannagetta, 1980). Based on petrographic, petrological and geochronological data, most macro- and micro-scale structures observed in the Koralpe are Cretaceous in age (Krohe, 1987; Tenczer et al., 2006). In the course of the eo-Alpine (=Cretaceous) convergence and subduction-related high-P metamorphism (e.g., Miller et al., 2005), large parts of the Koralpe crystalline were intensely deformed

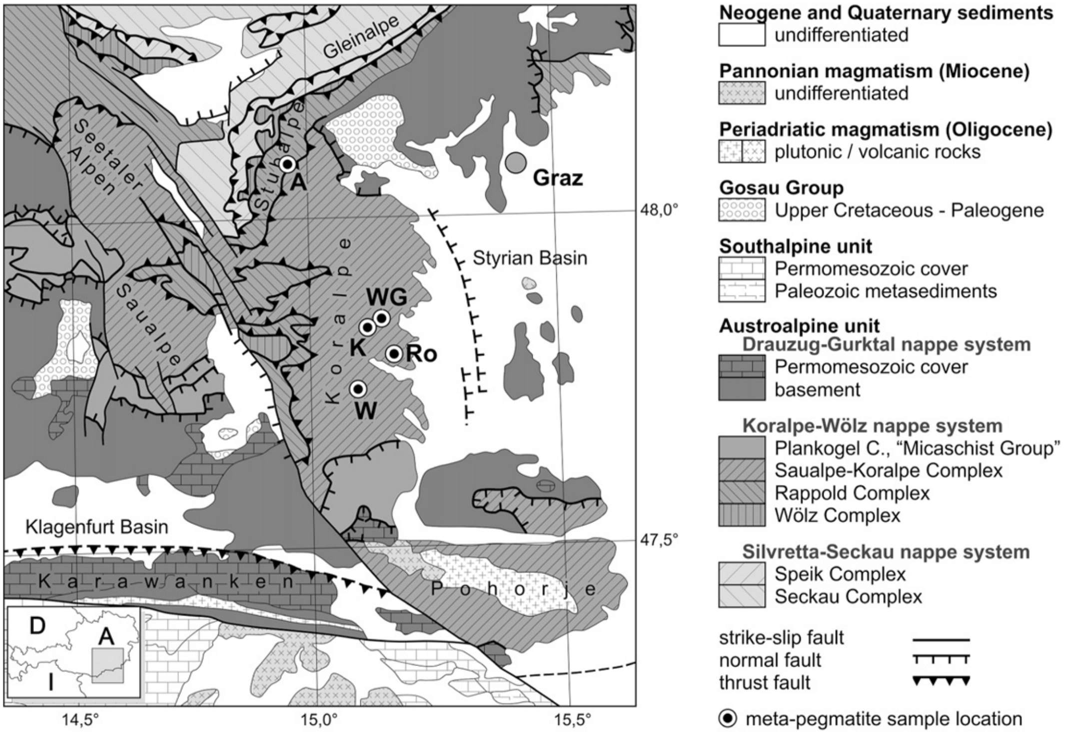

Fig. 1. Geologic-tectonic sketch of the eastern part of the central Eastern Alps, with sample localities. from Miller et al. (2005, modified). W=Wirtbartl, Ro=Rostockbach, K=Kuppergrund, WG=Wildbachgraben, A=Altes Almhaus.