Tracing the evolution of calc-alkaline magmas: in-situ Sm-Nd isotope studies of accessory minerals in the Bergell Igneous Complex, Italy

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Abstract

The common occurrence of Ca- and Nd-rich accessory minerals titanite, epidote, allanite and apatite in calc-alkaline plutonic suites makes them ideal targets for *in-situ* tracing of the temporal, chemical and isotopic evolution of tonalitic and granodioritic melts. The Sm-Nd isotope composition of accessory phases from the calc-alkaline Bergell Pluton and the peraluminous Novate leucogranite (central Alps) were investigated using laser ablation MC-ICPMS techniques. Grouping of individual LA-MC-ICPMS analyses produced average ε_{Nd} values with typical uncertainties of < 0.3 (2σ) epsilon units. SHRIMP dating of magmatic allanite cores of epidote grains from a Bergell gabbro yielded a Th-Pb age of 32.4 ± 0.4 Ma, which provides a new timing constraint on the emplacement of juvenile members within the Bergell intrusive sequence. The Bergell bulk-rock mantle-crust isotopic mixing curve was reproduced, demonstrating that integration of U-Th-rich accessory mineral Nd isotope compositions with crystallisation age is capable of tracing the geochemical evolution of magmatic systems over time. Crucially, the isotopic composition of the mantle end-member was successfully constrained by measurement of magmatic REE-epidote, highlighting the compositional versatility of accessory phases. The removal or addition of feldspar controls the Eu signature of both the bulk-rock and single minerals and therefore presents a unique trace element indicator of magmatic differentiation and assimilation processes in accessory minerals. Therefore the in-situ determination of age, Sm-Nd isotopes and trace elements in accessory minerals permits efficient and accurate reconstruction of complex magmatic processes in calc-alkaline plutonic suites. Sub-grain isotopic heterogeneity in magmatic monazite from the Novate leucogranite was identifiable by LA-MC-ICPMS analysis and emphasizes the additional value of a micro-analytical approach to understanding geological processes.

Key words: LA-MC-ICPMS, allanite, titanite, neodymium, U-Th-Pb dating

1. Introduction

The opportunity to obtain long-lived radiogenic isotope systematics *in-situ* from trace element-rich accessory phases that can also be dated by the U-Th-Pb method has only been realised with the emergence of laser ablation multiple-collection inductively coupled plasma mass spectrometry (LA-MC-ICPMS) systems. To date, such application has principally focussed on zircon as an isotopic tracer, with numerous studies successfully exploiting the high Hf and low Lu/Hf chemistry of this mineral to track petrogenetic processes (Griffin et al., 2000; Harrison et al., 2005; Hawkesworth and Kemp, 2006; Kemp et al., 2007; Scherer et al., 2007). Importantly, observations from the micro-analysis of Hf and U-Pb isotopes in zircon have revealed primary isotope compositions and the preservation of sub-grain isotopic heterogeneities, which were obscured by alteration or metamorphism, or no longer present in the rock record (e.g., Scherer et al., 2007).

Recently, LA-MC-ICPMS instrumentation has been used to integrate U-Th-Pb and Nd isotope information from other geochemically and geochronologically significant minerals, such as monazite (McFarlane and McCulloch, 2007) and apatite (Foster and Carter, 2007). These analytical advancements have opened up the way for the in-situ determination of Nd isotope compositions in accessory phases that can be routinely analysed for age and chemical information at the micron scale. The Sm-Nd isotope system has had widespread application in the earth sciences, notably in isotope tracer studies, where the Sm-Nd decay scheme has been used to investigate sediment provenance and crustal residence ages (McCulloch and Wasserburg, 1978; O'Nions et al., 1983; Allègre and Rousseau, 1984; Condie, 1993; McLennan et al., 1990; Vervoort et al., 1999), and early differentiation of the earth and meteorites, including the evolution of continental crust from mantle petrogenesis (e.g., DePaolo, 1980; Bennet et al., 1993; McCulloch and Compston, 1981; Bowring and Housh, 1995; Vervoort et al., 1996). In particular, Nd isotopes have been successfully applied in igneous petrology to "fingerprint" the source(s) and processes that contribute to the genesis of plutonic systems, such as continuous mantle melt extraction and assimilation of isotopically heterogeneous continental crust (e.g., DePaolo, 1981a; McCulloch and Chappell, 1982; von Blanckenburg et al., 1992).

To extract Nd isotope information with adequate precision and sufficient spatial resolution to discriminate isotopic heterogeneities at the grain-scale, LA-MC-ICPMS analysis has primarily targeted LREE-rich accessory phases for which between-run uncertainties of ~0.5 epsilon units are achieved (Foster and Vance, 2006; McFarlane and McCulloch, 2007).

Whereas this level of analytical uncertainty is a factor of ~2-3 greater than the precision attained by thermal ionization mass spectrometry (TIMS) measurements, crucial grain-scale textural and chemical information is retained.

The calc-alkaline magma series, which form the bulk of exposed granitic batholith belts, including a significant proportion of subduction-related plutonic rock associations (Wilson, 1989), commonly contain diverse LREE-accessory phase assemblages amenable to in-situ Nd isotope analysis (von Blanckenburg, 1992; Oberli et al., 2004). The isotopic characterisation of calc-alkaline plutonic suites potentially involves a range of isotopically distinct source components (DePaolo, 1981a, b; Hill et al., 1986; von Blanckenburg et al., 1992), however until now, LREE-accessory phases have been mainly targeted with the single aim of extracting magma crystallisation ages (Barth et al., 1994; Oberli et al., 2004).

In this paper, we extend this micro-analytical approach to a group of LREE-enriched accessory minerals that can be analysed for Nd isotope systematics using LA-MC-ICPMS. This Nd isotope tracer data is combined with accessory mineral trace element systematics to reconstruct the differentiation and assimilation history of the Oligocene (*c.* 30-32 Ma) calc-alkaline Bergell Igneous Complex, eastern Central Alps (Fig. 1). The Bergell Igneous Complex comprises co-genetic early mafic cumulates and intermediate to felsic differentiates that exhibit a range of bulk-rock initial Nd isotope compositions, and major and trace element compositions (von Blanckenburg et al., 1992). The studied rocks contain abundant accessory titanite, allanite, REE-epidote and apatite, which are known to be major hosts for trace elements in tonalites and granodiorites (Gromet and Silver, 1983; Bea, 1996; Oberli et al., 2004), and which record changes in melt trace element availability over time through the retention of primary chemical and U-Th-Pb isotopic zoning at the micron-scale (e.g., Oberli et al., 2004).

The youth (< 32 Ma) of the Bergell magmatic system minimizes time-integrated variations in $^{143}Nd/^{144}Nd$ and allows us to trace the temporal evolution of sequential magma pulses with an age resolution of < 0.5 Ma. It therefore presents an excellent case study with which to examine the magmatic occurrence, Nd isotope and trace element behaviour of LREE-accessory phases relative to bulk-rock. Previously published Nd isotope data determined for the Bergell suite from a combination of TIMS bulk-rock and mineral separates (von Blanckenburg, 1992; von Blanckenburg et al., 1992) are used for validation of the in-situ method used here. Sub-grain isotopic zoning in monazite, a peraluminous phase from the adjacent Novate leucogranite, provides a complementary example of the benefits of isotopic micro-analysis by LA-MC-ICPMS.

2. Geological setting

The Oligocene Bergell Pluton is situated in the eastern Central Alps (Fig. 1) at the boundary between the Tertiary-metamorphosed central Penninic and eastern Austroalpine nappes. These magmatic and metamorphic units are separated from the relatively unmetamorphosed Southern Alps by the Insubric Line, which forms part of the Periadriatic fault system (Berger et al., 1996; Trommsdorff and Nievergelt, 1983) representing the suture zone of Alpine continental collision. The Bergell pluton is a composite structure consisting primarily of a tonalite margin and a granodiorite core (Figure 1), which cooled rapidly at the eastern margin through their respective solidi at 32 Ma and 30 Ma (von Blanckenburg, 1992). Members of the Bergell suite also include early mafic dykes that intruded the surrounding country rock, minor amounts of gabbro, hornblendite and diorite blocks associated with the marginal tonalite (Fig. 1), and several generations of aplitic and pegmatitic granite stocks and dykes hosted within the granodiorite and in the adjacent country rock (Diethelm, 1989; Reusser, 1987).

The NE granodioritic margin has a laccolithic geometry and shallow level of emplacement (<5 kbar) as recorded by hornblende barometry (Reusser, 1987; Davidson et al., 1996). In contrast, the SW tonalitic margin represents a structurally deeper (~8 kbar) “feeder zone” for the main intrusion (e.g., Davidson et al., 1996), which experienced a protracted cooling history from 33 to 28 Ma (Oberli et al., 2004). At this margin the pluton narrows and takes on the sub-vertical geometry of the Southern Steep Belt adjacent to the Insubric Line. These changes in attitude and geometry have been ascribed to syn-intrusive deformation during Alpine N-S shortening and E-W extension (Davidson et al., 1996). Thus, a ≥10 km oblique section through the Bergell Pluton is exposed along a NE-SW transect (Berger and Gieré, 1995).

Isotopically, the members of the Bergell Pluton exhibit smooth mantle-crust isotope mixing trends ranging from initial mantle ε_{Nd} values of +4 to crustal values of -7, relative to CHUR at 30 Ma (Fig. 2; von Blanckenburg et al., 1992). On the basis of Sr, Nd and oxygen isotope geochemical arguments, von Blanckenburg et al. (1992) concluded that the evolution of the Bergell Pluton involved two stages: (1) partial melting of an enriched lithospheric mantle component that had been modified by mantle source contamination processes, from which early mafic dykes and cumulates were extracted; and (2) subsequent simultaneous

fractional crystallisation and contamination of the uprising magma (AFC mixing of DePaolo, 1981b). This second stage involved significant melting of the heterogeneous lower to middle Alpine crust to produce the main intermediate intrusive bodies, which typically show an increase in crustal contamination with degree of differentiation (von Blanckenburg et al., 1992).

3. Sample selection

Samples for LA-MC-ICPMS analysis were collected at the eastern margin of the Bergell Pluton to avoid the hydrothermal and metamorphic modification and solid-state syn-intrusive deformation observed at the southern tonalitic margin (Berger et al., 1996). LA-MC-ICPMS Nd isotope results are referenced to TIMS bulk-rock and mineral dilution studies of von Blanckenburg et al. (1992) and von Blanckenburg (1992), on samples from the eastern margin. Only a brief description of the Bergell intrusives that are relevant to the samples analysed (Table 1) is given here. An excellent overview of the regional geology and structural setting of the Bergell Pluton can be found in Schmid et al. (1996), Berger et al. (1996) and references therein.

MAL1: Basaltic-andesitic dyke sample collected in Val Malenco, east of the Bergell contact aureole. The un-recrystallised mafic dykes that crosscut the ultramafic Malenco unit are younger than the regional Alpine deformation, but older than the emplacement of the tonalite and granodiorite (Berger et al., 1996). MAL1 is representative of the mantle end-member (ε_{Nd} = +4; von Blanckenburg et al., 1992). Epidote grains separated from MAL1 were yellow-brown, ~200 µm in diameter and contained subordinate inclusions of a Ca-phosphate (most likely apatite).

SIS01: A hornblende gabbro, representative of the initial phase of the intrusion, was collected in Val Sissone (Table 1). A range of basic rock compositions are observed along the pluton margin, however, including blocks of cumulitic hornblendites to in-situ crystallised gabbro as enclaves in tonalite (Diethelm 1989). These rocks display a corresponding range in initial εNd from +2 to -6 (von Blanckenburg et al. 1992). Allanite, titanite and apatite from SIS01 were ≤200µm in diameter. Allanite grains were slightly opaque and typically rimmed by epidote. Titanite occurred as single grains but also as rims on ilmenite, which suggests it could have been a late-magmatic or sub-solidus phase.

SIS04: Representative sample of hornblende-rich tonalite collected in Val Sissone near SIS01. The tonalite displays a range Nd isotope composition from east to west (-4.8 to -2.7, respectively), suggesting that the tonalite was emplaced in several batches with different degrees of crustal contamination (von Blanckenburg et al., 1992). SIS04 is equivalent to the eastern tonalite sample Siss3 of von Blanckenburg et al. (1992). Separated allanite, titanite and apatite were inclusion-free and transparent. Allanite grains were dark brown and display a size increase from SIS01.

SIS07: Porphyritic K-feldspar-rich granodiorite sample from Val Sissone and representative of the granodioritic core of the pluton. Minor late-stage epidote and chlorite growth was observed along small shear planes and boundaries of K-feldspar porphyroclasts. Separated allanite and titanite grains are similar to those in SIS04, although apatite grains are significantly larger in size (>100 μm) than SIS04 apatite.

NOV1: Representative sample of the peraluminous garnet-bearing two mica Novate leucogranite. The Novate intrusion was emplaced at *c.*25-24 Ma according to the U-Pb system in monazite and zircon (Köppel and Grünenfelder, 1975; Liati et al., 2000), and represents the youngest intrusion in the area. The leucogranite is compositionally and genetically unrelated to the Bergell Pluton (Fig. 2) as it was derived from crustal melts (Kagami et al., 1985). It may, however, be associated with late-stage aplitic and pegmatitic dyke intrusions in gneisses north of the Insubric Line and crosscutting the Bergell Pluton (Reusser, 1987, von Blanckenburg et al., 1992). Monazite and apatite were separated from NOV1. Monazite grains were euhedral, transparent, ~200 μm in diameter and contain inclusions of quartz and feldspar.

4. Analytical method

Translucent grains that lacked significant zoning or alteration features (e.g. cracks, irregular domains) were hand picked using a binocular microscope. The grains were cleaned, mounted in epoxy, and polished to expose their mid-section. High-contrast backscatter electron (BSE) images were obtained using a Cambridge S360 scanning electron microscope at the Electron Microscopy Unit, ANU using an accelerating voltage of 15kV, beam current of 2-3 nA and a working distance of 20mm.

Trace element analyses of mineral separates were performed by LA–ICP-MS at the ANU Research School of Earth Sciences (RSES) using a pulsed 193 nm ArF Excimer laser operating at 100 mJ, 5 Hz repetition rate, and a 32 μm laser crater diameter (Eggins et al., 1998). Ablated aerosols were transported in a mixed He-Ar carrier gas to the ICPMS (Agilent 7500). External calibration was performed relative to NIST 612 SRM reference glass and results were check for accuracy using a BCR-2G microbeam glass standard. Preferred values

for BCR-2G were taken from the GeoReM compilation by K. P. Jochum and F. Nehring (available at http://georem.mpch-mainz.gwdg.de/). Allanite, titanite analyses were normalised to CaO values independently determined by electron microprobe. Stoichiometric values for Ce in monazite and CaO in apatite were used as internal standards for these accessory phases.

U-Th-Pb isotopes in allanite were measured using the Reverse Geometry Sensitive High Resolution Ion MicroProbe (SHRIMP RG) at the RSES, using a 3-4 nA, 10 kV primary O_2^- beam focussed to a ~ 20 μm diameter spot. The analytical procedure was similar to that described by Gregory et al. (2007). Each analysis consisted of six scans through the masses. Sputtered ^{208}Pb, ^{232}Th and ^{248}ThO ions were corrected to the reference allanite CAP run every fourth analysis (~276 Ma, Barth et al., 1994; Gregory et al., 2007). Poor calibration for the U-Pb system over the course of analysis prevented the use of allanite U-Pb data to calculate robust ages. Data reduction was carried out using RSES internal software. Data were corrected for common Pb using the measured $^{207}Pb/^{206}Pb$ according to Williams (1998) and a model common Pb composition of Stacey and Kramers (1975). Weighted mean plots were made using Isoplot/Ex software (Ludwig, 2000).

Sm-Nd isotope data was collected during three analytical sessions on a Thermo Finnigan Neptune MC-ICPMS coupled to a HelEx ArF excimer laser ablation system at the RSES (Eggins et al., 2005). The laser ablation system setup, Neptune MC-ICPMS amplifier and cup configurations, and data acquisition were according to McFarlane and McCulloch (2007) and are only briefly described here. Oxide/metal ratios were maintained at <0.5 % to monitor oxide interferences on LREEs (e.g., BaO). Spot diameter (24 μm to 105 μm) and laser repetition rate (4 Hz to 6 Hz) varied according to the mineral Nd content. Typical signal intensities were: >1 V ^{146}Nd for allanite at 47 μm (10 000 ppm for gabbro to 25 000 ppm for granodiorite); <2 V ^{146}Nd for REE-epidote at 105 μm (2 500 to 10 000 ppm for basaltic-andesite); 0.5-1.5 V ^{146}Nd for titanite at 81 μm (1 500 ppm for gabbro to 2 500 ppm for tonalite); 0.5-1 V ^{146}Nd for apatite at 105 μm (500 to 1 000 ppm); and >3 V ^{146}Nd for monazite at 24 μm (> 120 000 ppm).

Isotope ratios and gas blanks were measured using 50 cycles of 2 seconds integration. We have observed higher background levels associated with ablation of LREE-rich minerals such as monazite and allanite. As a result, low LREE concentration minerals such as apatite and titanite were analysed first, followed sequentially by minerals with progressively higher LREE content. For example, on-peak background levels were <0.05 mV for all analytes at the start of the session and during apatite and titanite ablation, but increased to ~0.1 mV during allanite and monazite analysis at the end of the analytical session. Data was processed offline on a cycle-by-cycle basis allowing the time-resolved data to be critically assessed. As outlined in McFarlane and McCulloch (2007), an independently determined $^{147}Sm/^{149}Sm$ was used to correct mass bias on $^{144}Sm/^{149}Sm$ using an exponential law. The latter was then used to correct for ^{144}Sm interference on ^{144}Nd. The interference-corrected $^{146}Nd/^{144}Nd$ (reference = 0.7219) was then used to normalise background and interference-corrected $^{143}Nd/^{144}Nd$ and $^{145}Nd/^{144}Nd$ (Wasserburg et al., 1981) using an exponential law. A systematic 40 ppm offset is observed between normalised MC-ICPMS and TIMS values (McFarlane and McCulloch, 2007), which has been documented elsewhere as relating to the inherent mass bias differences between plasma-source mass spectrometers and TIMS (Alberède et al., 2004; Vance and Thirlwall, 2002). The best comparison between MC-ICPMS and TIMS results is achieved by applying an empirical correction (+40 ppm) to our $^{143}Nd/^{144}Nd$ values. Isotope ratio errors are reported as 2σ absolute standard errors. Uncertainty on $^{147}Sm/^{144}Nd$ is not included in the final error calculation.

Secondary mineral standards characterised by solution Nd isotope MC-ICPMS (Trebilcock monazite and Daibosatsu allanite, McFarlane and McCulloch, 2007; Durango apatite, Foster and Vance, 2006; Fish Canyon Tuff titanite, McFarlane unpublished) were analysed periodically to verify external reproducibility. The LA-MC-ICPMS $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd(t)$ values for these natural mineral standards were identical within error to their known solution MC-ICPMS values. Results are provided in the electronic data repository (EDR Table 1).

5. Allanite major element chemistry

In the Bergell calc-alkaline samples, epidote and allanite major element composition changes along the solid solution join $Ca^{2+} + Fe^{3+}$ (epidote) $\leftrightarrow$ $REE^{3+} + Fe^{2+}$ (allanite) (Dollase, 1971). The major element (Ca, Si and Al) composition is correlated with bulk-rock composition and these elements decrease with increasing degree of differentiation. In general, total REE content measured by EMP increases with degree of bulk differentiation (~8 wt% to 19 wt%), particularly at the early stage of differentiation from MAL1 basaltic-andesite to SIS01 gabbro when allanite replaces REE-epidote as the most important LREE-carrier in the rock (Table 2).

6. Accessory mineral trace elements

Backscatter electron (BSE) images of the accessory minerals are shown in Fig. 3. Analysed allanite grains were typically only weakly zoned (Fig. 3d-f) and apatite was unzoned (Fig. 3j). REE-epidote displayed faint, planar-like zoning (Fig. 3k). Titanite grains were weakly to strongly oscillatory zoned and locally sector zoned (Fig. 3g & h). Monazite grains were oscillatory- to sector-zoned with local internal core-overgrowth structures (Fig. 3a & b).

Chondrite-normalised (McDonough and Sun, 1995) REE plots are shown in Fig. 4. Trace element data is given in Table 3. Allanite and REE-epidote are relatively enriched in the LREEs at different absolute abundances (Fig. 4a). The low La/Lu of epidote compared to allanite (La/Lu of ~360 and ~8 000-200 000, respectively), is due to crystal-chemical effects, whereby the incorporation of trivalent REEs into the A-sites (i.e., Ca^{2+} site) of allanite, is balanced by the presence of divalent cations, principally Fe^{2+}, which effectively distort the crystal structure to accommodate the relatively large LREEs (Bonazzi and Menchetti, 1995). Interestingly, allanite M-HREE abundances increase with degree of differentiation (e.g.,

SIS01 to SIS07, Table 3) despite decreasing Ca and Al contents (Table 2). This indicates that factors other than crystal-chemical effects contributed to decreasing La/Lu in allanite (Fig. 4a). Titanite and apatite show similar chondrite-normalised REE profiles, although the absolute REE concentration in apatite from the granodiorite is an order of magnitude lower than titanite (Fig. 4b and d). Notably, titanite is progressively LREE-depleted and M-HREE-enriched with increasing degree of differentiation, causing a decrease in La/Lu (~60 to 4) similar to allanite. This behaviour contrasts to bulk-rock LREE/HREE compositions, which typically increase with crustal contamination and degree of differentiation (Table 3; von Blanckenburg et al., 1992). Monazite from NOV1 shows a characteristic strongly LREE-enriched patterns (Fig. 4c) and a rimward decrease in Y and HREE concentrations (e.g., La/Lu varies from 2 500 to 4 000 rimward, Table 3).

Accessory mineral Eu anomalies become increasingly negative with degree of differentiation from MAL1 to NOV1 (Table 3, Fig. 4). Titanite and allanite show opposing trends in Th/U. With increasing magma differentiation Th/U in titanite decreases from 1.4 in SIS01 to 0.16 in SIS07 (Table 3). Overall, Th/U in REE-epidote and allanite increases from <1 in MAL1 to ~140 in SIS07, although SIS04 allanite has a Th/U of ~160, reflecting the high Th/U of the tonalite bulk-rock (Table 3). Thorium in monazite decreases from core to rim (Table 3). The Ba content of the accessory phases analysed in this study was typically < 2 ppm.

7. Accessory mineral Sm-Nd and U-Th-Pb isotopes

LA-MC-ICPMS Nd isotope results are given in Table 4 and Fig. 5 and include the bulk-rock and mineral isotope data of von Blanckenburg et al. (1992) and von Blanckenburg (1992) for comparison. The different sampling volumes of SIMS and laser ablation in-situ techniques (e.g., 1-2 μm versus ~10's μm deep pits) permit the direct coupling of U-Th-Pb and Sm-Nd isotope systematics for isotopic tracing using a single mineral target, a protocol successfully employed in Lu-Hf studies involving zircon (e.g., Harrison et al., 2005). The high fraction of common Pb of the total measured Pb in REE-epidote (f^{206}Pb > 0.95) precluded an age determination for MAL1. However similar mafic dykes analysed by von Blanckenburg et al. (1992), were corrected for ^{147}Sm decay assuming a Bergell age (at t = 30 Ma), which we adopt here for consistency. Following we discuss each sample in order of relative emplacement:

343 *MAL1 basaltic-andesite:* Five REE-epidote grains were analysed and had variable
344 inter-grain $^{147}Sm/^{144}Nd$ (0.083 to 0.113) due to epidote-group REE solid solution. The five
345 analyses produced a weighted mean $\varepsilon_{Nd}t$ of +3.85 ± 0.27 (MSWD 0.1), in agreement with the
346 TIMS bulk-rock value (Fig. 5a; von Blanckenburg et al., 1992).
347 *SIS01 gabbro:* Allanite grains were homogeneous in $^{147}Sm/^{144}Nd$ (~0.052 ± 0.002).
348 Analysis over two sessions produced $\varepsilon_{Nd}t$ values identical within error of -2.40 ± 0.18,
349 (MSWD 0.9) and -2.18 ± 0.41 (MSWD 0.5), respectively. Co-existing titanite was more
350 variable in $^{147}Sm/^{144}Nd$ (0.131 to 0.178) with some grains displaying up to 5 % (1σ) internal
351 variations. Only 3 of 9 titanite grains from SIS01 produced sufficient Nd counts to yield
352 acceptable errors (≤1 epsilon unit; Table 4). These three analyses gave an average $\varepsilon_{Nd}t$ of -
353 2.08 ± 0.39 (MSWD 0.4) and calculation inclusive of all analyses gives -2.39 ± 0.45
354 (MSWD 1.3). Apatites grains were too small for laser sampling due to relatively low Nd
355 concentrations (Table 3). The allanite and titanite results lie within the range previously
356 documented for the Bergell gabbros (Fig. 5c-d; von Blanckenburg et al., 1992). Allanite
357 separated from the Bergell gabbro was dated for the first time using the SHRIMP protocol of
358 Gregory et al. (2007) in order to corroborate the LA-MC-ICPMS Sm-Nd isotope systematics.
359 Fourteen analyses on allanite cores surrounded by epidote overgrowths produced a weighted
360 mean Th-Pb age of 32.4 ± 0.4 Ma (95 % c.l., MSWD 1.0; Table 5). Individual allanite Th-Pb
361 analyses are plotted in Fig. 6 against SHRIMP allanite ages of the Bergell tonalite and
362 granodiorite (Gregory et al., 2007), to illustrate the absolute timing sequence of each
363 intrusive body. Uranium-Pb data are not presented (refer to Section 4), however the
364 behaviour of the U-Pb system in allanite from the Bergell tonalite and granodiorite is
365 described in Gregory et al. (2007). Given the high Th/U and relatively young age of allanite
366 from SIS01, it is suspected that the U-Pb system of this sample would be affected by initial
367 ^{230}Th disequilibrium in the form of excess ^{206}Pb (e.g., Schärer, 1984) and therefore give old
368 U-Pb ages, in line with the U-Pb behaviour of allanite in SIS04 and SIS07 (von
369 Blanckenburg, 1992; Gregory et al., 2007).
370 *SIS04 tonalite:* Titanite in this sample showed variable intra-grain $^{147}Sm/^{144}Nd$ (up to
371 2.3 % at 1-sigma). Despite this compositional variation, the titanite analyses formed a
372 coherent Nd isotope population with a weighted mean $\varepsilon_{Nd}t$ of -5.41 ± 0.18 (MSWD 0.3),
373 which is within error of previous TIMS titanite analyses (Fig. 5f; von Blanckenburg, 1992).
374 Allanite however, consistently reproduced $\varepsilon_{Nd}t$ values that were ~40 ppm below those
375 obtained conventionally (Fig. 5e; von Blanckenburg, 1992), even after application of the

empirical correction to measured $^{143}Nd/^{144}Nd$ (see Section 4). This discrepancy is unlikely to be an analytical artifact because indistinguishable $\varepsilon_{Nd}t$ values for allanite were obtained from three separate analytical sessions: -5.66 ± 0.24 (MSWD 2.0), -5.63 ± 0.18 (MSWD 0.6), and -5.73 ± 0.40 (MSWD 0.2). In addition, allanite from SIS04 measured by LA-MC-ICPMS have identical $^{147}Sm/^{144}Nd$ (0.049 ± 0.002) to single grains analysed by TIMS (~0.0484; von Blanckenburg 1992). We will return to the significance of this discrepancy in the forthcoming discussion. The Th-Pb age of tonalitic allanite (31.5 Ma, von Blanckenburg, 1992) was also confirmed by Gregory et al. (2007), using in-situ techniques on the same separates (Fig. 6). Apatite in SIS04 was again too small for laser analysis.

SIS07 granodiorite: Allanite grains displayed variable $^{147}Sm/^{144}Nd$ (0.105 to 0.061, av. 0.069) and the results from two analytical sessions gave $\varepsilon_{Nd}t$ values of -6.18 ± 0.13 (MSWD 1.2) and -6.39 ± 0.38 (MSWD 0.8), which are identical to independent allanite analyses obtained by TIMS (Fig. 5g; von Blanckenburg, 1992). Similarly, ten titanite grains yielded $\varepsilon_{Nd}t$ of -6.20 ± 0.23 (MSWD 0.2), in agreement with TIMS results (Fig. 5g; von Blanckenburg, 1992). Only one apatite grain from SIS07 was large enough (> 150 μm diameter) to analyse and it yielded ε_{Nd} of -6.29 ± 1.05, overlapping with the allanite and titanite Sm-Nd data. This observation suggests that allanite, titanite, and apatite preserve Sm-Nd isotopic equilibrium. A $^{143}Nd/^{144}Nd$ versus $^{147}Sm/^{144}Nd$ isochron plot of allanite, apatite and titanite analyses from SIS07 (Fig. 7), yielded an initial $^{143}Nd/^{144}Nd$ intercept of -6.20 ± 0.18 in excellent agreement with the documented bulk-rock value of -6.29 ± 0.08 (von Blanckenburg, 1992). The multiple-phase Sm-Nd isochron age of 32 ± 5 Ma (1σ) is consistent with the known age of the Bergell Granodiorite of 30.1 ± 0.3 Ma determined by von Blanckenburg (1992) and confirmed by Gregory et al. (2007).

NOV1 monazite: $^{147}Sm/^{144}Nd$ in monazite averaged ~0.119, although monazite cores displayed greater down-hole Sm/Nd variability than rims. A population of intermediate BSE-intensity monazite domains (Fig. 3c) produced a weighted mean $\varepsilon_{Nd}t$ of -8.86 ± 0.22 (calculated at t = 25 Ma) identical to the bulk-rock TIMS value (Kagami et al. 1985). In contrast, two high BSE-intensity cores (Fig. 3a) record higher $\varepsilon_{Nd}t$ values of -7.36 and -7.65. Three apatite grains yielded $\varepsilon_{Nd}t$ of -8.78 ± 0.57 (MSWD 0.6), again within error of the bulk-rock value and co-existing monazite (Table 4; Fig. 5).

8. Discussion

8.1 Record of magma evolution in single crystals

Elevated bulk-rock Sr and oxygen isotopes relative to the mantle array (Fig. 2) were used as evidence by von Blanckenburg et al. (1992) to propose an enriched lithospheric mantle source for the origin of the Bergell calc-alkaline magmas due to metasomatism of the mantle wedge through dehydration of subducted oceanic material. Bulk-rock ε_{Nd} values are of mantle and crustal affinity, and define a smooth calc-alkaline mantle-crust mixing trend (Fig. 2). This trend is interpreted to reflect differentiation of uprising magma via simultaneous crustal assimilation and fractional crystallisation processes (von Blanckenburg et al., 1992). Such diversity in bulk-rock chemical and isotopic compositions provides an ideal setting to assess the value of accessory phase LA-MC-ICPMS Nd isotope analysis for tracing the isotopic evolution of igneous suites.

To extract a faithful history of the evolution of the Bergell magmatic system it was essential to separate Nd-rich accessory phases from each intrusive member. Crucially, the representative mafic end-member MAL1 contained magmatic REE-epidote, which was used to constrain the ε_{Nd} isotopic composition of the proposed mantle source ($\varepsilon_{Nd}t$ = +4, von Blanckenburg et al., 1992). Figure 8a is a summary of average accessory mineral $\varepsilon_{Nd}t$ values obtained by LA-MC-ICPMS against their known U-Th-Pb age determined either by SHRIMP (this study; Gregory et al., 2007) or TIMS techniques (Köppel and Grünenfelder, 1975; von Blanckenburg et al., 1992). First, this graph illustrates that the accessory phase Nd isotope compositions successfully reproduced the smooth mantle-crust mixing trend recorded by the Bergell igneous complex, from an $\varepsilon_{Nd}t$ of +3.9 for basaltic-andesite determined by REE-epidote, to an $\varepsilon_{Nd}t$ of -6.2 for granodiorite obtained using allanite, titanite and apatite. This dataset also demonstrates an absence of significant outliers, both analytical (instrumental bias) and geological (inherited isotopic components) in the accessory mineral results from Bergell. Second, when multiple accessory phases were analysed in a single sample the Nd isotope compositions of these phases were consistent (e.g., Fig. 7). This indicates that primary magmatic $^{143}Nd/^{144}Nd$ signatures were preserved and demonstrates mineral-melt isotopic equilibrium during crystallisation. This check on internal consistency is one of the most powerful benefits of the LA-MC-ICPMS approach. Because secondary alteration could affect different minerals in different proportions (e.g., preferential alteration of allanite compared to titanite) bulk-rock application in this situation could result in misrepresentation of the true isotopic value.

Neodymium isotope compositions of titanite and allanite from SIS01 ($\varepsilon_{Nd}t$ of -2.08 ± 0.39 and -2.36 ± 0.17, respectively) fall within the large range of bulk-rock $\varepsilon_{Nd}t$ documented for samples of Bergell gabbro (Fig. 2; von Blanckenburg et al., 1992), yet they do not correspond to a specific bulk-rock Nd isotope composition. The bulk mineralogy of SIS01 analysed in this study corresponds most closely to the Siss1 hornblende gabbro described by von Blanckenburg et al. (1992), however the latter has a more juvenile composition (ε_{Nd} = +0.4) compared to that of the accessory phases (Table 4). Considering the range of bulk compositions for gabbro in the Bergell igneous complex (e.g., primitive cumulates to tonalite cumulates; Diethelm, 1989), the discrepancy between the in-situ data and previous conventional results is most likely a sampling artifact. This hypothesis is supported by the excellent agreement of titanite and allanite results despite substantial differences in $^{147}Sm/^{144}Nd$ and total Nd content, and the fact that simultaneously measured $^{145}Nd/^{144}Nd$ values were identical within error of the natural ratio (Table 4).

In-situ Nd isotope analyses of allanite from the SIS04 tonalite are ~40 ppm (~0.8 epsilon units) lower than previous TIMS results for this mineral (Fig. 5; von Blanckenburg, 1992). This offset also includes LA-MC-ICPMS analyses of the Siss3 allanite separates of von Blanckenburg (1992), which immediately removes the possibility of a sampling bias. However, the SIS04 allanites were analysed concurrently with those from SIS07 and Daibosatsu and these samples both returned accurate LA-MC-ICPMS results (Fig. 5; EDR Table 1). In addition, allanite grains separated from SIS04 and SIS07 for in-situ analysis were inclusion-poor, lacked obvious signs of alteration and displayed similar internal zoning in BSE images (Fig. 3). Given these factors, it is hard to reconcile why potential instrument bias would only affect the measurement of a single mineral sample. Encouragingly, the in-situ analyses of co-existing titanite were within error of their known isotopic value (Fig. 5) and importantly, they agreed with the Nd isotope results obtained from allanite (Fig. 5). The in-situ data therefore point to the fact that the TIMS results for allanite might not be accurate, for either analytical or geological reasons. It is evident from Fig. 8a that the Nd isotope composition of SIS04 allanite determined by LA-MC-ICPMS lies within the mantle-crust mixing trend, and thus is considered geologically accurate.

The in-situ Nd isotope results for monazite and apatite from the Novate leucogranite (NOV1) are shown in Fig. 8a. The Sm-Nd system in apatite recorded an $\varepsilon_{Nd}t$ of -8.78 ± 0.57, which is consistent with the bulk-rock (-8.6; Kagami et al., 1985). However, in BSE images, co-existing monazite is not homogeneous. For example, the high BSE-intensity monazite

core shown in Fig. 3a and the oscillatory- to sector-zoned monazite in Fig. 3c displayed Nd isotope *variations* with $\varepsilon_{Nd}t$ values of -7.4 ± 0.4 and -8.4 ± 0.5, respectively. Oscillatory- to sector-zoned monazites were, however, more common in NOV1, and the in-situ results indicate that this monazite type was in isotopic equilibrium with the crystallising host magma (Fig. 5). In comparison, a low BSE-intensity monazite core shown in Fig. 3b gave a markedly lower $\varepsilon_{Nd}t$ of -13.2 ± 0.3. This core is inclusion-rich and BSE imaging indicates that it is of a different composition to the monazite overgrowth. It also displays an irregular and discontinuous contact with the overgrowth (Fig. 3b). Combined, the texture, chemical gradients, resorptive boundary and Nd isotopes all suggest that the core is inherited. Isotopic inheritance in monazite is not uncommon for peraluminous leucogranites (e.g., Copeland et al., 1988; Harrison et al., 1995) given the limited solubility of monazite in these melts (Montel, 1993). Consequently, the ability to recognise inherited isotopic components and thus their potential to skew bulk Sm-Nd measurements is one of the most important advantages of in-situ analysis.

8.2 Bulk-rock versus accessory phase trace elements

Because certain bulk-rock trace element ratios change in response to crustal assimilation and degree of differentiation, e.g., Ba/Sr, Ce/Sr, Ba/Y (Table 3; von Blanckenburg et al., 1992), it could be expected that accessory phase trace element ratios might also be modified and, integrated with in-situ Nd isotopes, provide insight into petrogenetic processes. An index of differentiation encompassing both bulk-rock and accessory mineral behaviour would thus be ideal to characterise such processes. This was investigated with a comparison of mineral trace element compositions determined by LA-ICP-MS in this study, and bulk-rock trace element data of von Blanckenburg et al. (1992).

Bulk-rock Ba/Y is a sensitive monitor of crustal assimilation (Table 3). Measured Ba concentrations in the studied accessory phases however, were very low (< 2 ppm), which prevented the use of Ba systematics at the mineral-scale as a sensor for differentiation. Similarly, bulk-rock Ce/Sr increased with decreasing $\varepsilon_{Nd}t$, whereas Ce/Sr in allanite and titanite displayed contrasting behaviour: Ce/Sr increased in allanite and decreased in titanite (Table 3). In these minerals, Sr does not vary systematically with index of differentiation (Table 3). More important, however, is the ability of these accessory phases to effectively fractionate trace elements in a melt, principally REEs, Y, Th and U (Gromet and Silver, 1983; Bea, 1996; Oberli et al., 2004), since these elements are essential structural

components. As a result, even low degrees of mineral-melt fractionation by these phases can control trace element enrichment or depletion of an evolving magma (e.g., Oberli et al., 2004). The progressive LREE-depletion in titanite indicated in Fig. 4b is thus attributed to allanite fractionation, given that allanite is the principal host of LREEs in granodioritic and tonalitic rocks (Gromet and Silver, 1983; Oberli et al., 2004). Consequently, this poses some difficulty in directly linking the behaviour of trace element ratios from bulk-rock and accessory mineral data.

Unlike other REEs, the fractionation of Eu in a melt is typically governed by feldspar, which displays a strong affinity for Eu^{2+} (Bea, 1996) and is a major mineral constituent in most calc-alkaline igneous rocks. As a result, fractional crystallisation of magmatic plagioclase and K-feldspar is reflected in the Eu anomaly (or Eu/Eu*) of the bulk-rock and its minerals. This situation is clearly illustrated for the Bergell samples in Fig. 8b, which shows that accessory mineral Eu/Eu* values decrease systematically with $\varepsilon_{Nd}t$. Such trends are interpreted to reflect the progressive Eu depletion of the host magma through increasing plagioclase or K-feldspar fractionation (von Blanckenburg et al., 1992).

Fig. 8b also highlights a difference in titanite and allanite Eu/Eu*. This is a second order effect related to Eu oxidation state, and is dependent on the propensity of the crystal lattice to incorporate Eu^{2+}. The data suggest that titanite has a higher affinity for Eu^{2+} than allanite in the same rock. This is consistent with trace element data from Bea (1996), which indicate relatively Eu-depleted REE contents in allanite compared to titanite. A similar feature is also observed for contemporaneously formed titanite (Eu/Eu* ~1.5) and allanite (Eu/Eu* ~1.1) in metamorphic orthogneisses (Gregory et al., in review; Gregory, 2008). It is therefore suggested that crystal chemical effects play a role in Eu^{2+} fractionation in titanite and allanite.

The Eu anomaly showed the most uniform behaviour when considering all accessory phases analysed for Nd isotopes, and thus provides the most reliable trace element indicator of differentiation index at the mineral-scale. Unfortunately the bulk-rock data of von Blanckenburg et al. (1992) does not contain Gd, which prohibits comparison of Eu/Eu* mineral to bulk-rock data.

8.3 Utility of accessory mineral Sm-Nd isotopes in igneous rocks

Accessory minerals suitable for Nd isotope analysis by LA-MC-ICPMS crystallised over the entire range of bulk-rock compositions investigated from the Bergell igneous complex, from fine-grained basaltic-andesite to porphyritic granodiorite (Fig. 8a), and therefore have wide-ranging application to the study of igneous rocks.

The precision of in-situ Nd isotope measurements obtained in this study (down to ~20 ppm at 2σ level; Table 4) was degraded by a factor of ~3 compared to that of ID-TIMS accessory mineral data (< 10 ppm at 2σ level; Thöni et al., 2008). Nonetheless, the in-situ method presented here enables mineral zones of different Nd isotope composition to be distinguished, and permits the targeting of any chemically or texturally anomalous domains identified in BSE images (e.g., Fig. 3), including domains previously analysed for U-Th-Pb isotopes. The analytical and spatial resolution required for isolating sub-grain domains was routinely achieved using high-Nd monazite and allanite (Fig. 5). Because the precision of in-situ isotope measurements is primarily a function of total Nd content (Foster and Vance, 2006; McFarlane and McCulloch, 2007), the utility of titanite for high-resolution work remains dependent on LREE abundances in this mineral: in this study > 1000 ppm total Nd was required in order to apply a 81μm laser spot diameter.

The laser ablation MC-ICPMS technique outlined in this paper offers a direct approach to measure the Sm-Nd isotope systematics of U-Th accessory minerals with application to calc-alkaline igneous rocks. Such potential application includes “juvenile” tonalite-trondhjemite-granodiotite (TTG) series granitoids whose bulk compositions are favourable for magmatic titanite and allanite crystallisation, and which dominate early Archaean terrane (Nutman et al., 2001), including the oldest crustal remnants (e.g., Bennett et al., 1993; Bowring and Williams, 1999). Potential applications also extend to orthogneisses whose initial bulk-rock isotope signatures have been blurred due to later metamorphic reworking (e.g., Bingen et al., 1996; Finger et al., 1998; Berger et al., 2008). For example, granite to tonalite orthogneisses located along the southern margin of the Central Alpine orogen in Switzerland, preserve igneous allanite cores within metamorphic allanite grains, despite undergoing bulk-rock modification during Alpine high-grade metamorphism and melting (Berger et al., 2008; Gregory, 2008). Using in-situ dating techniques (Gregory et al., 2007) to first assess the behaviour of the U-Th-Pb system, it was established that the Pb in relict igneous allanite was not affected by volume diffusion and retained Permain magmatic ages (Gregory, 2008). It is thus expected that the Sm-Nd isotope system in allanite was also undisturbed by the tectonometamorphic overprint, considering the relatively slow

diffusivities of REEs compared to Pb in other accessory phases, such as titanite (Cherniak, 1993; 1995). Consequently, the extraction of primary Sm-Nd isotope information from igneous rocks that have seen varying degrees of alteration or metamorphism, offers a significant application for microbeam analysis. The procedure described here opens up the way for petrogenetic applications to exploit information held in U-Th-Pb and Nd isotopes at the micrometer scale, in a manner similar to current U-Pb and Hf isotope studies on zircon (e.g., Harrison et al., 2005; Hawkesworth and Kemp, 2006; Scherer et al., 2007).

9. Conclusions

Based on this study, titanite and epidote-allanite present themselves as key minerals for targeted in-situ Sm-Nd isotope analysis and trace element characterisation of calc-alkaline plutonic suites. Importantly, the mineral isotopic investigation of the entire Bergell intrusive suite and the Novate leucogranite has shown that the range of bulk-rock compositions containing (co-existing) accessory phases amenable to Sm-Nd isotope analysis by LA-MC-ICPMS is broad. Constraining the isotopic composition of the mantle or crustal-sourced magmatic end-members is crucial in order to successfully extract an accurate account of magmatic evolution. We have demonstrated here that LA-MC-ICPMS can be used to determine the Sm-Nd isotope composition of accessory phases with variable Nd (1 500 to 100 000 ppm) and Sm/Nd (~0.5 to 0.05) contents within a single analysis, and with a precision that allows targeting of different mineral domains (down to ~20 ppm at 2σ level). Grouped averages of Nd isotope data yielded an analytical precision (< 0.3 epsilon units, 2σ) approaching that of TIMS single mineral data (von Blanckenburg 1992). We have also shown, using monazite from leucogranite, that in-situ accessory phase Nd isotopes are able to communicate the same information as that of bulk-rock techniques but with an added level of detail. Therefore, these minerals are capable in-situ indicators for bulk-rock crustal contamination processes, and integrated with in-situ U-Th-Pb ages present an innovative approach for tracing the temporal, chemical and isotopic evolution of calc-alkaline melts.

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Tables

Table 1: LA-MC-ICPMS sample description and location.

Table 2: Allanite and REE-epidote major element composition determined by electron microprobe.

Table 3: Representative mineral trace element compositions determined by LA-ICP-MS. Bulk-rock trace element compositions after von Blanckenburg et al. (1992).

Table 4: LA-MC-ICPMS determined accessory mineral Sm-Nd isotope data.

Table 5: SHRIMP Th-Pb isotope data from SIS01 allanite (gabbro).

Electronic data repository

EDRTable: Secondary mineral standard Nd isotope data determined by LA-MC-ICPMS.

Figures

Fig. 1: Simplified geological map of the Bergell Pluton and Novate Intrusion showing the sample locations used in this study. After Schmid et al. (1996). SSB: Southern Steep Belt, LM: Lago di Mezzola.

Fig. 2: Bulk-rock initial εNd versus epsilon εSr values of the igneous members of the Bergell Pluton investigated in this study. After von Blanckenburg et al. (1992), including isotopic data of the Novate Intrustion from Kagami et al. (1985). The “mantle array” is after DePaolo (1988). The smooth mantle-crust trend represents mixing of picrobasaltic partial melt originating from an enriched mantle source (εNd = +4) and European crust (von Blanckenburg et al. 1992).

Fig. 3: High-resolution electron backscatter images of accessory minerals analysed by LA-MC-ICPMS. Dotted circles are locations of laser ablation analysis. Numbers are initial εNd values including 2-sigma uncertainties (in brackets). Minerals: (a) NOV1 monazite with high BSE core, (b) NOV1 monazite with low BSE, inclusion-rich core, (c) NOV1 monazite intermediate BSE, (d) SIS04 allanite unzoned, (e) SIS07 allanite, (f) SIS01 allanite with epidote rim, (g) SIS07 titanite sector-zoned, (h) SIS04 titanite, (i) SIS01 titanite, (j) NOV1 apatite unzoned, (k) MAL1 REE-epidote with titanite rim.

Fig. 4: Chondrite-normalised (McDonough and Sun, 1995) mineral REE patterns determined by LA-ICP-MS.

Fig. 5: Allanite Th-Pb ages determined by SHRIMP for Bergell gabbro (this study), tonalite and granodiorite (Gregory et al. 2007).

Fig. 6: Summary of initial (^{147}Sm decay-corrected) εNd values determined by LA-MC-ICPMS for the Bergell minerals. Error bars are 2σ absolute standard errors. Grey shading indicates corresponding TIMS εNd*t* values (at 2-sigma) after von Blanckenburg et al. (1992) and von Blanckenburg (1992). Unfilled squares are statistical outliers and unfilled circles are core analyses. Six analyses of SIS01 titanite (indicated by stars) with large uncertainties due to low counting statistics (<0.5 V ^{146}Nd) were not included in the weighted mean calculation specified by full black lines (see text for discussion).

Fig. 7: Sm-Nd isochron of uncorrected LA-MC-ICPMS mineral analyses from SIS07 granodiorite. The initial ^{143}Nd/^{144}Nd intercept is identical to that of the bulk-rock value (0.512277; von Blanckenburg et al. 1992).

Fig. 8: (a) Mineral εNd*t* versus age plot. Age of basaltic-andesite dyke MAL1 estimated at ≥33 Ma based on field observations and geochemical and isotopic data. SIS01, SIS04 and SIS07 allanite ages: SHRIMP Th-Pb (Gregory et al. 2007, and this study); SIS04 and SIS07 titanite ages: TIMS U-Pb (von Blanckenburg et al. 1992); SIS07 apatite age: TIMS U-Pb (von Blanckenburg, 1992); NOV1 monazite age: TIMS U-Pb (Köppel and Grünenfelder, 1975 as reported by Hansmann, 1996); (b) Mineral Eu/Eu* versus age plot.