



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.

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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; McLennan et al., 1990; Condie, 1993; 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; McCulloch and Compston, 1981; Bennett et al., 1993; Bowring and Housh, 1995; Vervoort et al., 1996). In particular, Nd isotopes have been successfully applied in igneous

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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 primarily used to extract 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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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 (Trommsdorff and Nievergelt, 1983; Berger et al., 1996) 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 (Fig. 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, hornblende 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 (Reusser, 1987; Diethelm, 1989).

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

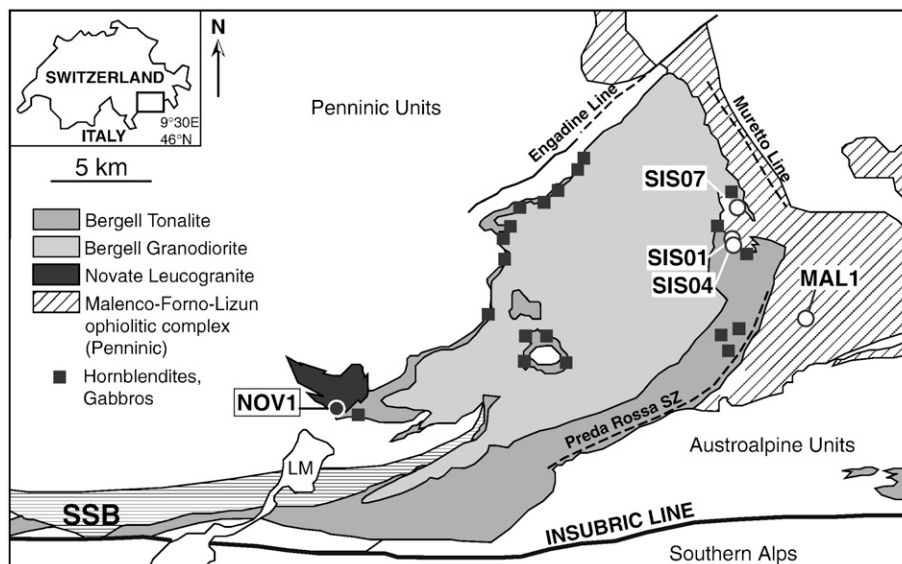


Fig. 1. Simplified geological map of the Bergell Pluton and Novate Intrusion showing the sample locations used in this study. After Schmid et al. (1996). SSB: Southern Steep Belt, LM: Lago di Mezzola.

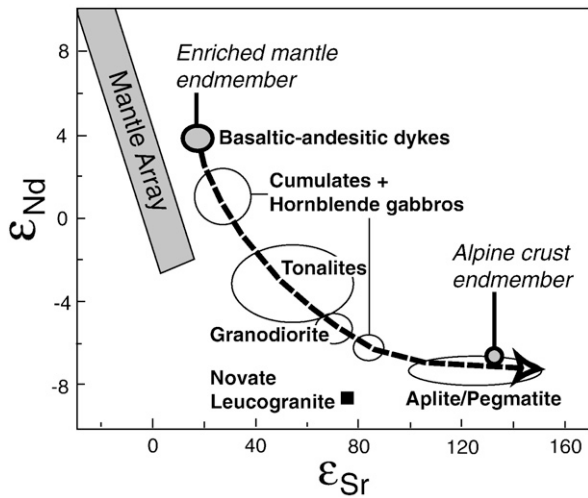


Fig. 2. Bulk-rock initial ϵ_{Nd} versus ϵ_{Sr} values of the igneous members of the Bergell Pluton investigated in this study. After von Blanckenburg et al. (1992), including isotopic data of the Novate Intrusion from Kagami et al. (1985). The “mantle array” is after DePaolo (1988). The smooth mantle-crust trend represents mixing of picobasaltic partial melt originating from an enriched mantle source ($\epsilon_{\text{Nd}} = +4$) and European crust (von Blanckenburg et al., 1992).

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-andesite dyke 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 proposed mantle end-member ($\epsilon_{\text{Nd}} = +4$; 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: Hornblende gabbro, representative of the initial phase of magmatic intrusion, was collected in Val Sissone (Table 1). A range of basic rock compositions, however, are observed along the pluton margin from blocks of cumulitic hornblendites to in-situ crystallised gabbro as enclaves in tonalite (Diethelm, 1989). These rocks display a corresponding range in initial ϵ_{Nd} from +2 to –6 (von Blanckenburg et al., 1992). Allanite, titanite and apatite from SIS01 were ≤ 200 μm 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 in Nd isotope compositions 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 commonly larger in size than those 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 were similar in appearance 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

Table 1
Sample description

Sample	Coordinates ^a	Location	Rock type	Major minerals	Accessories	Description	Separates ^b
MAL1	4616.96 0949.81	Val Malenco	Basaltic-andesite dyke	Pl, Hbl	Ep, Ap	Very fine-grained, homogeneous dyke ~ 1 m, intruding cumulate dunite	Ep, Ttn
SIS01	4618.14 0945.43	Val Sissone	Gabbro	Hbl, Pl, Cpx	Aln, Ttn, Ap	Boulder, undeformed, homogeneous	All, Ttn
SIS04	4618.14 0945.43	Val Sissone	Tonalite	Hbl, Bt, Pl, Kfs, Qtz	Ep, Aln, Ttn, Ap, Zrn	Boulder, homogeneous	All, Ttn
SIS07	4618.73 0946.09	Val Sissone	Granodiorite	Kfs, Pl, Qtz, Hbl, Bio	Aln, Zr, Ap, Ttn	Boulder, Kfs megacrysts, minor late-stage chlorite and epidote	All, Ttn, Ap
NOV1		Novate Quarry, East of L. Mezzola	Leucogranite	Bt, Ms, Pl, Qtz, Kfs, Grt	Mnz, Ap, Uraninite	Relatively undeformed, homogeneous	Mnz, Ap

^a Coordinates given in Global degrees.

^b Analysed by LA-MC-ICPMS for Sm–Nd isotopes.

Table 2
Average EMP major element composition of REE-epidote and allanite

	MAL1 REE-epidote	SIS01 allanite	SIS04 allanite	SIS07 allanite
SiO ₂	34.8	32.7	31.8	31.2
TiO ₂	0.83	0.46	0.43	0.78
Al ₂ O ₃	22.4	18.1	17.2	14.9
MgO	0.09	1.13	1.01	1.32
CaO	20.2	15.1	14.6	13.1
MnO	0.93	0.21	0.37	0.47
FeO _{total}	10.8	12.4	13.6	14.6
La ₂ O ₃	1.56	5.72	5.77	5.25
Ce ₂ O ₃	2.95	7.74	9.23	9.46
Pr ₂ O ₃	0.46	0.66	0.61	1.10
Nd ₂ O ₃	1.25	1.87	2.06	3.09
Sm ₂ O ₃	0.26	0.13	0.14	0.28
Gd ₂ O ₃	0.18	0.05	0.08	0.12
Y ₂ O ₃	0.35	0.03	0.04	0.09
SrO	0.05	0.05	bdl	0.05
ThO ₂	0.01	2.21	2.49	2.15
Total	97.1	98.6	99.5	97.9
REE+Th	0.19	0.55	0.59	0.67

bdl = below detection.

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, transpar-

ent, ~200 µm in diameter and contained inclusions of quartz and feldspar.

4. Analytical method

Mineral grains were separated using conventional heavy liquids and magnetic methods. 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 15 kV, beam current of 2–3 nA and a working distance of 20 mm.

Major-element analyses of allanite were performed using a Cameca SX100 electron microprobe at the Research School of Earth Sciences, ANU, working at 15 kV and 20 nA, with a defocused electron beam (5 µm). A detailed description of EMP analytical protocols is provided in Gregory et al. (2007). Trace element analyses of mineral separates were performed by LA-ICP-MS at the ANU Research School of Earth Sciences 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 checked 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 and titanite analyses were normalised to CaO values independently determined by electron microprobe. Stoichiometric values for

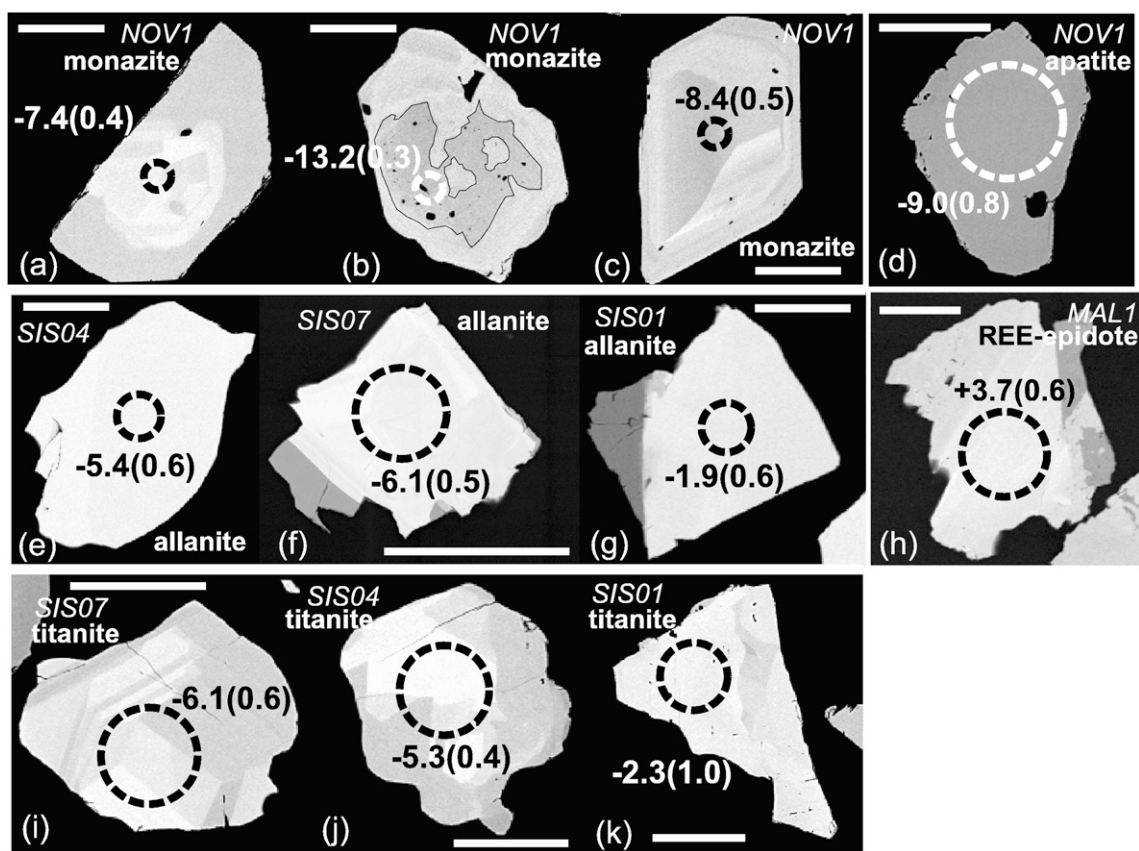


Fig. 3. High-resolution electron backscatter images of accessory minerals analysed by LA-MC-ICPMS. Dotted circles are locations of laser ablation analysis. Numbers are initial ϵ_{Nd} values including 2-sigma uncertainties (in brackets). Minerals: (a) NOV1 monazite with high BSE core, (b) NOV1 monazite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

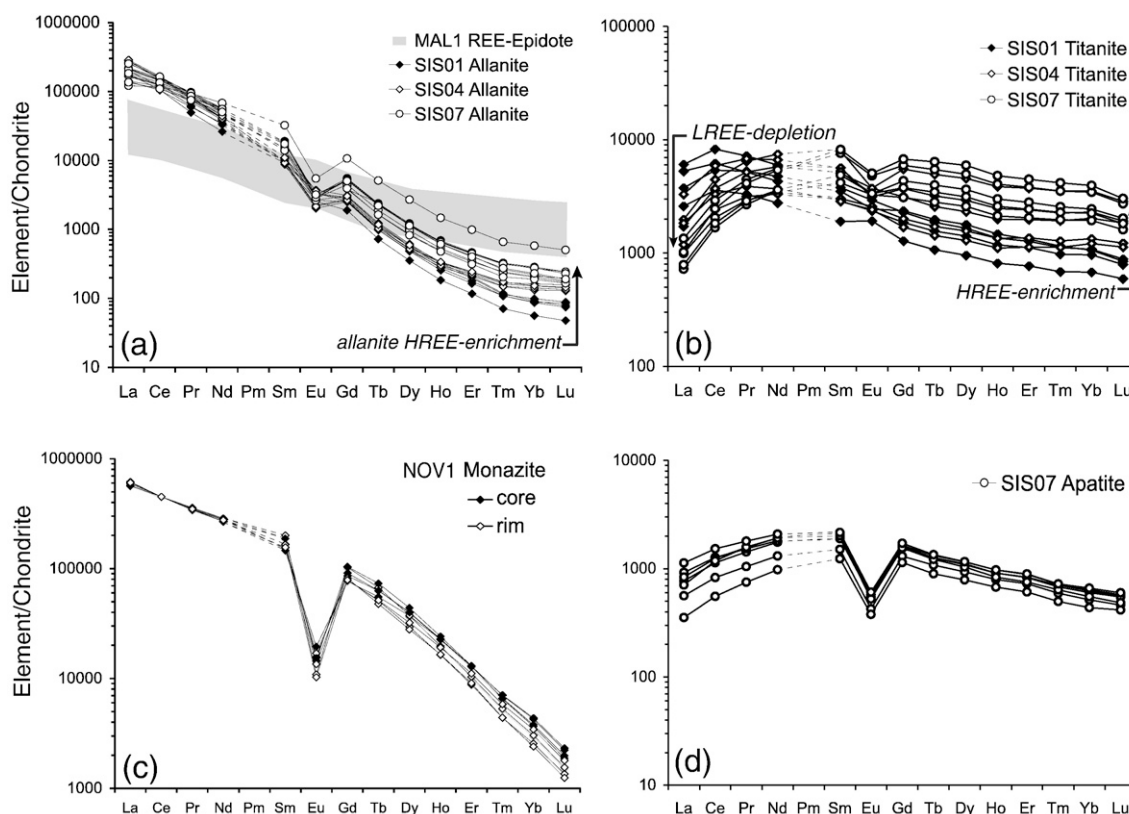


Fig. 4. Chondrite-normalised (McDonough and Sun, 1995) mineral REE patterns determined by LA-ICP-MS.

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 μ m 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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 were 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 μ m to 105 μ m) 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 μ m (10 000 ppm for gabbro to 25 000 ppm for granodiorite); <2 V ^{146}Nd for REE-epidote at 105 μ m (2500 to 10 000 ppm for basaltic-andesite); 0.5–1.5 V ^{146}Nd for titanite at 81 μ m (1500 ppm for gabbro to 2500 ppm for tonalite); 0.5–1 V ^{146}Nd for apatite at 105 μ m (500 to 1000 ppm); and >3 V ^{146}Nd for monazite at 24 μ m (>120 000 ppm).

Isotope ratios and gas blanks were measured using 50 cycles of 2 s 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 $^{147}\text{Sm}/^{149}\text{Sm}$ was applied to correct mass bias on $^{144}\text{Sm}/^{149}\text{Sm}$ using an exponential law. The latter was being used to correct for ^{144}Sm interference on ^{144}Nd . The interference-corrected $^{146}\text{Nd}/^{144}\text{Nd}$ (reference=0.7219) was then applied to normalise background and interference-corrected $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{145}\text{Nd}/^{144}\text{Nd}$ (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 (Vance and Thirlwall, 2002; Albrède et al., 2004). The best comparison between MC-ICPMS and TIMS results is achieved by applying an empirical correction (+40 ppm) to our $^{143}\text{Nd}/^{144}\text{Nd}$ values. Isotope ratio errors are reported as 2 σ absolute standard errors. Uncertainty on $^{147}\text{Sm}/^{144}\text{Nd}$ 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 $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}(t)$ 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 $\text{Ca}^{2+} + \text{Fe}^{3+}$ (epidote) $\rightarrow \text{REE}^{3+} + \text{Fe}^{2+}$ (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 and h). Monazite grains were oscillatory- to sector-zoned with local internal core-overgrowth structures (Fig. 3a and 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 ~8000–200,000, 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 characteristic strongly LREE-enriched patterns (Fig. 4c) and a rimward decrease in Y and HREE concentrations (e.g., La/Lu varies from 2500 to 4000 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

Table 3
Average bulk-rock (XRF, INAA, ID)^a and mineral (LA-ICP-MS)^b trace element compositions (in ppm)

	BCR-2G ^c		Mafic Dyke		Gabbro			Tonalite			Granodiorite				Leucogranite	
	BCR-2G ^c	BCR-2G ref ^d	WR ^a	REE-epidote	WR ^a	Titanite	Allanite	WR ^a	Titanite	Allanite	WR ^a	Titanite	Allanite	Apatite	Monazite core	Monazite rim
Sc	33	33	39	92	117	5.2	55	25	5.3	50	9.0	11	98	0.33	0.07	0.12
V	435	425	331	1360	316	1210	989	181	1170	753	70	980	646	9.0	1.4	0.4
Rb	54	47	2.4	<0.1	5.1	0.27	0.45	91	0.71	<0.1	200	1.0	0.15	0.30	4.1	3.1
Sr	320	342	327	469	78	18	154	320	21	156	346	20	124	194	47	99
Y	31	35	19	2670	1.9	1380	338	18	3170	458	4.0	4900	882	1256	29,300	22,400
Zr	159	184	74	684	21	305	4.8	131	404	7.6	129	305	6.5	0.46	4.7	15
Nb	12.1	12.5	–	<0.02	–	1730	<0.02	–	3580	0.08	–	9450	0.14	<0.01	0.21	0.20
Ca	1.25	1.16	–	<0.09	–	0.08	0.25	–	0.10	<0.09	–	0.17	<0.09	<0.03	<0.03	<0.03
Ba	663	683	92	1.1	28	<0.2	0.59	556	0.58	1.7	852	0.42	0.38	0.32	0.29	0.50
La	23.8	24.7	6.7	9630	2.8	954	41,800	29	475	57,500	33	230	45,900	179	136,000	144,000
Ce	51.3	53.3	17	20,200	6.4	3160	67,900	60	2420	92,800	63	1330	86,200	679	276,000	276,000
Pr	6.4	6.7	–	2220	–	423	5470	–	472	7520	–	316	8310	129	32,700	32,500
Nd	27.7	28.9	13	7970	6.3	1740	14,700	27	2460	19,000	24	1970	25,300	770	126,000	127,000
Sm	6.46	6.59	3.7	1120	2.1	373	1190	5.7	727	1520	4.6	888	2740	272	25,700	25,000
Eu	1.86	1.97	1.3	289	0.50	113	157	1.2	176	139	1.0	223	180	29	858	727
Gd	6.19	6.71	–	814	–	321	481	–	638	577	–	950	1090	299	18,600	17,000
Tb	0.93	1.02	0.60	95	0.30	48	35	0.8	100	42	0.60	160	87	43	2400	1960
Dy	6.13	6.44	–	514	–	295	120	–	622	146	–	996	305	256	10,100	7800
Ho	1.19	1.27	–	92	–	55	14	–	117	19	–	181	37	47	1270	980
Er	3.3	3.7	–	238	–	149	27	–	339	40	–	498	73	127	2070	1570
Tm	0.47	0.51	–	31	–	20	2.6	–	50	4.3	–	72	7.8	16	170	123
Yb	3.13	3.39	2.8	192	1.3	128	14	2.8	335	26	1.5	452	44	93	661	461
Lu	0.48	0.5	0.40	26	0.20	16	1.9	0.50	44	3.7	0.20	55	5.7	13	53	37
Hf	4.36	4.84	2.3	11	1.3	23	0.37	4.8	58	0.38	4.8	29	0.33	0.10	1.5	1.5
Ta	0.77	0.78	–	<0.04	–	181	0.03	–	1000	<0.03	–	1100	<0.04	<0.02	0.28	0.20
Pb	11	11	–	115	–	2.5	55	–	4.5	96	–	4.4	66	6.1	203	113
Th	5.4	5.9	1.9	133	1.0	490	14,600	11	238	26,100	19	91	17,000	50	95,700	62,700
U	1.66	1.69	0.60	232	0.30	478	305	2.3	806	170	12	520	157	36	6780	5000
Ba/Y			4.8		15			31			213					
Th/U			3.2	0.6	3.3	1.0	48	4.8	0.3	154	1.6	0.2	108	1.4	14	13
Eu/Eu*			–	0.9	–	1.0	0.6	–	0.8	0.5	–	0.7	0.3	0.3	0.1	0.1

^a Bulk-rock analysis taken from von Blanckenburg et al. (1992).

^b Mineral contents are single representative analyses.

^c BCR-2G average values obtained as secondary standards during the course of trace element measurement, using CaO=7.06 wt.% as internal standard (from GeoREM).

^d BCR-2G GeoREM preferred values (<http://georem.mpch-mainz.gwdg.de/>).

Table 4

Nd isotopic compositions of Bergell accessory phases determined by laser ablation MC-ICPMS

Sample	Analysis	Spot size (microns)	Session	Measured $^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	2σ	$^{144}\text{Nd}/^{145}\text{Nd}$	2σ	Initial epsilon Nd	$2\sigma^a$
<i>Andesite dyke-MAL1</i>										
TIMS (WR, von Blanckenburg et al., 1992)				0.1741	0.512841	7			4.05	0.14
REE-epidote	andep01	105	2	0.0834	0.512814	47	0.348403	39	3.86	0.91
	andep02	105	2	0.0924	0.512810	46	0.348429	36	3.75	0.89
	andep03	105	2	0.1128	0.512828	72	0.348390	66	4.03	1.41
	andep04	105	2	0.1018	0.512810	31	0.348422	27	3.72	0.60
	andep05	105	2	0.0867	0.512814	19	0.348417	10	3.86	0.36
<i>Gabbro-SIS01</i>										
TIMS (Hornblende gabbro, von Blanckenburg et al., 1992)				0.2007	0.512660	23			0.41	0.45
TIMS (in-situ crystallised gabbro, von Blanckenburg et al., 1992)				0.1615	0.512324	9			-6.13	0.18
Allanite	gaball01	47	2	0.0480	0.512507	29	0.348424	20	-1.98	0.56
	gaball02	47	2	0.0504	0.512474	38	0.348403	18	-2.63	0.75
	gaball03	47	2	0.0501	0.512499	24	0.348406	15	-2.16	0.47
	gaball04	47	2	0.0530	0.512476	20	0.348404	12	-2.61	0.40
	gaball05	47	2	0.0525	0.512490	27	0.348418	15	-2.34	0.52
	gaball06	47	2	0.0548	0.512481	18	0.348407	15	-2.52	0.35
	gaball07	47	2	0.0511	0.512487	36	0.348409	25	-2.38	0.70
	gaball01	47	3	0.0528	0.512497	87	0.348397	70	-2.20	1.69
	gaball02	47	3	0.0500	0.512512	39	0.348410	23	-1.89	0.76
	gaball03	47	3	0.0551	0.512486	31	0.348411	20	-2.42	0.61
Titanite	gaball04	47	3	0.0540	0.512507	55	0.348396	70	-2.00	1.07
	gabtttn01*	81	2	0.0830	0.512469	164	0.348414	130	-2.87	3.19
	gabtttn03	81	2	0.1312	0.512525	42	0.348417	14	-1.92	0.59
	gabtttn05*	81	2	0.1478	0.512471	102	0.348410	80	-3.07	1.98
	gabtttn06*	81	2	0.1088	0.512495	143	0.348407	74	-2.45	2.79
	gabtttn07*	81	2	0.0864	0.512430	62	0.348402	34	-3.63	1.22
	gabtttn08*	81	2	0.1489	0.512334	198	0.348397	101	-5.74	3.87
	gabtttn09	81	2	0.1781	0.512517	55	0.348400	32	-2.30	1.07
	gabtttn10	81	2	0.1474	0.512521	43	0.348419	30	-2.09	0.83
<i>Granodiorite-SIS07</i>										
TIMS (WR, von Blanckenburg et al., 1992)				0.1160	0.512300	4			-6.29	0.08
TIMS (allanite, von Blanckenburg, 1992)				0.0682	0.512290	18			-6.30	0.35
Allanite	granall01	47	2	0.0683	0.512259	26	0.348409	17	-6.91	0.50
	granall02	47	2	0.0668	0.512308	31	0.348407	51	-5.94	0.60
	granall03	47	2	0.0641	0.512299	20	0.348415	11	-6.10	0.40
	granall04	47	2	0.0690	0.512295	22	0.348403	11	-6.20	0.43
	granall05	47	2	0.0659	0.512283	36	0.348389	21	-6.43	0.70
	granall06	47	2	0.0950	0.512296	16	0.348405	28	-6.28	0.31
	granall07	47	2	0.0926	0.512303	20	0.348408	98	-6.13	0.40
	granall08	47	2	0.0718	0.512296	16	0.348405	15	-6.19	0.32
	granall09	47	2	0.1000	0.512307	28	0.348415	18	-6.08	0.55
	granall10	47	2	0.0602	0.512300	17	0.348415	15	-6.07	0.33
	granall01	47	3	0.1054	0.512312	49	0.348416	17	-6.01	0.95
	granall02	47	3	0.0808	0.512291	39	0.348402	17	-6.33	0.76
	granall03	47	3	0.0678	0.512301	51	0.348403	21	-6.08	1.00
	granall04	47	3	0.0627	0.512267	29	0.348402	26	-6.73	0.57
TIMS (titanite, von Blanckenburg, 1992)				0.2558	0.512338	19			-6.08	0.37
Titanite	granttn01	81	2	0.2458	0.512339	48	0.348421	52	-6.09	0.93
	granttn02	81	2	0.2865	0.512332	23	0.348413	27	-6.34	0.45
	granttn03	81	2	0.2661	0.512342	38	0.348401	23	-6.05	0.74
	granttn04	81	2	0.2733	0.512338	32	0.348398	20	-6.16	0.62
	granttn06	81	2	0.3005	0.512346	29	0.348402	25	-6.12	0.57
	granttn07	81	2	0.2458	0.512348	67	0.348382	35	-5.86	1.30
	granttn08	81	2	0.2820	0.512341	47	0.348419	59	-6.15	0.91
	granttn09	81	2	0.3023	0.512332	36	0.348408	16	-6.40	0.70
	granttn10	81	2	0.3225	0.512362	122	0.348408	76	-5.90	2.39
TIMS (apatite, von Blanckenburg, 1992)				0.1701	0.512319	18			-6.12	0.35
Apatite	granap02	105	2	0.2115	0.512319	54	0.348400	37	-6.28	1.05
<i>Tonalite-SIS04</i>										
TIMS (WR, von Blanckenburg et al., 1992)				0.1300	0.512378	5			-4.82	0.09
TIMS (allanite, von Blanckenburg, 1992)				0.0484	0.512362	19			-4.78	0.37
Allanite	tonall01	47	2	0.0577	0.512309	26	0.348410	22	-5.89	0.50
	tonall03*	47	2	0.0470	0.512292	32	0.348401	16	-6.17	0.63
	tonall04	47	2	0.0477	0.512328	29	0.348408	20	-5.48	0.57
	tonall05	47	2	0.0476	0.512319	26	0.348409	15	-5.65	0.50
	tonall06	47	2	0.0465	0.512318	24	0.348403	14	-5.67	0.46
	tonall07	47	2	0.0466	0.512312	30	0.348407	19	-5.78	0.59
	tonall08	47	2	0.0517	0.512312	20	0.348413	15	-5.80	0.40
	tonall09	47	2	0.0526	0.512322	23	0.348411	14	-5.62	0.45
	tonall10	47	2	0.0639	0.512344	31	0.348418	23	-5.23	0.61

(continued on next page)

Table 4 (continued)

Sample	Analysis	Spot size (microns)	Session	Measured					Initial	
				$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	2 σ	$^{144}\text{Nd}/^{145}\text{Nd}$	2 σ	epsilon Nd	2 σ^a
Tonalite-SIS04										
	tonall01	47	3	0.0472	0.512307	30	0.348412	18	-5.89	0.58
	tonall02	47	3	0.0652	0.512322	36	0.348419	26	-5.67	0.71
	tonall03	47	3	0.0487	0.512320	45	0.348398	28	-5.64	0.88
	2.1	47	1	0.0437	0.512309	18	0.348418	14	-5.83	0.35
	3.1	47	1	0.0514	0.512302	17	0.348418	12	-5.99	0.33
	4.1	47	1	0.0463	0.512315	19	0.348427	12	-5.72	0.38
	5.1	47	1	0.0527	0.512304	17	0.348416	11	-5.97	0.33
	7.1	47	1	0.0569	0.512332	15	0.348423	11	-5.44	0.30
	8.1	47	1	0.0437	0.512333	15	0.348420	14	-5.36	0.30
	9.1	47	1	0.0583	0.512316	17	0.348439	14	-5.75	0.33
TIMS (titanite, von Blanckenburg, 1992)				0.1901	0.512380	18			-5.01	0.35
Titanite										
	tonttn01	81	2	0.2043	0.512364	24	0.348404	19	-5.38	0.47
	tonttn02	81	2	0.1834	0.512363	33	0.348403	21	-5.32	0.65
	tonttn03	81	2	0.1611	0.512339	23	0.348412	15	-5.70	0.45
	tonttn04	81	2	0.1618	0.512349	30	0.348408	20	-5.50	0.59
	tonttn05*	81	2	0.1653	0.512311	34	0.348398	22	-6.26	0.66
	tonttn06	81	2	0.1944	0.512361	28	0.348423	21	-5.40	0.54
	tonttn07	81	2	0.2135	0.512370	22	0.348410	14	-5.29	0.43
	tonttn08	81	2	0.1874	0.512356	58	0.348417	34	-5.48	1.14
	tonttn09	81	2	0.1772	0.512365	28	0.348392	34	-5.26	0.54
	tonttn10	81	2	0.1642	0.512363	72	0.348406	73	-5.24	1.41
Leucogranite-NOV1										
TIMS (WR, Kagami et al., 1985)									-8.57	
monazite										
	novmon02	24	3	0.1233	0.512185	32	0.348397	17	-8.61	0.63
	novmon03 (core)*	24	3	0.1171	0.511947	16	0.348395	11	-13.23	0.30
	novmon04	24	3	0.1232	0.512195	24	0.348399	14	-8.41	0.47
	novmon05 (core)	24	3	0.1013	0.512157	26	0.348390	24	-9.09	0.52
	novmon06 (core)	24	3	0.1268	0.512249	19	0.348404	73	-7.36	0.36
	novmon07	24	3	0.1478	0.512237	25	0.348405	11	-7.66	0.48
	novmon08	24	3	0.1080	0.512181	45	0.348395	29	-8.63	0.88
	novmon09	24	3	0.1227	0.512155	22	0.348408	43	-9.19	0.43
	novmon10	24	3	0.1286	0.512145	54	0.348400	47	-9.41	1.05
	novmon11	24	3	0.0851	0.512167	40	0.348410	29	-8.83	0.78
apatite										
	novap01	105	2	0.4901	0.512264	48	0.348406	45	-8.23	0.93
	novap02	105	2	0.4292	0.512287	96	0.348417	103	-7.56	1.88
	novap03	105	2	0.4443	0.512236	39	0.348419	48	-8.62	0.77

Initial values are corrected for ^{147}Sm decay based on U–Pb ages of 30 Ma for the Bergell Pluton and 25 Ma for the Novate Leucogranite.

*Not included in weighted mean calculations.

^a Error on corrected epsilon Nd values are calculated from $^{143}\text{Nd}/^{144}\text{Nd}(\text{error})/^{143}\text{Nd}/^{144}\text{Nd} * 10,000$.

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 ($f^{206}\text{Pb} > 0.95$) 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:

MAL1 basaltic-andesite: Five REE-epidote grains were analysed and had variable inter-grain $^{147}\text{Sm}/^{144}\text{Nd}$ (0.083 to 0.113) due to epidote-group REE solid solution. The five analyses produced a weighted mean $\epsilon_{\text{Nd}}t$ of $+3.85 \pm 0.27$ (MSWD 0.1), in agreement with the TIMS bulk-rock value (Fig. 5a; von Blanckenburg et al., 1992).

SIS01 gabbro: Allanite grains were homogeneous in $^{147}\text{Sm}/^{144}\text{Nd}$ ($\sim 0.052 \pm 0.002$). Analysis over two sessions produced $\epsilon_{\text{Nd}}t$ values identical within error of -2.40 ± 0.18 , (MSWD 0.9) and -2.18 ± 0.41 (MSWD 0.5), respectively. Co-existing titanite was more variable in $^{147}\text{Sm}/^{144}\text{Nd}$ (0.131 to 0.178) with some grains displaying up to 5% (1σ) internal variations. Only 3 of 9 titanite grains from SIS01 produced sufficient Nd counts to yield acceptable errors (≤ 1 epsilon unit; Table 4). These three analyses gave an average $\epsilon_{\text{Nd}}t$ of $-2.08 \pm$

0.39 (MSWD 0.4) and calculation inclusive of all analyses gives -2.39 ± 0.45 (MSWD 1.3). Apatites grains were too small for laser sampling due to relatively low Nd concentrations (Table 3). The allanite and titanite results lie within the range previously documented for the Bergell gabbros (Fig. 5c–d; von Blanckenburg et al., 1992). Allanite separated from the Bergell gabbro was dated for the first time using the SHRIMP protocol of Gregory et al. (2007) in order to corroborate the LA-MC-ICPMS Sm–Nd isotope systematics. Fourteen analyses on allanite cores surrounded by epidote overgrowths produced a weighted mean Th–Pb age of 32.4 ± 0.4 Ma (95% c.l., MSWD 1.0; Table 5). Individual allanite Th–Pb analyses are plotted in Fig. 6 against SHRIMP allanite ages of the Bergell tonalite and granodiorite (Gregory et al., 2007), to illustrate the absolute timing sequence of each intrusive body. Uranium–Pb data are not presented (refer to Section 4), however the behaviour of the U–Pb system in allanite from the Bergell tonalite and granodiorite is described in Gregory et al. (2007). Given the high Th/U and relatively young age of allanite from SIS01, it is suspected that the U–Pb system of this sample would be affected by initial ^{230}Th disequilibrium in the form of excess ^{206}Pb (e.g., Schärer, 1984) and therefore give old U–Pb ages, in line with the U–Pb behaviour of allanite in SIS04 and SIS07 (von Blanckenburg, 1992; Gregory et al., 2007).

SIS04 tonalite: Titanite in this sample showed variable intra-grain $^{147}\text{Sm}/^{144}\text{Nd}$ (up to 2.3% at 1-sigma). Despite this compositional variation, the titanite analyses formed a coherent Nd isotope population with a weighted mean $\epsilon_{\text{Nd}}t$ of -5.41 ± 0.18 (MSWD 0.3),

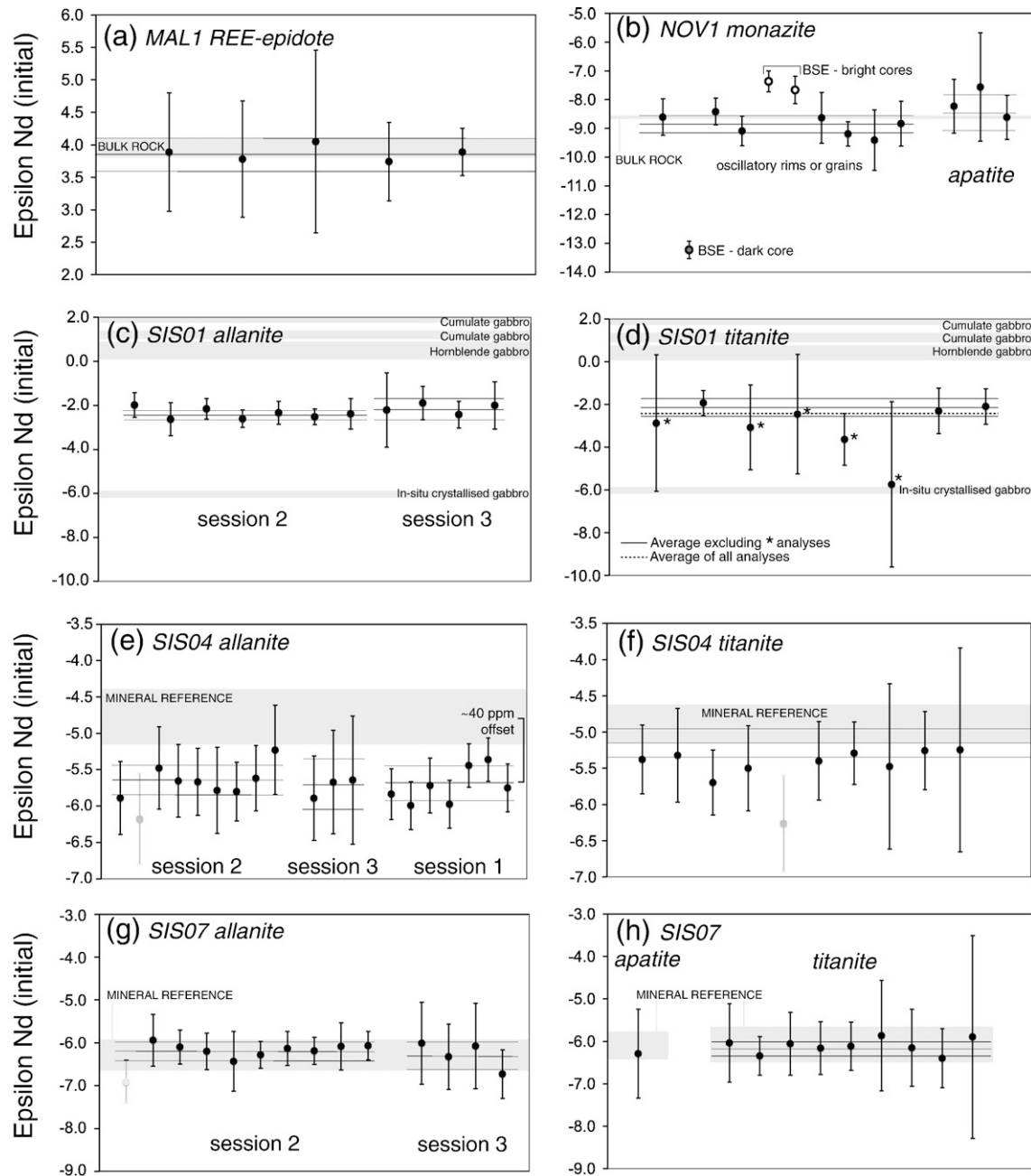


Fig. 5. Summary of initial (^{147}Sm decay-corrected) ϵ_{Nd} values determined by LA-MC-ICPMS for the Bergell minerals. Error bars are 2σ absolute standard errors. Grey shading indicates corresponding TIMS ϵ_{Nd} values (at 2-sigma) after von Blanckenburg et al., 1992 and von Blanckenburg (1992). Unfilled 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 ($<0.5 \text{ V } ^{146}\text{Nd}$) were not included in the weighted mean calculation specified by full black lines (see text for discussion).

which is within error of previous TIMS titanite analyses (Fig. 5f; von Blanckenburg, 1992). Allanite however, consistently reproduced ϵ_{Nd} values that were ~ 40 ppm below those obtained conventionally (Fig. 5e; von Blanckenburg, 1992), even after application of the empirical correction to measured $^{143}\text{Nd}/^{144}\text{Nd}$ (see Section 4). This discrepancy is unlikely to be an analytical artifact because indistinguishable ϵ_{Nd} 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 $^{147}\text{Sm}/^{144}\text{Nd}$ (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 $^{147}\text{Sm}/^{144}\text{Nd}$ (0.105 to 0.061, av. 0.069) and the results from two analytical sessions gave ϵ_{Nd} 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 ϵ_{Nd} 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 ($> 150 \mu\text{m}$ 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 $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{147}\text{Sm}/^{144}\text{Nd}$ isochron plot of allanite, apatite and titanite analyses from SIS07

Table 5
SHRIMP Th–Pb age data

Label	% ²⁰⁸ Pb ^a	²⁰⁸ Pb*/ ²³² Th	1σ	Th–Pb age (Ma)	1σ ^b
SIS01-1.1	89	0.00152	0.00004	30.7	0.8
SIS01-2.1	91	0.00166	0.00003	33.4	0.7
SIS01-3.1	84	0.00169	0.00005	34.2	0.9
SIS01-4.1	91	0.00157	0.00003	31.7	0.6
SIS01-5.1	94	0.00158	0.00004	31.9	0.7
SIS01-6.1	93	0.00160	0.00004	32.2	0.8
SIS01-7.1	85	0.00162	0.00004	32.6	0.8
SIS01-8.1	75	0.00164	0.00004	33.2	0.9
SIS01-9.1	75	0.00159	0.00004	32.2	0.8
SIS01-10.1	87	0.00158	0.00006	31.9	1.3
SIS01-11.1	90	0.00161	0.00002	32.4	0.4
SIS01-12.1	90	0.00157	0.00002	31.7	0.5
SIS01-13.1	90	0.00163	0.00004	33.0	0.7
SIS01-14.1	90	0.00160	0.00002	32.3	0.5

^a Denotes the radiogenic portion of the total ²⁰⁸Pb content, which is estimated using a ²⁰⁷Pb/²⁰⁶Pb based correction.

^b 1.6% (1SD) uncertainty on the CAP standard calibration is included in the errors provided.

(Fig. 7), yielded an initial ¹⁴³Nd/¹⁴⁴Nd 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: ¹⁴⁷Sm/¹⁴⁴Nd 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 $\epsilon_{\text{Nd}t}$ 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 $\epsilon_{\text{Nd}t}$ values of -7.36 and -7.65 . Three apatite grains yielded $\epsilon_{\text{Nd}t}$ 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 Blancken-

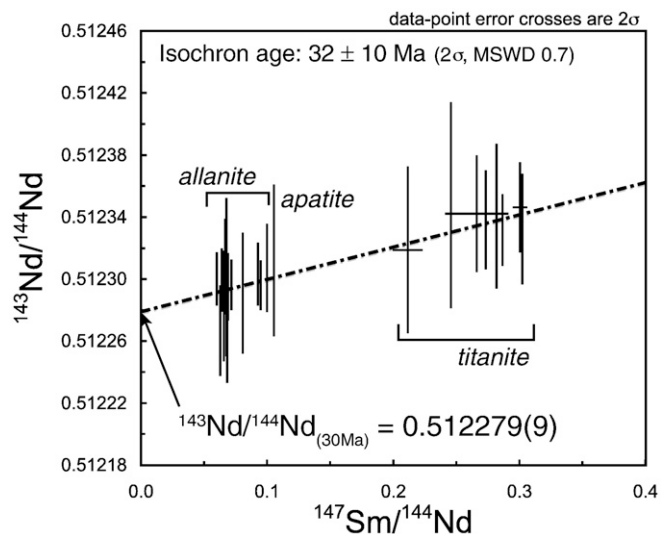


Fig. 7. Sm–Nd isochron of uncorrected LA-MC-ICPMS mineral analyses from SIS07 granodiorite. The initial ¹⁴³Nd/¹⁴⁴Nd intercept is identical to that of the bulk-rock value (0.512277; von Blanckenburg et al., 1992).

burg 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 ($\epsilon_{\text{Nd}t} = +4$, von Blanckenburg et al., 1992). Fig. 8a is a summary of average accessory mineral $\epsilon_{\text{Nd}t}$ 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 $\epsilon_{\text{Nd}t}$ of $+3.9$ for basaltic–andesite determined by REE-epidote, to an $\epsilon_{\text{Nd}t}$ 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 ¹⁴³Nd/

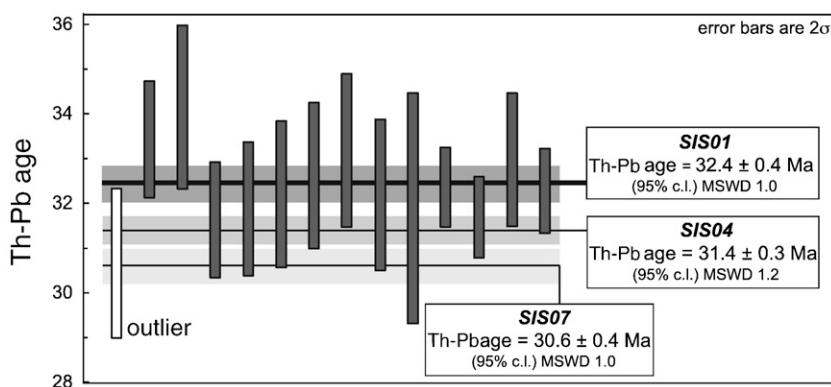


Fig. 6. Allanite Th–Pb ages determined by SHRIMP for Bergell gabbro (this study), tonalite and granodiorite (Gregory et al., 2007).

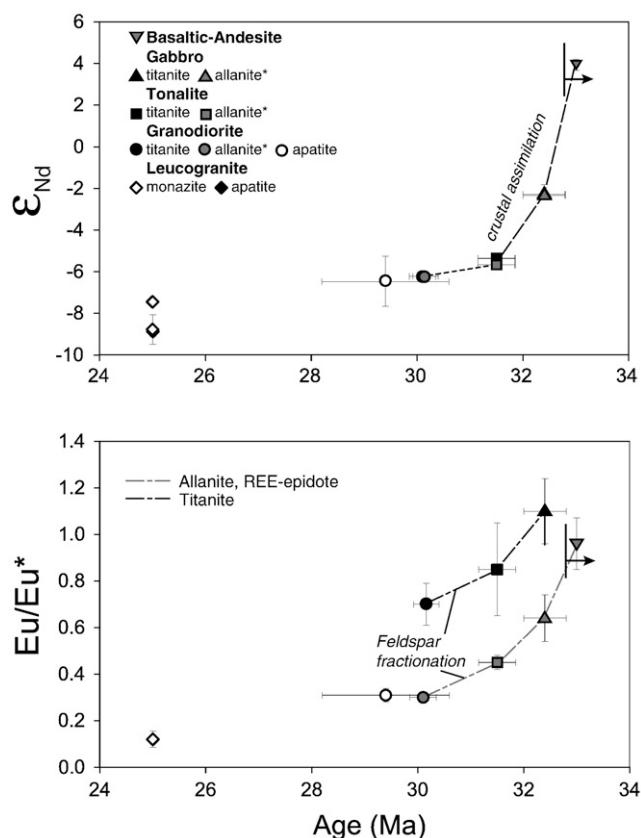


Fig. 8. (a) Mineral ϵ_{Nd} versus age plot. Age of basaltic-andesite dyke MAL1 estimated at ≥ 33 Ma based on field observations and geochemical and isotopic data. SIS01, SIS04 and SIS07 allanite ages: SHRIMP Th–Pb (Gregory et al., 2007, and this study); SIS04 and SIS07 titanite ages: TIMS U–Pb (von Blanckenburg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

^{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 can 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 (ϵ_{Nd} of -2.08 ± 0.39 and -2.36 ± 0.17 , respectively) fall within the large range of bulk-rock ϵ_{Nd} 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 ($\epsilon_{Nd} = +0.4$) 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 ϵ_{Nd} 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 ϵ_{Nd} 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 ϵ_{Nd} 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 ϵ_{Nd} , 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 ε_{Nd} . 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 ($\text{Eu}/\text{Eu}^* \sim 1.5$) and allanite ($\text{Eu}/\text{Eu}^* \sim 1.1$) in metamorphic orthogneisses (Gregory et al., in press; 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 $81 \mu\text{m}$ 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-granodiorite (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 Permian 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 (1500 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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Appendix A

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2008.12.003.

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