

Allanite behaviour during incipient melting in the southern Central Alps

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Abstract

The response of allanite to incipient melting was investigated in migmatites from the Tertiary Barrovian-type sequence of the Central Alps (southern Switzerland, northern Italy). Inheritance and new mineral growth were recorded in composite allanite grains sampled from meta-granitoids and leucosomes. Ion microprobe (SHRIMP) dating of high Th/U allanite cores in meta-granitoids yield Permian ages consistent with magmatic crystallisation dating protolith intrusion. In contrast, low Th/U allanite overgrowths and weakly-zoned allanite in meta-granitoids and leucosomes yield Alpine U–Pb intercept ages between 30 ± 4 and 20 ± 5 Ma; these date allanite formation during the Barrovian cycle. Major and accessory mineral REE compositions suggest that Alpine allanite crystallised in the presence of a low-temperature melt. Whereas new zircon growth is rare in the migmatites, allanite readily recorded growth during the Alpine cycle. Allanite U–Th–Pb isotopes may therefore present a complementary approach to zircon for dating low-temperature partial melting, where the preservation of allanite is aided by low LREE solubility in hydrous granitic melt. The Th–Pb age is preferred to date high-Th magmatic allanite, however the U–Pb and Th–Pb ages of allanite overgrowths may differ (by up to 25%), and this demands a comparison of both U–Pb and Th–Pb isotopic systems to obtain a best estimate for the timing of low-Th allanite crystallisation. Protolith allanite preserves a substantial memory of its initial age in spite of upper amphibolite facies re-working during migmatitisation ($T = 620$ – 700 °C), which places strong constraints on Pb closure temperature. Magmatic allanite contains <30% of initial (non-radiogenic) Pb, allanite in migmatites is characterised by an initial Pb of 20–70%, and subsolidus allanite has >60% of initial Pb. Therefore, the initial Pb may be useful as a sensor for the amount of melt present during allanite formation. The Pb isotope composition of allanite overgrowths indicates $\leq 5\%$ inherited radiogenic Pb from precursor allanite, which suggests efficient redistribution and homogenisation of Pb isotopes during the Alpine partial melting period.

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1. INTRODUCTION

The epidote-group mineral allanite occurs most commonly as an accessory phase in metaluminous granites (Gromet and Silver, 1983) and in low- to medium-grade regional metamorphic terranes (Finger et al., 1998; Wing

et al., 2003), and is an important host of thorium (Th), uranium (U) and light rare earth elements (LREE) in both types of occurrences (Gromet and Silver, 1983; Janots et al., 2008). Such features have made allanite a prospective U–Th–Pb chronometer in magmatic (Barth et al., 1994; Oberli et al., 2004) and metamorphic rocks (Catlos et al., 2000; Parrish et al., 2006; Gregory et al., 2009a) as well as an important mineral-scale tracer of geochemical processes involving the REEs (Hermann, 2002; Oberli et al., 2004; Gregory et al., 2009a). As in other U–Th-bearing minerals, allanite can be heterogeneous in chemistry and

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texture and thus the development of high-resolution dating protocols specific to this mineral (Catlos et al., 2000; Cox et al., 2003), in particular using the Sensitive High Resolution Ion Microprobe (SHRIMP, Gregory et al., 2007), has enhanced its use in geochronological studies by providing texturally-sensitive information and the ability to target individual mineral zones.

Dating of allanite has proven most useful for samples in which zircon, the most commonly used U–Pb chronometer, is rare or inherited (e.g. von Blanckenburg et al., 1992). For example, allanite forms readily during subsolidus metamorphism (Smith and Barreiro, 1990; Wing et al., 2003; Janots et al., 2008; Krenn and Finger, 2009; Rasmussen and Muhling, 2009), and the phase relationships of allanite and monazite can be used to date prograde mineral reactions in Barrovian-type sequences (Janots et al., 2009). Allanite may also form as a high-pressure mineral replacing monazite (Janots et al., 2006; Gabudianu et al., 2009) and zoisite (Tribuzio et al., 1996; Hermann, 2002; Spandler et al., 2003), making it a target for dating subduction-related metamorphism (Parrish et al., 2006; Rubatto et al., 2008; Gabudianu et al., 2009). These studies have shown that under subsolidus conditions allanite may retain its isotopic signature with subsequent heating (Janots et al., 2009) or decompression (Parrish et al., 2006; Rubatto et al., 2008; Gabudianu et al., 2009). However, significant fluid interaction and deformation can expose allanite to open-system isotopic behaviour, even at low metamorphic temperatures (Gabudianu et al., 2009).

In comparison, allanite formation in high-grade rocks, and the response of U–Th–Pb isotope systematics within allanite to superimposed metamorphism and anatexis, is poorly understood. Allanite can newly grow during upper amphibolite facies events, providing direct ages of metamorphism (Gregory et al., 2009a). Although there are no diffusion experiments to provide a direct quantitative basis for the closure temperature of allanite in metamorphic rocks, estimates have been derived from other empirical data. Heaman and Parrish (1991) dated allanite from high grade gneisses by ID-TIMS and found that when metamorphosed to second sillimanite zone, protolith allanite still preserved a component of its original age. Parrish (2001) concluded based on U–Pb isotope systematics that the closure temperature of allanite is likely ~ 650 °C. Isotopic inheritance in the form of inherited cores has not been reported for allanite. Owing to its tendency to incorporate Pb on crystallisation, however, allanite may inherit radiogenic Pb from precursor minerals (Romer and Siegesmund, 2003), thereby complicating the correction for non-radiogenic Pb in U–Th–Pb isotope analyses (Gabudianu et al., 2009). In order to interpret ages obtained from allanite in high grade rocks, it is thus important to understand the mechanisms of isotopic resetting and new mineral growth, such as diffusion versus overgrowth processes that affect allanite. In particular, overgrowth processes can be problematic for geochronology unless microanalytical techniques are used (i.e. SHRIMP). Barth et al. (1994) observed that the Th–Pb and U–Pb age systems of magmatic allanite may differ, and suggested that these two geochronometers are decoupled from each other. There are few

studies providing explanations of this feature (inherited Pb, Romer and Siegesmund, 2003; excess ^{206}Pb , Oberli et al., 2004), or how these systems behave in metamorphic allanite with low Th/U (Gabudianu et al., 2009). All of these effects have significant implications for allanite geochronology.

This paper details the response of allanite to incipient melting and its performance as a chronometer by examining its occurrence, trace element composition, and age in migmatites from the Barrovian-type sequence of the Central Alps (southern Switzerland, northern Italy). The Central Alps have provided previous opportunities to study the isotope systematics of igneous and subsolidus allanite (Oberli et al., 2004; Janots et al., 2009). Here they are the ideal setting to examine allanite in high-grade rocks whose protolith was allanite-bearing (Berger et al., 2008), and where the young age of Alpine metamorphism enables multiple allanite crystallization events to be recorded using SHRIMP and LA-ICPMS techniques (Gregory et al., 2007). Allanite has high and variable trace element contents and is therefore susceptible to matrix-induced variations in ion microprobe $^{206}\text{Pb}^+/^{238}\text{U}^+$ and $^{208}\text{Pb}^+/^{232}\text{Th}^+$ analyses (Catlos et al., 2000) similar to xenotime (Fletcher et al., 2004) and monazite (Stern and Berman, 2000; Fletcher et al., 2010). Matrix effects are a potential problem in this study because the ages of the rocks (Permian and Tertiary) require $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$ ratios. Gregory et al. (2007) demonstrated that magmatic allanite can be dated accurately ($2\text{--}3\% \pm 2\sigma$) for samples with LREE + Th of 0.5–0.9 cpfu. Potential complications for allanite dating caused by matrix effects, initial radioactive disequilibrium and the composition of non-radiogenic Pb are discussed in the context of both Th–Pb and U–Pb age systems in magmatic and metamorphic grains. The new allanite ages obtained in this study provide constraints on the closure temperature of allanite and enable the timing of migmatization to be determined in samples for which new zircon growth is rare.

2. GEOLOGICAL SETTING

The Central Alpine orogen of southern Switzerland and northern Italy underwent Barrovian-type metamorphism in the mid-Tertiary following continental collision of Africa with Europe. Regional metamorphism in the Central Alpine Lepontine domain is delineated by Barrovian mineral zones, which indicate an increasing metamorphic grade to the south from sub-greenschist to upper-amphibolite facies conditions (Engi et al., 1995; Todd and Engi, 1997). This Barrovian-type metamorphic sequence terminates at the Insubric fault line (Schmid et al., 1989), a major tectonic lineament through the Alpine orogen. This fault juxtaposes the high-grade metamorphic core of the Lepontine domain against the units of the Southern Alps, which underwent only weak metamorphism during the Alpine orogeny (Fig. 1). The current tectonic architecture is derived from the south-vergent subduction of the European continental margin beneath the Apulian plate and subsequent lithospheric uplift (Schmid et al., 1996).

Peak metamorphic conditions of 685 ± 50 °C and 0.6–0.8 GPa, determined by amphibole-plagioclase thermobarometry on granitic leucosome from the Southern Steep

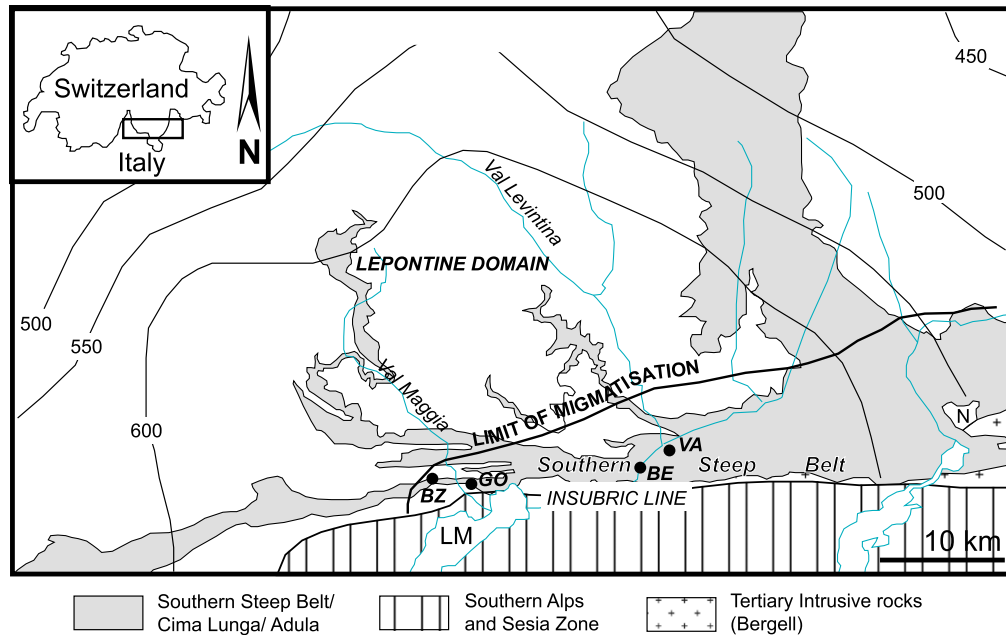


Fig. 1. Schematic geological map of the Central Alps with the sample locations (after Engi et al., 2004). Solid lines are isograds determined from metamorphic mineral assemblages (Engi et al., 2004). Limit of migmatisation based on field observations by Burri et al. (2005). VA = Val d'Arbedo, BE = Bellinzona, GO = Golino, BZ = Berzona, N = Novate leucogranite, LM = Lago Maggiore.

Belt (SSB) (Burri et al., 2005), were reached immediately north of the Insubric Line (Fig. 1). The SSB is a highly deformed rock package comprising poly-deformed Variscan basement intruded by Permian granitoids; now metamorphosed granitic gneisses (Schaltegger and Gebauer, 1999). The pre-Alpine units are intercalated at the metre to kilometre-scale with Alpine units consisting of marbles, calc-silicate and metasedimentary rocks, mafic to ultramafic rocks (Engi et al., 1995; Burri et al., 2005; Berger et al., 2005) and high-pressure relicts (Gebauer, 1996). Consequently, workers have interpreted the SSB to represent part of a tectonic mélange zone (Engi et al., 2001).

Partial melting associated with Alpine metamorphism was dominantly fluid-assisted, and limited to amphibolite-grade rocks of the SSB (Burri et al., 2005). In situ melting of granitic gneisses occurred in the mid-crust at temperatures close to the wet granite solidus ($\sim 630^\circ\text{C}$) and in some cases produced up to ~ 30 vol.% leucosomes (Burri et al., 2005). At outcrop, leucosomes are variably deformed and heterogeneously distributed even within a common protolith (Burri et al., 2005). Only relatively small melt volumes were produced by hydrate-breakdown reactions in muscovite-bearing rocks (Burri et al., 2005). This led Burri et al. (2005) and Berger et al. (2008) to infer a causal relationship between mid-crustal deformation, fluid flow, and migmatization within the SSB.

The nature of incipient Alpine melting and complex association of high-grade rocks in the SSB has complicated geochronology and the determination of Alpine ages (Romer et al., 1996). The long-accepted age for peak metamorphism in the SSB (~ 28 Ma, Engi et al., 1995) is broadly coincident with igneous activity related to the emplacement of the Bergell Pluton (Berger et al., 1996; Oberli et al.,

2004). Zircon and allanite in the western segment of the Bergell tonalite record a protracted magmatic history lasting from 33 to 28 Ma (Oberli et al., 2004). Accessory mineral ages from syn- and post-kinematic pegmatites and aplites within the SSB also span several million years, from 29 to 25 Ma (Schärer et al., 1996; Romer et al., 1996; Liati et al., 2000). The age of related amphibolite-grade metamorphism, determined by Sm–Nd analysis of garnet, falls within this period (~ 27 Ma, Vance and O'Nions, 1992). In fact, Alpine igneous activity continued to at least ~ 24 Ma with the emplacement of the Novate leucogranite stocks (Liati et al., 2000). Together, these data suggest a long-lasting thermal history for the SSB. Recent ion microprobe dating of zircon in migmatites from the SSB indicates that the duration of melting in this area was from about 32–22 Ma (Rubatto et al., 2009).

The best evidence of Alpine in situ melting is preserved in granitic gneisses (Burri et al., 2005). The gneisses were derived from ~ 280 to 300 Ma calc-alkaline granitoids (Romer et al., 1996; Schaltegger and Gebauer, 1999), many of which were originally allanite-bearing (Berger et al., 2008). They have been interpreted as only being metamorphosed during Alpine events. The migmatites studied for geochronology contain abundant allanite and zircon and occur in an east-west profile through the SSB (Fig. 1). The principal deformation structures in the migmatites are Alpine in origin (Berger et al., 2005, 2008).

3. SAMPLE DESCRIPTION

Samples collected in the migmatite zone of the Southern Steep Belt (Burri et al., 2005; Berger et al., 2008) represent leucosome (suffix "L") referring to thick leucocratic

Table 1
Summary of samples containing allanite used for U–Th–Pb analysis.

Sample	Rock type	Location	Temp in °C	Assemblage	
VAM1	Metatonalite	Arbedo (725 100, 119 350)		pl-qtz-hbl-bt ± Kfs	zrn-ttn-aln-ap-mag
VAL1	Discordant leucosome	Arbedo (725 100, 119 350)	630–670	pl-qtz-hbl Kfs	zrn-aln-ttn
VAM2	Metatonalite	Arbedo (725 100, 119 350)	<700	pl-qtz-hbl-bt ± Kfs	zrn-ttn-aln-ap
VAL2	Discordant leucosome	Arbedo (725 100, 119 350)	630–680	pl-qtz-hbl Kfs	zrn-aln-ttn
BEM1	Metagranodiorite	Bellinzona (722 500, 118 700)	640–690	pl-qtz-Kfs-bt-hbl	zrn-aln-ap
BEL1	Leucosome	Bellinzona (722 500, 118 700)	610–670	pl-qtz-Kfs-bt-hbl	zrn-aln-ap
GOL03	Metagranite	Golino (701 621, 113 762)		Kfs-qtz-pl-bt-hbl	zrn-aln-ap
GOL06	Metadiorite	Golino (701 621, 113 762)		hbl-pl-qtz-Kfs-bt	zrn-aln-ap-ttn
BER1	Metagranite	Berzona (691 206, 117 274)		Kfs-qtz-pl-bt	zrn-aln-ap ± ttn

Temperature estimates taken from Ti-in-zircon thermometry ([Rubatto et al., 2009](#)).

Mineral abbreviations are according to Bucher and Frey (1994).

Swiss grid coordinates.

segregations resulting from melt crystallization, and orthogneisses (suffix “M” for mesosome) referring to country rock containing relatively small amounts of leucosome. The country rocks have granitic to tonalitic protoliths and are thus meta-granites or meta-tonalites. Some of the samples studied here (VAM1–VAL1, VAM2–VAL2 and BEM1–BEL1) are the same as investigated in [Rubatto et al. \(2009\)](#) for zircon geochronology. Sample details are summarised in Table 1.

Two structurally controlled sample pairs of meta-tonalite and leucosome (VAM1–VAL1 and VAM2–VAL2) were collected in Val d’Arbedo ([Fig. 1](#)) from a road cut that exposes a cross section of the sequence. Samples VAM1 and VAM2 are derived from meta-tonalite and contain diffuse leucosome with a weak subvertical fabric ([Fig. 2a](#)). They have a shared mineral assemblage of plagioclase, quartz, green amphibole and biotite, with abundant accessory zircon, apatite, titanite and allanite. The amphiboles form porphyroblasts that are commonly poikiloblastic and include plagioclase; K-feldspar is rare or absent. Leucosomes VAL1 and VAL2 are discordant to the main fabric in the meta-tonalites ([Fig. 2a](#)). Although structurally younger, they preserve a weak foliation defined by subordinate biotite and VAL1 is openly folded ([Fig. 2b](#)). The leucosomes are coarse-grained and contain large green amphibole ([Fig. 2b](#)), abundant zircon, but only minor titanite and allanite.

A migmatite (BEM1 and BEL1) was sampled from road outcrop near Bellinzona, between Carasso and Gorduno ([Fig. 1](#); see also [Berger et al., 2008, 2009](#)). The migmatites are intensely folded with a penetrative subvertical foliation and contain distinct leucosomes of different structural ages (i.e. stromatic to discordant) ([Fig. 2c](#)). BEM1 comprises alternating mm- to cm-size bands of biotite and leucocratic material with abundant allanite, apatite and zircon. Allanite is large (up to 1 mm), zoned and commonly associated with biotite. Leucosome BEL1 formed axial planar to isoclinal folding and is plagioclase-rich with allanite, apatite and zircon, rare green amphibole and minor biotite indicating a weak foliation. The leucosome contains accessory allanite, apatite and multiple generations of metamorphic zircon ([Rubatto et al., 2009](#)).

The Melezza river between Golino and Intragna exposes large outcrops of banded, biotite-rich migmatite. These migmatites are intensely deformed. Sample GOL03 is granitic in composition with layer-parallel leucosomes and a structurally late, plagioclase-rich leucosome ([Fig. 2d](#)). The migmatites contain quartz, plagioclase, K-feldspar, biotite, and rare green amphibole. Zircon and apatite are common in leucocratic zones, whereas allanite is often in contact with biotite. Allanite grains are 200–700 µm in length and show core to rim zonation. Small (50–200 µm) idiomorphic grains are weakly zoned in comparison. Sample GOL06 comes from a metre-sized boudin of mafic gneiss within the migmatite (most likely meta-diorite). It contains diffuse leucosome and a foliation marked by green amphibole. Allanite is less common in the meta-diorite but is texturally similar to allanite in GOL03.

Sample BER1 was collected from a biotite-rich migmatite outcropping in the Bordione River near Berzona ([Fig. 1](#)). The migmatite contains minimum melt composition leucosomes concordant to a penetrative fabric marked by biotite ([Fig. 2e](#)). Rare discordant, plagioclase-rich veins were observed to truncate the main fabric. BER1 derives from a granitic protolith and contains thin bands of leucosome rimmed by biotite selvages ([Fig. 2e](#)). The accessory mineral assemblage includes apatite, zircon, allanite and minor titanite. Allanite is commonly found with biotite.

4. ANALYTICAL METHODS

Allanite grains in mounts and thin section were imaged by scanning electron microscope in backscattered electron mode (SEM-BSE), and analysed for major and minor elements using a wavelength dispersive electron microprobe (EMP), prior to isotopic analysis. SEM-BSE imaging revealed the internal structure of allanite grains defined primarily by rare earth element (REE) zoning, and EMP analysis provided a quantitative chemical characterisation of the allanite samples, used to assess the effects of compositional variation on ion microprobe analyses, and to calibrate the LA-ICPMS geochemical data. Major and trace element analyses on selected bulk rock samples were done by wavelength dispersive X-ray fluorescence (XRF). Details

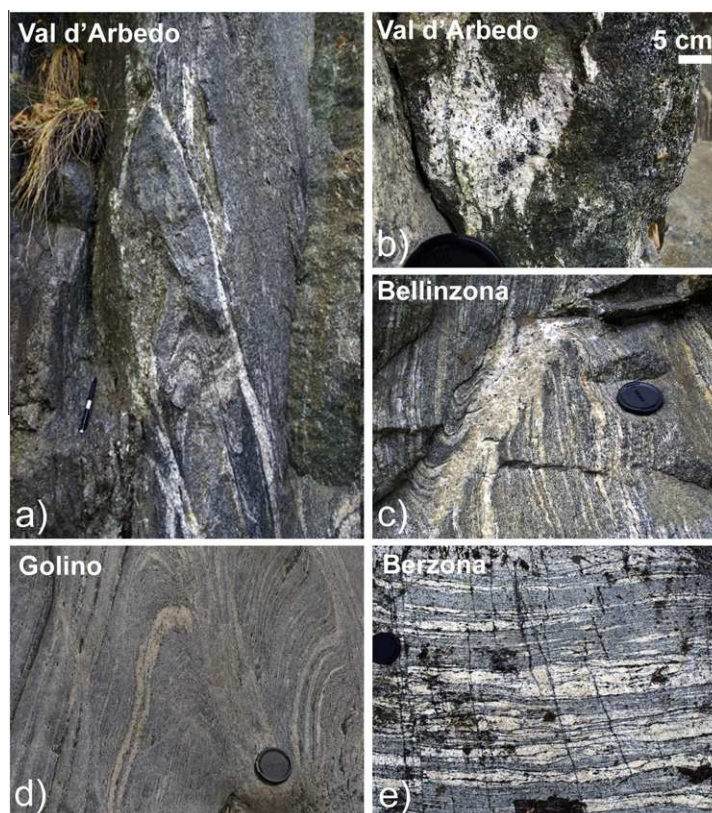


Fig. 2. Field occurrence of migmatites in the SSB (a) Val d'Arbedo migmatite with deformed leucosome VAL1 and country rock with thin, layer-parallel leucosomes (VAM1). (b) Detail of leucosome VAL1 showing large poikilitic amphibole grains and a weak foliation. (c) Typical outcrop appearance of migmatites at the locality of Bellinzona. Note the different generations of cross-cutting leucosomes. (d) Deformed migmatite at the locality of Golino. (e) Berzona migmatite with layer-parallel leucosome and biotite selvages.

of the instrument parameters and analytical procedures used for SEM-BSE imaging, EMP and XRF analysis are provided in the [Electronic annex supplement](#).

4.1. Sensitive High Resolution Ion Microprobe

U–Th–Pb dating of allanite was conducted over five separate sessions using the SHRIMP II and SHRIMP RG (Reverse Geometry) ion microprobes at the Research School of Earth Sciences, ANU. Analyses were performed on allanite in polished grain mounts with a 2.0–3.5 nA, 10 kV primary O_2^- beam focused through a $\sim 100\ \mu\text{m}$ aperture to form a $\sim 20\text{--}25\ \mu\text{m}$ diameter spot. Operating procedure was broadly similar to that used for zircon (Williams, 1998), except that the post-collector retardation lens on SHRIMP II was fully activated during analysis to suppress low-energy scattered ions. At a mass resolution of >5100 ($M/\Delta M$ at 1% peak height) the Pb, Th and U isotopes were resolved from all major interferences. Data acquisition for allanite followed that of Gregory et al. (2007) and each analysis consisted of six scans through the mass stations. Allanite standards were cast in the same grain mount as the samples and analysed after every three unknowns.

U–Th–Pb ratios were corrected by using 2-dimensional power law Pb/U–UO/U and Pb/Th–ThO/Th relationships (Gregory et al., 2007) and normalised to reference allanite

(CAP, ID-TIMS mean Th–Pb age = 275.5 ± 1.5 Ma, $n = 4$; mean U–Pb age = 278.4 ± 5.8 Ma, $n = 3$; Barth et al., 1994). The U–Pb system of the CAP allanite is affected by uncertainties associated with initial radioactive disequilibrium due to ^{230}Th -derived excess ^{206}Pb (estimated at <4 Ma for U–Pb ages, Barth et al., 1994), and by the partial loss of U-derived Pb isotopes in some high Th/U crystal domains (Barth et al., 1994). Data sets for the CAP allanite were vetted for low $^{206}\text{Pb}/^{238}\text{U}$ outliers ($\pm 2\sigma$), which typically constitute $\sim 10\%$ of standard measurements. Minimum 1σ external precisions of 3.0% for the U–Pb system and 2.0% for the Th–Pb system were assigned to the allanite standard. No corrections were made for potential matrix effects in $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ measured from allanite.

To monitor the accuracy of the standard calibration, four secondary allanite standards, including Siss (ID-TIMS Th–Pb age = 31.5 ± 0.4 Ma, von Blanckenburg et al., 1992), Bona (ID-TIMS Th–Pb age = 30.1 ± 0.3 Ma, von Blanckenburg et al., 1992), BC ('98–19' ID-TIMS zircon U–Pb age = 90.8 ± 1.0 Ma, (Butler et al., 2002) and Tara (SHRIMP Th–Pb age = 415 ± 3 Ma, Gregory et al., 2007) were analysed with the sample unknowns in two of the sessions. The results are presented in the [Electronic annex supplement](#). The $^{208}\text{Pb}/^{232}\text{Th}$ ages obtained by SHRIMP are identical within error of their reference ages. The elevated SHRIMP $^{206}\text{Pb}/^{238}\text{U}$ ages for Siss, Bona and

98–19 allanites, however, reflect radioactive disequilibrium-related bias in form of excess ^{206}Pb (von Blanckenburg et al., 1992; Oberli et al., 2004).

The dependence of ion microprobe $^{206}\text{Pb}^+/\text{U}^+$ and $^{208}\text{Pb}^+/\text{Th}^+$ analyses on sample chemistry can compromise the use of this technique for dating chemically complex minerals if suitable matrix-matched standards are unavailable. Whereas the investigated allanites display a range of REE and Th contents (LREE + Th = 0.2–0.8 cations per formula unit) (see Sections 5 and 6), the magmatic standards have typically high LREE and Th contents of 0.5–0.9 cfpu (Gregory et al., 2007). Such compositional differences can offset standard and sample $\text{ThO}_n^+/\text{ThO}_n^+$ and $\text{UO}_n^+/\text{UO}_n^+$ ($n = 0–2$) used for Th–Pb and U–Pb calibrations, respectively (e.g. allanite, Catlos et al., 2000; monazite, Fletcher et al., 2010). We monitored matrix effects by comparing standard and sample $\ln[\text{ThO}^+/\text{Th}^+]$ and $\ln[\text{UO}^+/\text{U}^+]$ measurements from the same session (listed with the U–Th–Pb isotope data in the [Electronic annex supplement](#)). Matrix effects on Th–Pb isotope ratios from metamorphic allanite were identified (i.e. different $\ln[\text{ThO}^+/\text{Th}^+]$ values) and are discussed in Section 9.2.

All raw data were processed using SQUID-2 (rev. 2.50) software (Ludwig, 2009), which reproduces the procedure described by Gregory et al. (2007) for allanite. Listed uncertainties for radiogenic isotope ratios and ages are $\pm 1\sigma$ and include all components of statistical precision, including uncertainty on the estimation of non-radiogenic Pb and uncertainty on the Pb/U and Pb/Th calibrations, which range from 0.33% to 1.2% and 0.23% to 0.52% (1σ), respectively. The 1σ external reproducibility of Th–Pb and U–Pb ages measured from the allanite standard were quadratically propagated into the final uncertainties on all single spot ages and ratios, since there is no a priori reason to believe all sample allanites are a homogeneous population. The final age uncertainties do not include potential unquantified uncertainties in $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ arising from matrix effects in allanite analyses. To compare ages from both the U–Pb and Th–Pb systems in allanite, the final $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ ratios of each analysis are plotted on 2-dimensional U–Th–Pb concordia diagrams (Section 6). Age calculations and plots were made using Isoplot/Ex (Ludwig, 2003). Pooled ages are cited at 95% confidence limits (cl.) unless otherwise stated.

4.2. Laser ablation ICP-MS

Large (<500 μm) allanite grains observed in polished thin section from BER1 meta-granite were dated in situ (in thin section) using laser ablation ICPMS (LA-ICPMS) techniques. The LA-ICPMS method was used initially as a reconnaissance tool, to provide a rapid assessment of the age of allanite overgrowths in a migmatite sample that contained no new zircon growth. U–Th–Pb analyses were performed using a 193 nm ArF Excimer laser system couple to an Agilent 7500S quadrupole ICP-MS housed at RSES, ANU. Instrument parameters were generally as described by Eggins et al. (1998) and data acquisition and reduction followed that of Gregory et al. (2007). The laser was focused to a spot size of 32 μm using a laser pulse rate of 5 Hz and

laser irradiance of approximately 10–12 J/cm². The analyte was ablated into a mixed He–Ar (1:3) carrier gas (gas flow ~ 1.2 L/min). Each isotope analysis was of 65 s duration in time-resolved (peak hopping) analysis mode, including 40 s of ablation and 25 s monitoring gas blank. The depth of laser drilling was $\sim 20–25$ μm per analysis. A post-plasma oxide was used to monitor the production of molecular compounds ($\text{ThO}/\text{Th} < 0.5\%$) and lead hydride interferences were checked on a pure Pb sample. Torch position (~ 5.6 mm) and lens tuning were adjusted to maximise sensitivity for the Pb isotopes, Th and U; ^{204}Pb was not measured due to a systemic ^{204}Hg interference.

Raw data was processed offline using an in-house macro-based EXCEL spreadsheet. Each analysis was corrected for background gas blank and for laser-induced element fractionation processes, which occur during stationary laser sampling (e.g. Eggins et al., 1998). External calibration of $^{208}\text{Pb}/^{232}\text{Th}$ was done against an allanite standard (AVC, ID-TIMS Th–Pb age = 276.3 ± 2.2 Ma, Barth et al., 1994). Element (Th, U, P, Si, Ca and REE) concentrations were referenced directly to a NIST SRM 610 glass. Both materials were re-analysed once after every 8 sample analyses. Internal precision on the matrix normalisation factor ($F = ^{208}\text{Pb}/^{232}\text{Th}_{\text{reference}} \div ^{208}\text{Pb}/^{232}\text{Th}_{\text{measured}}$) determined from the allanite standard is 0.6% (1σ) and the external reproducibility based on repeat standard analyses is 1.25% (1σ) for AVC ($n = 10$). The CAP allanite was analysed as a secondary standard and used to calibrate AVC for inter-comparison of reference materials. Eleven analyses of CAP yielded a Th–Pb isochron age of 289 ± 12 Ma (MSWD = 0.36, $n = 11/11$) and 10 analyses of AVC yielded an age of 281 ± 23 Ma (MSWD = 0.13, $n = 10/10$) ([Electronic annex Table 5](#)).

Th–Pb ages were calculated from LA-ICPMS analyses using a 2-dimensional isochron plot, a method suited to analyses of Th-rich minerals for which accurate determination of non-radiogenic Pb is particularly crucial. The Th–Pb isochrons are constructed using the non-radiogenic portion of ^{206}Pb , instead of ^{204}Pb , as the reference isotope. The measured $^{232}\text{Th}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ are adjusted accordingly: $^{232}\text{Th}/^{206}\text{Pb}_{\text{initial}} = ^{232}\text{Th}/^{206}\text{Pb}_{\text{measured}} \div f_{206}$ (Gregory et al., 2007). The uncertainties in the measured ratios, the calculation of non-radiogenic Pb and the external precision of the allanite standard are added in quadrature into the final uncertainty on all isotope ratios. Calculation of isochron ages (quoted at 95% cl.) was done using Isoplot/Ex (Ludwig, 2003).

Rare earth element (REE) and trace element concentrations of silicate and accessory minerals were determined by LA-ICPMS, using similar working conditions to U–Th–Pb isotope analysis, and laser spot sizes of 24–84 μm . The analytical protocol for REE analysis is outlined in the [Electronic annex supplement](#).

4.3. Estimation of initial Pb in allanite from ^{207}Pb abundance

Allanite can have high contents of initial Pb (Pb included at mineral formation) that make calculated $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ ages sensitive to uncertainty in the choice of non-radiogenic Pb correction (all Pb

components, except in situ accumulated radiogenic Pb, are thus dominated by initial Pb and include a minor or irrelevant amount of Pb from surface contamination). In this study, the non-radiogenic Pb content of an analysis is given as a fraction or percentage of total measured ^{206}Pb (f-206) or ^{208}Pb (f-208), an expression routinely used by the ion probe community for the purpose of data interrogation.

Isotopic analyses by both SHRIMP and LA-ICPMS are burdened with isobaric interferences on the mass 204 that could be neither avoided with the current techniques, nor accurately subtracted (Gregory et al., 2007). In addition, the uncertainty associated with measuring the very small 204 peak can be significant for geologically “young” minerals. These problems can be circumvented by the estimation of initial Pb from the abundance of ^{207}Pb rather than ^{204}Pb (Gregory et al., 2007). The f-206 (and f-208) is thus calculated from the measured $^{207}\text{Pb}/^{206}\text{Pb}$, assuming U–Pb concordance (Williams, 1998). The equations used to calculate f-206 and f-208 are stated in the [Electronic supplement](#).

The ^{207}Pb -based approach is model-dependent and is therefore potentially less accurate than the “classical” approach based on measurements of all Pb isotopes in minerals with low $\text{U}/^{204}\text{Pb}$ and $\text{Th}/^{204}\text{Pb}$. For example, the f-208 and f-206 estimates depend on assumed concordance and may be inaccurate if the systems are discordant. The ^{207}Pb correction method is generally suited to “young” Phanerozoic samples for which the range of potential radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ is small and it is often valid to assume near concordance (Williams, 1998). For the purpose of this study, we have compared the f-206 and f-208 values calculated using ^{204}Pb -corrected data in some samples with the ^{207}Pb -corrected data (see [Electronic supplement](#)), in order to evaluate the affect of potential isotopic discordance and/or unquantified spectral interferences on the 204 peak during ion probe analysis (cf. Stern and Berman, 2000). The estimates of initial Pb based on ^{204}Pb are generally comparable to the model-dependent ^{207}Pb corrected data for most of the analysed allanites.

The initial $^{207}\text{Pb}/^{206}\text{Pb}$ used was based on a model Pb isotopic composition (Stacey and Kramers, 1975) at the approximate age of the sample. When the initial $^{207}\text{Pb}/^{206}\text{Pb}$ approximates the modelled Pb isotope composition, a single spot correction method is applicable, however this cannot be assumed for Pb-rich minerals such as allanite. An independent check on the initial $^{207}\text{Pb}/^{206}\text{Pb}$ was done by regressing total $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{238}\text{U}/^{206}\text{Pb}$ data using an inverse concordia (Tera–Wasserburg) plot. A comparison of the initial $^{207}\text{Pb}/^{206}\text{Pb}$ in allanite determined by this method with the modelled composition is discussed in Sections 6 and 9. The relationship between f-206 and f-208 and the ^{207}Pb -corrected $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ ages in samples with relatively uniform Th/U contents is also used as a tool to assess the choice of initial Pb composition.

5. ALLANITE MAJOR ELEMENT COMPOSITION

The chemistry of allanite was determined prior to ion microprobe dating to assess the extent of compositional zoning in allanite grains used for U–Th–Pb isotope analysis. The major element compositions of allanite grains are given

in Table 2. Element (CaO, Fe_{total} and Th_2O) maps of representative allanite dated in this study from meta-tonalite VAM1 clearly illustrate a strong internal zonation (Fig. 3a). From core to overgrowth, Th_2O content decreases dramatically and is almost absent in epidote, whereas CaO content increases overall and Fe_{total} decreases only slightly. The compositional variation between allanite cores and overgrowths define a solid solution between the allanite and epidote end-members (Fig. 3b) where REE are primarily incorporated into allanite via: $\text{Ca}^{2+} + \text{Fe}^{3+} \rightarrow \text{REE}^{3+} + \text{Fe}^{2+}$ (Petrík et al., 1995; Gieré and Sorenson, 2004). The cores and overgrowths from meta-granite samples fall within or slightly below the end-member chemical classification for allanite ($\text{REE} + \text{Th} \geq 0.5$ cations per formula unit). In contrast, overgrowths from meta-tonalite samples are classified as REE-epidote ($\text{REE} + \text{Th} < 0.2$ cpfu).

6. ALLANITE AGES AND TRACE ELEMENT COMPOSITION

Allanite rare earth element data are provided in Table 3. Allanite U–Th–Pb data determined by SHRIMP and LA-ICPMS are compiled in tables in the [Electronic annex](#) and presented in Figs. 4–8.

6.1. Val d’Arbedo

Zoned allanites $<400\text{ }\mu\text{m}$ in length were identified in the VAM1 and VAM2 meta-tonalites by optical analysis and backscattered electron (BSE) imaging. They consist of a high-BSE intensity core, a low-BSE intensity rim and an unzoned, moderate-BSE intensity overgrowth (Fig. 4a). The different zones correspond to allanite (av. $\text{LREE} + \text{Th} = 0.6$ cpfu), epidote (<0.1 cpfu) and REE-epidote (~ 0.14 cpfu) (Table 2). In VAL1 leucosome, REE-epidote occurs as unzoned overgrowths on epidote grains; the large allanite cores are absent. Some allanite cores in VAM1 and all cores in VAM2 have patchy and irregular zoning that proceeds from core boundaries and along fractures (Fig. 4a). These zones are low-BSE intensity and therefore low-REE and are interpreted as secondary alteration. The allanite cores are characterised by highly fractionated REE patterns (av. $\text{La}_\text{N}/\text{Lu}_\text{N} \sim 2800$), moderate negative Eu anomalies ($\text{Eu}/\text{Eu}^* \sim 0.4$) and high Th/U (~ 100 – 200) (Fig. 4b, Table 3). In contrast, the REE-epidote overgrowths in VAM1 and VAL1 have low La/Lu ($\text{La}_\text{N}/\text{Lu}_\text{N} = 150$ – 170), small Eu anomalies ($\text{Eu}/\text{Eu}^* \sim 0.7$ – 0.8) and low Th/U (~ 7 – 9).

Eleven U–Th–Pb analyses of allanite cores from VAM1 meta-tonalite were obtained by SHRIMP. They have high radiogenic ^{208}Pb contents ($>96\%$ of the total ^{208}Pb) compared to ^{206}Pb (68–81% of the total ^{206}Pb) ([Electronic annex Table 1](#)). From 11 analyses a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 286 ± 5 Ma (MSWD = 0.7) and a $^{206}\text{Pb}/^{238}\text{U}$ age of 276 ± 7 Ma (MSWD = 0.9) can be calculated (Fig. 4c). The U–Pb age is lower than but within uncertainty of the Th–Pb age. Four SHRIMP analyses were made on altered allanite cores from VAM2 meta-tonalite. The analyses do not define a statistical population and scatter along U–Th–Pb concordia from ~ 282 to ~ 163 Ma (Fig. 4c).

Table 2

Average major element composition of allanite determined by EMP analysis.

	VAM1			BEM1		GOL03			GOL06		BER1		
	c	ep	ov	ep	ov	c	ep	ov	c	ov	c	r	ov
<i>n</i>	2	5	11	4	4	4	2	11	6	7	1	4	16
SiO ₂	32.3	36.8	35.7	35.8	34.9	31.1	32.5	31.5	31.8	33.7	32.8	33.3	33.1
TiO ₂	0.31	0.19	0.19	0.14	0.17	1.06	0.17	0.21	1.26	0.36	0.17	0.14	0.13
Al ₂ O ₃	18.2	24.7	23.4	24.1	22.8	14.1	19.1	18.2	16.3	21.6	20.4	21.9	21.5
MgO	0.91	0.18	0.30	0.26	0.35	0.94	0.41	0.50	1.08	0.58	0.85	0.46	0.38
CaO	14.2	23.4	21.8	22.1	20.9	11.2	15.9	14.5	12.4	17.5	12.3	15.1	15.4
MnO	0.39	0.23	0.29	0.28	0.27	0.86	1.18	1.20	0.33	0.25	0.39	0.52	0.78
FeO	12.2	9.76	10.1	9.72	10.4	14.8	13.0	12.9	11.9	8.95	10.5	10.8	11.7
La ₂ O ₃	5.41	0.45	1.10	0.63	1.22	6.40	2.51	3.19	7.01	3.69	4.22	3.10	2.68
Ce ₂ O ₃	8.92	0.89	2.22	1.29	2.61	11.1	4.87	5.93	10.7	6.52	9.24	6.51	5.71
Pr ₂ O ₃	0.93	0.14	0.29	0.19	0.33	1.14	0.63	0.73	0.95	0.67	0.86	0.61	0.60
Nd ₂ O ₃	2.73	0.53	1.13	0.80	1.34	3.43	2.05	2.52	2.59	2.03	3.07	2.25	2.21
Sm ₂ O ₃	0.22	0.12	0.16	0.20	0.28	0.28	0.37	0.39	0.18	0.18	0.30	0.29	0.33
Gd ₂ O ₃	0.09	0.06	0.11	0.33	0.30	0.16	0.39	0.43	0.09	0.07	0.18	0.16	0.31
Y ₂ O ₃	0.05	0.15	0.10	0.79	0.51	0.13	1.32	1.17	0.07	0.05	0.07	0.27	0.48
SrO	0.02	0.20	0.08	0.09	0.08	0.02	0.01	0.02	0.01	0.04	0.21	0.15	0.04
ThO ₂	1.35	0.08	0.20	0.27	0.54	1.31	1.77	2.21	1.75	0.85	1.25	1.28	1.17
Total	98.2	97.9	97.2	97.0	97.0	98.0	96.2	95.6	98.4	97.0	96.8	96.8	96.5
LREE + Th	0.60	0.06	0.14	0.13	0.20	0.79	0.43	0.51	0.74	0.41	0.65	0.45	0.42

n = number of EMP analyses used for average; c = core; ep = epidote; ov = overgrowth; LREE + Th given in cations per formula unit on the basis of 12.5 oxygens.

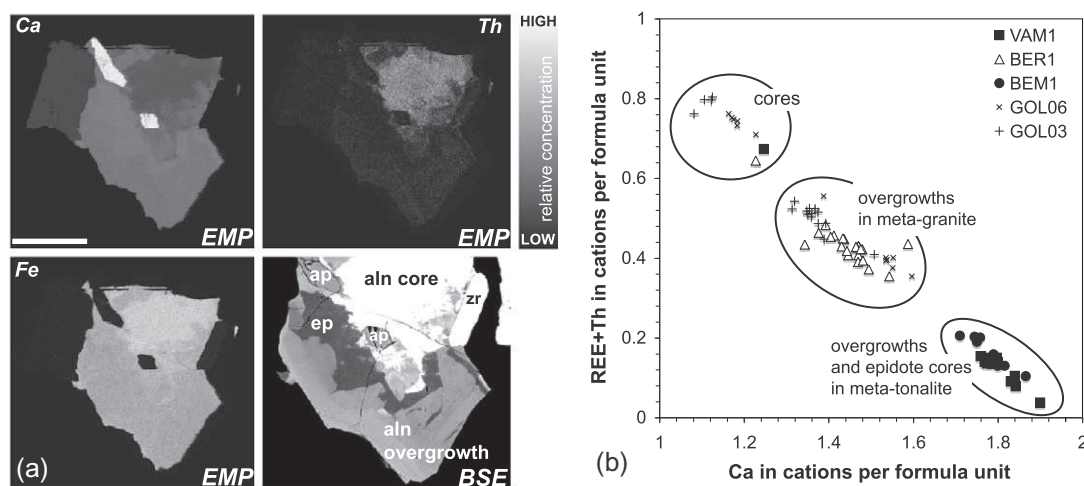


Fig. 3. (a) Element (CaO, Fe_{total} and Th₂O) maps determined by electron microprobe and BSE image of allanite grain from sample VAM1 metatonalite. (b) Summary of allanite EMP data from allanite dated in this study.

Nonetheless, they confirm that allanite cores in this sample are pre-Alpine in age. Two analyses (VAM2-10.2, 13.1) of alteration zones have relatively low Th/U (~37) and high non-radiogenic Pb contents (Electronic annex Table 1).

Thirteen SHRIMP analyses were obtained on REE-epidote overgrowths from VAM1. The calculated proportion of radiogenic Pb for each analysis is extremely low, particularly for the U-²⁰⁶Pb system (~3–14% of the total ²⁰⁶Pb) (Electronic annex Table 1). The 13 analyses calculate a weighted mean ²⁰⁸Pb/²³²Th age of 23.1 ± 1.3 Ma (MSWD = 1.8). The corresponding ²⁰⁶Pb/²³⁸U age is lower than the ²⁰⁸Pb/²³²Th age and thus, the analyses are shifted to

the left of U–Th–Pb concordia (Fig. 4d). The same analyses yield lower intercept U–Pb age of 24.1 ± 2.4 Ma and an initial ²⁰⁷Pb/²⁰⁶Pb composition of 0.86 ± 0.10 Ma (2σ, MSWD = 1.3) by extrapolating the total ²³⁸U/²⁰⁶Pb–²⁰⁷Pb/²⁰⁶Pb data along a non-radiogenic Pb mixing line (Fig. 4e). Although less precise, the intercept age is preferred over the single-spot ²⁰⁶Pb/²³⁸U ages because it does not rely on the choice of non-radiogenic Pb correction, which is significant for this sample. The U–Pb intercept age is within uncertainty of the Th–Pb age and both indicate that the REE-epidote overgrowths in meta-tonalite are of Alpine-age and therefore younger than the allanite cores.

Table 3

Average trace element composition of allanite samples determined by LA-ICP-MS analysis.

	VAM1			VAL1	VAM2			VAL2	BEM1			
	c	ep	ov	ov	c	ov	wz	ov	c	alc	ep	ov
Trace elements in ppm												
	<i>n</i> = 5	<i>n</i> = 8	<i>n</i> = 14	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 3	<i>n</i> = 3	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 2
P	118	238	212	163	139	129	129	130	174	61	68	53
Sc	51	147	146	185	34	123	23	130	91	133	538	301
V	514	398	378	353	293	387	218	384	711	556	373	366
Cr	69	30	38	38	160	137	122	335	100	217	131	109
Rb	0.15	0.26	0.43	0.15	—	0.21	—	0.23	0.19	0.20	0.52	0.37
Sr	603	1080	548	532	986	410	1290	389	118	155	293	301
Y	355	743	1000	1190	355	1111	197	1560	1070	2160	5560	3630
Zr	2	19	16	16	3	16	3	15	4	5	15	12
Nb	0.18	0.09	0.03	0.02	0.04	—	0.03	0.02	0.11	0.07	—	0.03
Ba	0.96	2.90	2.27	1.72	1.38	2.37	1.4	2.40	1.43	0.63	1.63	1.1
La	43,000	2980	6820	7500	32,900	12,500	24,900	14,000	59,200	33,000	5400	8340
Ce	73,200	6670	14,900	15,600	55,400	23,900	41,700	28,600	106,000	68,400	12,400	18,400
Pr	6540	792	1770	1770	4970	2470	3650	3230	9850	8000	1520	2170
Nd	18,800	3270	7220	6910	14,600	8550	10,500	12,200	29,270	30,000	6670	9090
Sm	1480	648	1310	1270	1360	1290	869	1960	2740	4380	1940	2280
Eu	106	145	269	248	96	289	66	367	174	333	397	385
Gd	546	470	851	856	557	824	326	1210	1120	2030	1790	1800
Tb	40	50	79	86	43	84	24	120	91	181	302	260
Dy	134	219	311	363	147	353	80	499	350	712	1570	1190
Ho	16	30	40	48	16	46	9	64	45	89	231	158
Er	28	55	72	87	26	84	14	120	89	165	394	256
Tm	3	5	7	8	2	8	1	12	10	17	31	20
Yb	13	22	32	39	10	40	5	60	55	87	120	89
Lu	1.8	3	4	5	1.3	5	1	7	7	11	10	8
Hf	0.11	0.77	0.70	0.77	0.15	0.79	0.15	0.82	0.29	0.25	0.91	0.62
Ta	0.02	—	—	—	0.02	—	—	—	0.02	0.01	—	—
Pb	258	36	28	29	122	33	39	32	405	529	31	32
Th	12,200	443	1090	1900	8900	3980	6370	3360	13,900	18,600	2330	3780
U	67	65	145	201	63	257	38	516	76	438	689	548
La _N /Lu _N	2580	122	175	154	2630	252	4090	207	859	327	58	105
Eu/Eu*	0.36	0.80	0.78	0.73	0.34	0.86	0.38	0.73	0.30	0.34	0.65	0.58
Th/U	222	8	8	9	178	15	168	7	187	42	3	8
	BEL1			GOL03			GOL06			BER1		
	ep		ov	c	ep	ov	c	ep	ov	c	r	ov
Trace elements in ppm												
	<i>n</i> = 3		<i>n</i> = 4	<i>n</i> = 3	<i>n</i> = 1	<i>n</i> = 4	<i>n</i> = 3	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 4
P	144		111	93	69	76	122	76	72	47	53	57
Sc	269		284	116	257	241	37	76	74	38	17	125
V	433		443	463	207	191	676	474	455	164	83	138
Cr	356		324	18	39	28	154	180	160	9	33	20
Rb	0.59		5	3	1.9	1.8	0.13	0.21	0.94	0.13	0.15	1.3
Sr	292		260	57	133	120	118	245	183	3550	3120	984
Y	4301		4920	1350	12,610	11,300	550	608	515	545	1040	2830
Zr	15		13	5	3	3	4	10	9	4	4	4
Nb	0.03		0.31	0.44	0.12	0.15	1.96	0.05	0.03	0.09	0.03	0.47
Ba	4		17	0.48	0.18	0.22	0.70	1.4	4	21	26	7
La	11,400		14,000	60,700	24,300	26,700	60,900	25,600	29,400	43,600	31,900	24,900
Ce	24,400		29,500	110,000	49,800	55,100	89,700	53,900	55,100	81,800	55,500	48,000
Pr	2790		3380	10,300	5430	5990	6900	5440	5100	7990	4960	4900
Nd	10,900		13,200	31,400	19,500	21,400	18,100	17,500	15,500	25,700	14,800	16,700
Sm	2180		2650	3250	3810	4130	1500	1700	1370	2640	1440	2630
Eu	430		455	87	396	375	120	226	186	80	196	304
Gd	1790		2180	1420	3110	3280	651	764	617	928	658	1550
Tb	222		267	118	454	458	52	56	46	66	70	186
Dy	1130		1320	446	2630	2540	188	196	162	198	288	799

(continued on next page)

Table 3 (continued)

	BEL1		GOL03			GOL06			BER1		
	ep	ov	c	ep	ov	c	ep	ov	c	r	ov
Ho	171	196	57	462	420	24	25	21	23	39	114
Er	351	403	120	1180	1030	45	47	40	43	81	232
Tm	36	41	14	152	131	4	4	4	5	9	26
Yb	175	209	87	920	805	24	23	20	33	58	147
Lu	20	25	12	112	99	3	3	3	4	7	17
Hf	0.80	0.75	0.25	0.32	0.24	0.22	0.48	0.43	0.10	0.24	0.18
Ta	0.02	0.34	0.04	0.05	0.05	0.11	–	0.02	0.02	–	0.03
Pb	37	36	364	74	75	313	44	44	367	358	116
Th	3390	4380	12,400	18,400	20,900	12,000	5480	6620	12,100	8270	9130
U	687	1140	69	1360	1010	193	410	326	422	1540	964
La _N /Lu _N	59	60	533	23	28	2062	863	1120	1090	518	157
Eu/Eu*	0.67	0.58	0.12	0.35	0.31	0.37	0.61	0.62	0.16	0.62	0.46
Th/U	5	4	180	14	22	62	13	20	29	5	11

c = core; ep = epidote; ov = overgrowth; wz = cloudy to weak oscillatory zoning; alc = altered core; La_N = chondrite normalised La; Eu/Eu* = europium anomaly.

Eight U–Th–Pb analyses of REE-epidote overgrowths from VAL1 leucosome yield a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 29.1 ± 2.0 Ma (MSWD = 2.4) and a significantly lower $^{206}\text{Pb}/^{238}\text{U}$ age of 22.6 ± 0.9 Ma (MSWD = 1.0) (Fig. 4d). The Th–Pb and U–Pb age systems have similarly low amounts of radiogenic Pb to overgrowths in VAM1 (~12–21% of the total ^{206}Pb and ^{208}Pb) (Electronic annex Table 1). The ages indicate, at least, that the REE-epidote overgrowths in leucosome are of Alpine origin.

REE-epidote overgrowths are present in VAM2 metatonalite and VAL2 leucosome (Fig. 5a). The overgrowths are similar in composition to those in VAM1 and VAL1, including low La/Lu (La_N/Lu_N = 200–250), small negative Eu anomalies (Eu/Eu* = 0.74–0.86) and low Th/U (av. ~15 and ~7) (Fig. 5b, Table 3). Allanite grains characterised by cloudy to weak-oscillatory zoning also occur in the metatonalite (Fig. 5a). The allanite REE patterns are HREE-depleted with respect to L-MREEs (av. La_N/Lu_N = 4090) and have moderate negative Eu anomalies (av. Eu/Eu* = 0.38) (Fig. 5b). The weakly zoned allanites have variable but high Th/U compositions (av. Th/U = 168) similar to allanite cores (Table 3).

Seven SHRIMP analyses of REE-epidote overgrowths from VAL2 leucosome yield a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 28.1 ± 0.8 Ma (MSWD = 0.8) and a significantly lower $^{206}\text{Pb}/^{238}\text{U}$ age of 22.6 ± 1.2 Ma (MSWD = 2.0) (Fig. 5c). The ages are identical to those measured from overgrowths in VAL1 (Fig. 4d) and the Th–Pb and U–Pb analyses have similarly low amounts of radiogenic Pb (~27–34% of the total ^{206}Pb and ^{208}Pb) (Electronic annex Table 1). Two analyses (VAM2.10-1 and 7.1) of low Th/U, REE-epidote overgrowths from VAM2 give high $^{208}\text{Pb}/^{232}\text{Th}$ ages of ~30 and ~32 Ma, and low $^{206}\text{Pb}/^{238}\text{U}$ ages of ~22 and ~26 Ma (Fig. 5c).

Nine analyses were obtained on weak oscillatory-zoned allanite from VAM2 meta-tonalite. One analysis (VAM2.8-1) is almost free of radiogenic Pb and was not considered in age calculations (outlier in Fig. 5c). The proportion of radiogenic Pb in each analysis is low and variable accounting for 1–16% of the total ^{206}Pb and 16–67% of the total

^{208}Pb (Electronic annex Table 1). The eight analyses calculate a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 35 ± 2 Ma (MSWD = 2.7) and a $^{206}\text{Pb}/^{238}\text{U}$ age of 30 ± 3 Ma (MSWD = 0.6) (Fig. 5c). The same data give a lower intercept U–Pb age of 30 ± 4 Ma and a tightly constrained initial $^{207}\text{Pb}/^{206}\text{Pb}$ composition of 0.839 ± 0.004 (2 σ , MSWD = 0.8) (Fig. 5d), which is identical to the model value of Stacey and Kramers (1975) at the assumed sample age (~30 Ma).

6.2. Bellinzona

Allanite in BEL1 leucosome occurs as thin (<50 μm) unzoned overgrowths on idiomorphic epidote crystals (Fig. 6a). In BEM1 meta-granodiorite, allanite occurs as large (<1 mm) composite grains comprised of high-BSE intensity cores and low-BSE intensity epidote rims (Fig. 6b). Rare overgrowths of REE-epidote (av. REE + Th = 0.20 cpfu) are found on composite grains, similar to allanite overgrowths in BEL1. Secondary alteration of allanite cores is observed, indicated by regions of patchy, low-BSE intensity zoning at core boundaries and adjacent to fine fractures (Fig. 6b). The high-BSE intensity cores are LREE-enriched (av. La_N/Lu_N = 860), have moderate negative Eu anomalies (av. Eu/Eu* = 0.3) and high Th/U (av. ~185) (Table 3, Fig. 6c). The overgrowths in BEL1 and BEM1 are less LREE-enriched (av. La_N/Lu_N = 60 and 105, respectively) with small negative Eu anomalies (Eu/Eu* = 0.6) and low Th/U (av. <10).

Six U–Th–Pb analyses were obtained by SHRIMP on low Th/U allanite overgrowths in BEL1. The radiogenic ^{206}Pb and ^{208}Pb contents of each analysis are similar: 38–53% of the total ^{206}Pb and 30–34% of the total ^{208}Pb (Electronic annex Table 2). A total $^{238}\text{U}/^{206}\text{Pb}$ – $^{207}\text{Pb}/^{206}\text{Pb}$ plot of the six analyses yields an imprecise initial $^{207}\text{Pb}/^{206}\text{Pb}$ composition of 0.78 ± 0.11 (95% cl.) and lower intercept age of 20 ± 5 Ma (MSWD = 3.9, 95% cl., Electronic annex Fig. 1). The initial Pb composition determined from allanite overgrowths is lower than but within uncertainty of the model Pb isotope composition (Stacey and Kramers,

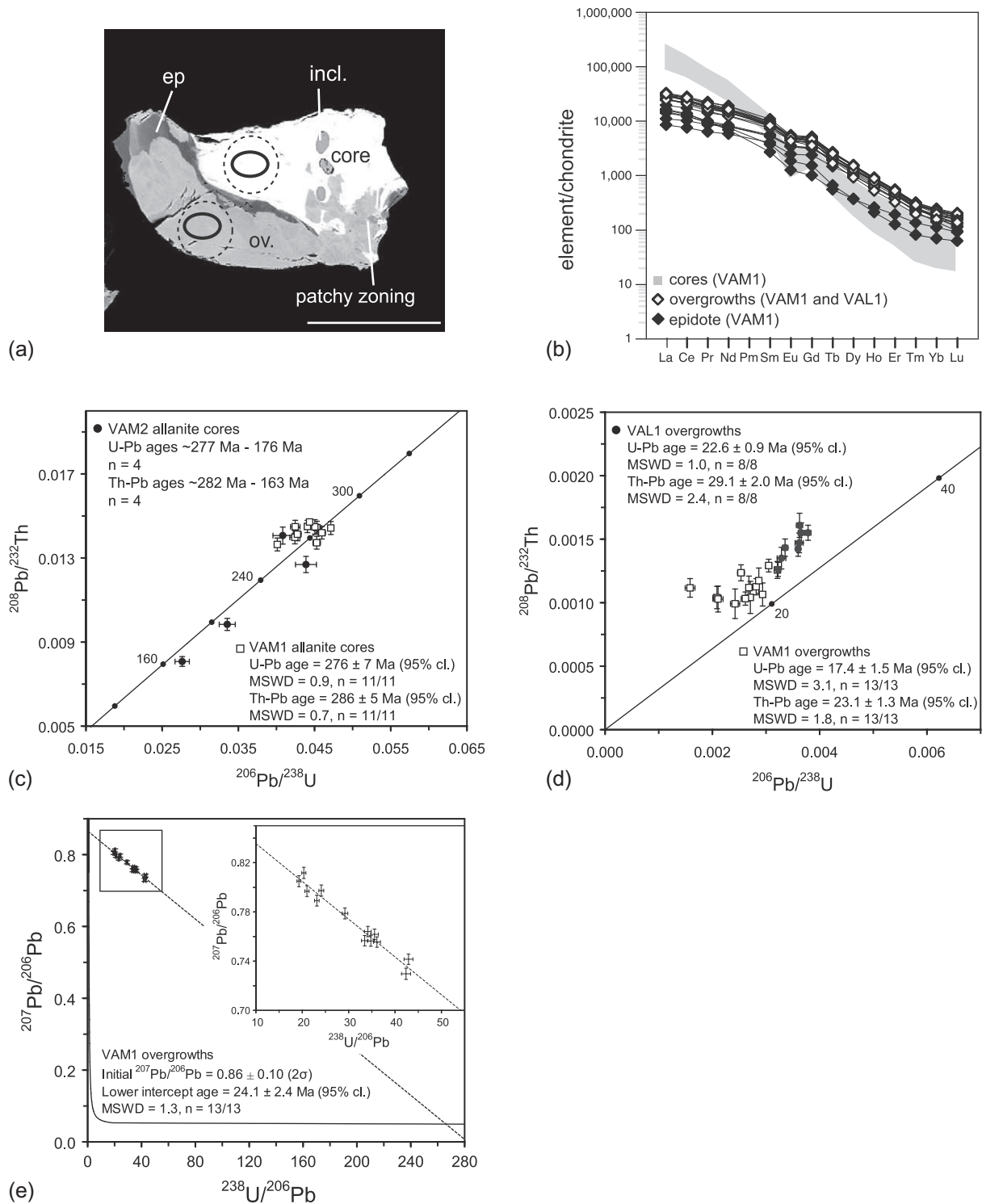


Fig. 4. Allanite age and trace element data for Val d'Arbedo. (a) SEM-BSE image of composite allanite grain from VAM1 meta-tonalite. Dashed and solid circles indicate LA-ICPMS and SHRIMP analysis locations, respectively. Ep = epidote, ov = overgrowth, incl = inclusion (apatite) and alt core = secondary alteration of core. White bar is 100 μm . (b) Chondrite-normalised REE patterns of allanite cores from VAM1 and REE-epidote overgrowths from VAM1 and VAL1 leucosome. (c) $^{206}\text{Pb}/^{238}\text{U}$ versus $^{208}\text{Pb}/^{232}\text{Th}$ diagram of ^{207}Pb -corrected single-spot ages determined by SHRIMP for allanite cores in VAM2 meta-tonalite and VAM1 meta-tonalite. Quoted ages are weighted mean ages. (d) $^{206}\text{Pb}/^{238}\text{U}$ versus $^{208}\text{Pb}/^{232}\text{Th}$ diagram of ^{207}Pb -corrected single-spot ages determined by SHRIMP for REE-epidote overgrowths in VAM1 meta-tonalite and VAL1 leucosome. Quoted ages are weighted mean ages. (e) Inverse concordia of uncorrected allanite U-Pb analyses from VAM1. Error crosses are 1 sigma for all plots.

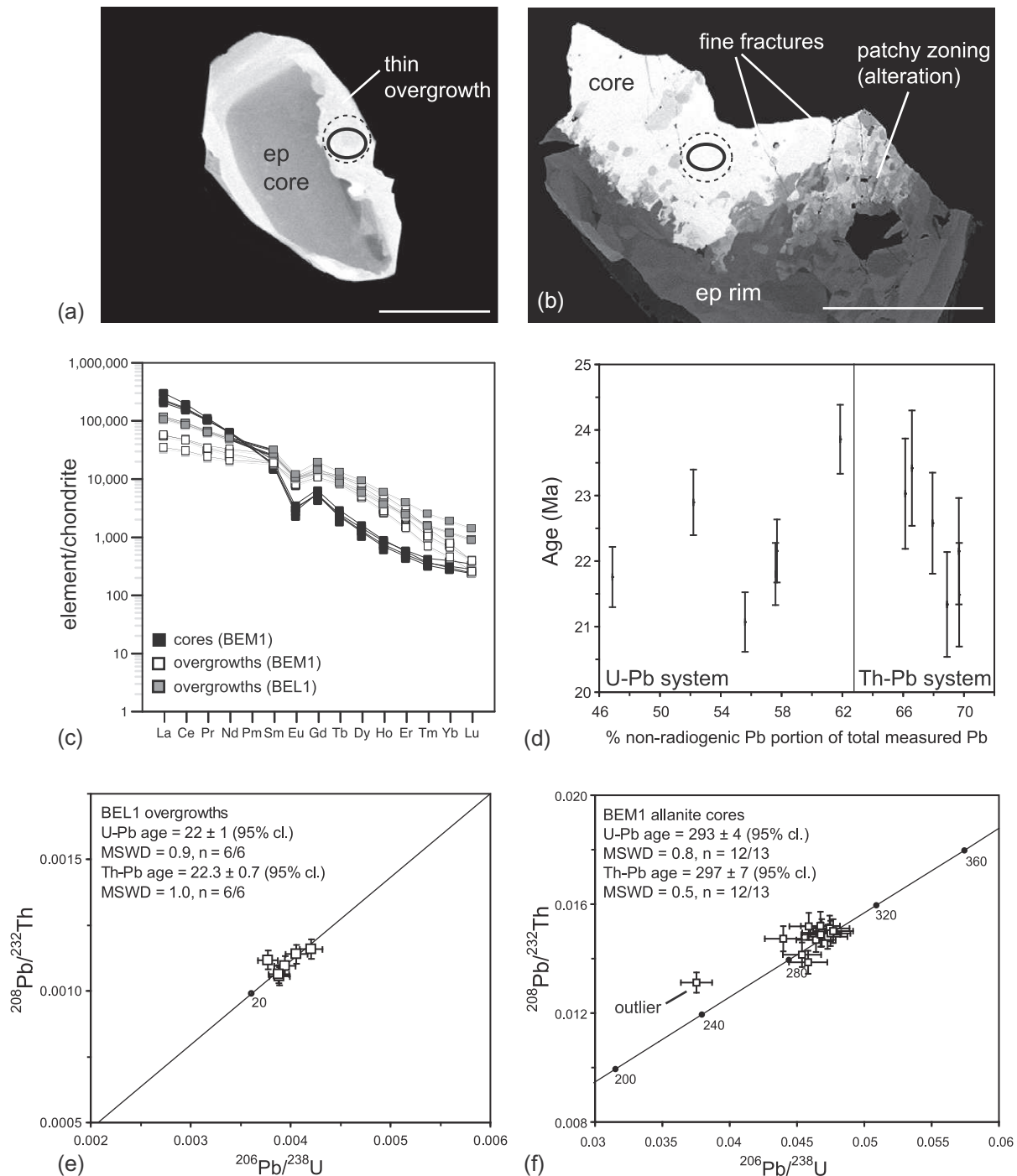


Fig. 6. Allantite age and trace element data for Bellinzona. (a) SEM-BSE image of epidote grain with allanite overgrowth in BEL1 leucosome. Dashed and solid circles indicate LA-ICPMS and SHRIMP analysis locations, respectively. Ep = epidote. White bar is 50 μm . (b) SEM-BSE image of composite allanite grain from BEM1 meta-granodiorite. Alt core = alteration of core (patchy, irregular zoning). White bar is 100 μm . (c) Chondrite-normalised REE patterns of allanite cores from BEM1 and REE-epidote and allanite overgrowths from BEM1 and BEL1. (d) $^{206}\text{Pb}/^{238}\text{U}$ versus $^{208}\text{Pb}/^{232}\text{Th}$ diagram of ^{207}Pb -corrected single-spot ages determined by SHRIMP for allanite overgrowths in BEL1 leucosome. Quoted ages are weighted mean ages. (e) $^{206}\text{Pb}/^{238}\text{U}$ versus $^{208}\text{Pb}/^{232}\text{Th}$ diagram of ^{207}Pb -corrected single-spot ages determined by SHRIMP for allanite cores in BEM1 meta-tonalite. Quoted ages are weighted mean ages. (f) Age versus non-radiogenic Pb portion of total measured Pb for both U-Pb and Th-Pb systems in allanite from BEL1. Error bars and crosses are 1 sigma for all plots.

1975). The lack of correlation between the corrected $^{206}\text{Pb}/^{238}\text{U}$ ages and the amount of non-radiogenic Pb in

each analysis (Fig. 6d), suggests that the choice of non-radiogenic Pb correction used for the allanite overgrowths

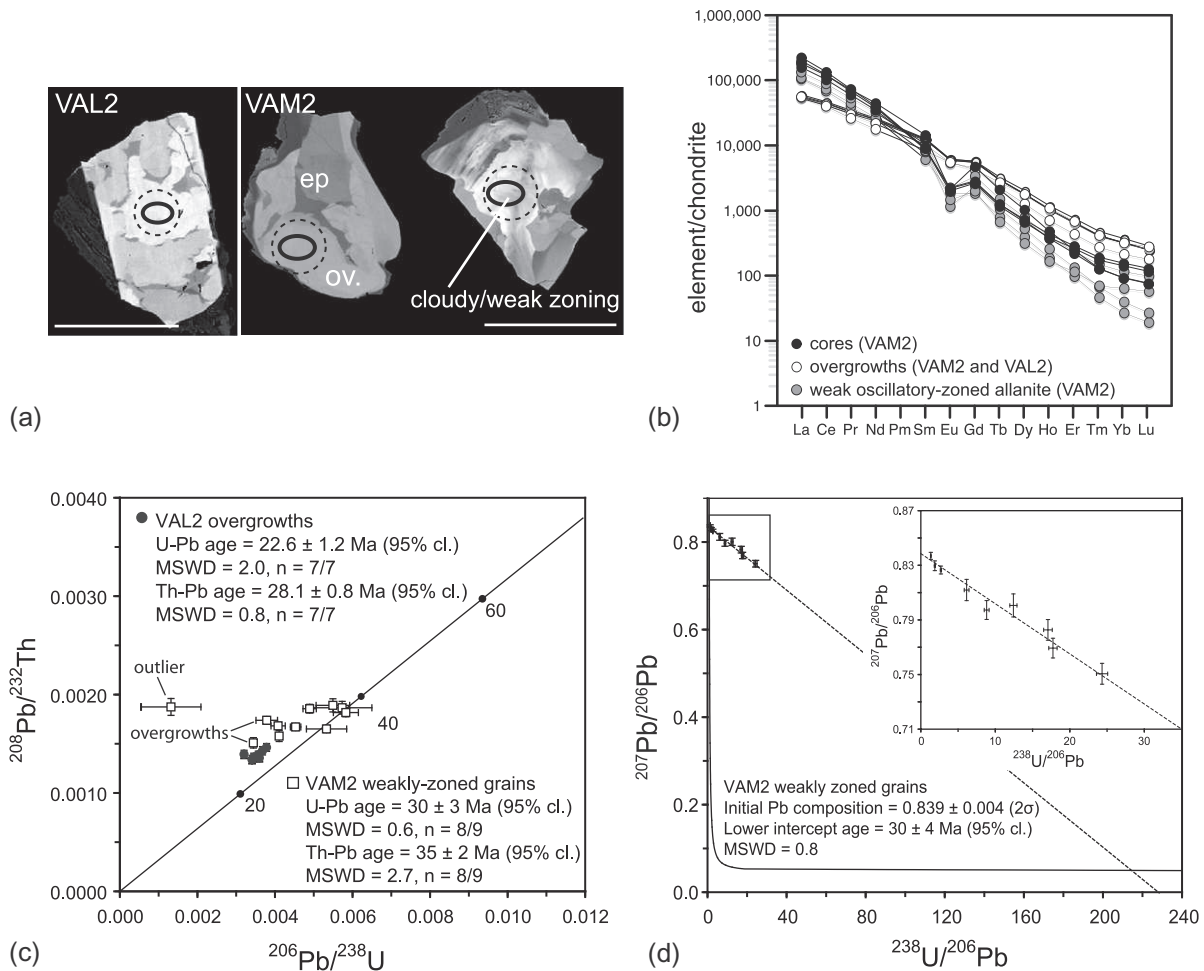


Fig. 5. Allanite age and trace element data for Val d'Arbedo. (a) SEM-BSE images of REE-epidote overgrowths in VAL2 leucosome and VAM2 meta-tonalite and cloudy/weak oscillatory zoned allanite in VAM2. Dashed and solid circles indicate LA-ICPMS and SHRIMP analysis locations, respectively. Ep = epidote and ov = overgrowth. White bar is 100 μm . (b) Chondrite-normalised REE patterns of allanite cores from VAM2, and REE-epidote overgrowths and weakly zoned allanite from VAM2 and VAL2. (c) $^{206}\text{Pb}/^{238}\text{U}$ versus $^{208}\text{Pb}/^{232}\text{Th}$ diagram of ^{207}Pb -corrected single-spot ages determined by SHRIMP for REE-epidote overgrowths in VAL2 and weakly zoned allanite in VAM2. Quoted ages are weighted mean ages. (d) Inverse concordia of uncorrected allanite U-Pb analyses from VAM2. Error crosses and bars are 1 sigma for all plots.

is robust. The six analyses lie along U-Th-Pb concordia (Fig. 6e) and yield a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 22.3 ± 0.7 Ma (MSWD = 1.0) and an identical $^{206}\text{Pb}/^{238}\text{U}$ age of 22.2 ± 0.8 Ma (MSWD = 0.9).

Thirteen analyses were obtained on high Th/U allanite cores in sample BEM1 meta-granodiorite. They contain >97% radiogenic ^{208}Pb of the total ^{208}Pb compared to 53–73% radiogenic ^{206}Pb (Electronic annex Table 2). Twelve of the 13 analyses calculate a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 297 ± 7 Ma (MSWD = 0.5), which agrees well with the weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 293 ± 4 Ma (MSWD = 0.8) (Fig. 6f). One analysis (BEM.3-2) was made on an alteration zone and was omitted from age calculation (Electronic annex Table 2). The alteration zone has low Th/U (~ 60) compared to unaltered cores and gives low $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages (~ 268 and ~ 238 Ma, respectively), which are offset from U-Th-Pb concordia (Fig. 6f).

6.3. Golino

Allanites in GOL03 meta-granite and GOL06 meta-diorite occur as unzoned overgrowths on epidote and as large (<500 μm) grains comprising a high-BSE intensity core (av. REE + Th = 0.7–0.8 cpfu) and a low-BSE intensity overgrowth or rim (av. REE + Th > 0.4–0.5 cpfu) (Fig. 7a, Table 3). Secondary alteration of allanite cores is indicated by patchy, low-BSE intensity zones that occur mainly at the core-rim boundary (Fig. 7a). Allanite cores in GOL03 and GOL06 have large to moderate negative Eu anomalies (av. $\text{Eu}/\text{Eu}^* = 0.1$ and 0.4, respectively) and highly fractionated REE patterns showing LREE enrichment (av. $\text{La}_\text{N}/\text{Lu}_\text{N} \sim 500$ and ~ 2000) (Table 3, Fig. 7b). In contrast, allanite overgrowths in GOL03 have low LREE with respect to M- (av. $\text{La}_\text{N}/\text{Lu}_\text{N} \sim 28$), and smaller negative Eu anomalies (av. $\text{Eu}/\text{Eu}^* = 0.3$) (Fig. 7b). REE patterns of allanite overgrowths in GOL06 are HREE-depleted (Fig. 7b), which

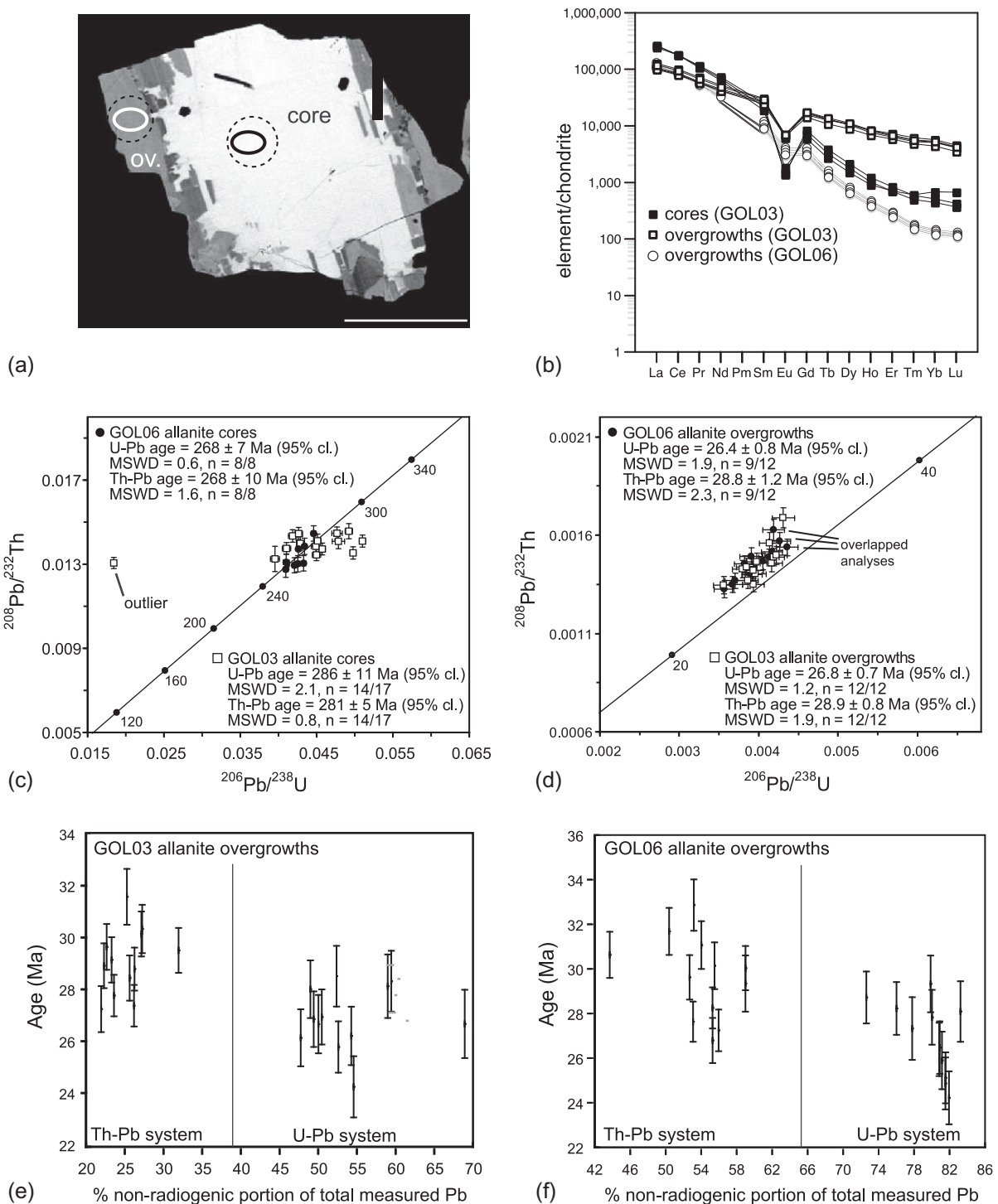


Fig. 7. Allantite age and trace element data for Golino. (a) SEM-BSE image of composite allanite grain from GOL03 meta-granite. Dashed and solid circles indicate LA-ICPMS and SHRIMP analysis locations, respectively. Ov = overgrowth. White bar is 100 μm . (b) Chondrite-normalised REE patterns of allanite cores and overgrowths from GOL03 and allanite overgrowths from GOL06 meta-diorite. (c) $^{206}\text{Pb}/^{238}\text{U}$ versus $^{208}\text{Pb}/^{232}\text{Th}$ diagram of ^{207}Pb -corrected single-spot ages determined by SHRIMP for allanite cores in GOL03 and GOL06. Quoted ages are weighted mean ages. (d) $^{206}\text{Pb}/^{238}\text{U}$ versus $^{208}\text{Pb}/^{232}\text{Th}$ diagram of ^{207}Pb -corrected single-spot ages determined by SHRIMP for allanite overgrowths in GOL03 and GOL06. Quoted ages are weighted mean ages. (e) Age versus non-radiogenic Pb portion of total measured Pb for both U-Pb and Th-Pb systems in allanite overgrowths in GOL03. (f) Age versus non-radiogenic Pb portion of total measured Pb for both U-Pb and Th-Pb systems in allanite overgrowths in GOL06. Error bars and crosses are 1 sigma for all plots.

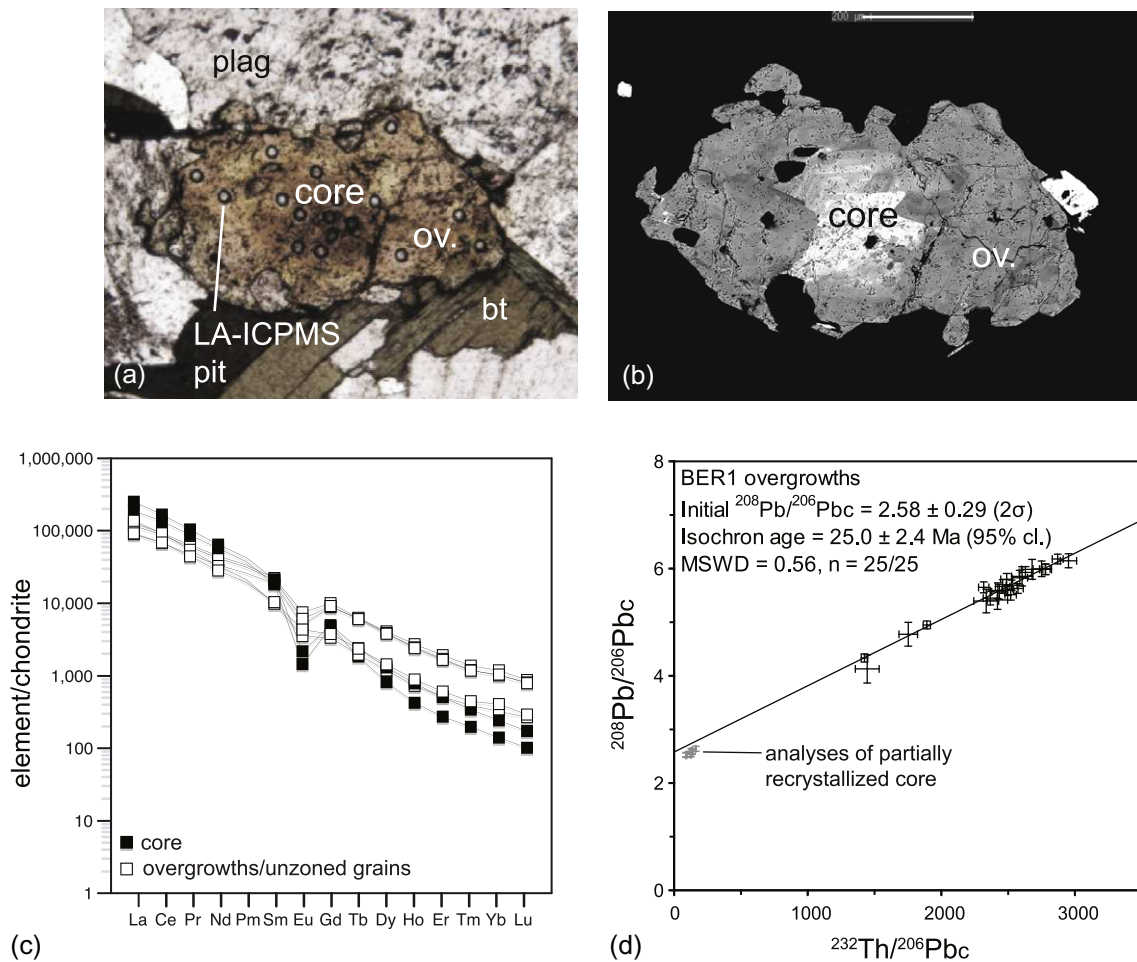


Fig. 8. Allanite age and trace element data for Berzona. (a) Photomicrograph of composite allanite grain in BER1 meta-granite (PPL); bt = biotite, plag = plagioclase. Circles in allanite are LA-ICPMS analysis pits (b) SEM-BSE image of grain in (a) showing bright-BSE, partially recrystallised core and darker-BSE overgrowth. White bar is 200 µm. (c) Chondrite-normalised REE patterns of allanite cores and overgrowths from BER1. (d) Th–Pb isochron of uncorrected allanite Th–Pb data determined by LA-ICPMS for BER1; Pbc denotes the non-radiogenic Pb component. Error bars and crosses are 1σ for all plots.

may reflect the presence of HREE-bearing amphibole in this sample and/or the bulk rock composition of the meta-diorite. The cores and overgrowths have distinct Th/U compositions in both the meta-granite (core Th/U = 145–185, overgrowth Th/U = 14–40), and in the meta-diorite (core Th/U = 53–76, overgrowth Th/U = 17–38) (Electronic annex Table 3).

Seventeen U–Th–Pb analyses of allanite cores in GOL03 meta-granite were determined by SHRIMP. The proportion of radiogenic ^{208}Pb (>94% of total ^{208}Pb) in each analysis is higher than radiogenic ^{206}Pb (>53% of total ^{206}Pb) (Electronic annex Table 3). Fourteen of 17 SHRIMP analyses from sample GOL03 yield a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 281 ± 5 Ma (MSWD = 2.1) and a $^{206}\text{Pb}/^{238}\text{U}$ age of 286 ± 11 Ma (MSWD = 1.6). One analysis (GOL03.11-2) overlapped core and overgrowth zones (outlier in Fig. 7c), and two analyses (GOL03.21-1 and 24.2) were measured on alteration zones and thus omitted from age calculation. The alteration zones yield U–Pb and Th–Pb ages lower than the weighted averages (Electronic annex Table 3). Eight

analyses were obtained on allanite cores in GOL06 that displayed varying degrees of secondary alteration. Grouped together, they yield a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 268 ± 10 Ma (MSWD 1.6), identical to the $^{206}\text{Pb}/^{238}\text{U}$ age of 268 ± 7 Ma (MSWD = 0.6) (Fig. 7c).

Twelve analyses of allanite overgrowths in GOL03 and GOL06 were obtained by SHRIMP. The calculated proportion of radiogenic Pb in each analysis is 69–79% (of total ^{208}Pb) and 31–53% (of total ^{206}Pb) for GOL03 and 41–56% (^{208}Pb) and 17–27% (^{206}Pb) for GOL06 (Electronic annex Table 3). From 12 analyses a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 28.9 ± 0.8 Ma (MSWD = 1.9) and a lower $^{206}\text{Pb}/^{238}\text{U}$ age of 26.8 ± 0.7 Ma (MSWD = 1.2) can be calculated for sample GOL03 (Fig. 7d). Similarly, nine of 12 analyses for GOL06 calculate a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 28.8 ± 1.2 Ma (MSWD = 2.3) and a lower $^{206}\text{Pb}/^{238}\text{U}$ age of 26.4 ± 0.8 Ma (MSWD = 1.9). Three analyses (GOL06.10-1, 5-1 and 8.1) overlapped the core-rim boundary and were omitted (Fig. 7c). For both samples, the low U–Pb ages relative to Th–Pb shift the data

to the right of U–Th–Pb concordia (Fig. 7d). There is no correlation between the ^{207}Pb -corrected single-spot ages and the amount of non-radiogenic ^{206}Pb (and ^{208}Pb) in each analysis (Fig. 7e and f), which suggests that initial Pb isotope composition of the sample does not deviate significantly from the model Pb composition used (see Section 9.1). A total $^{238}\text{U}/^{206}\text{Pb}$ – $^{207}\text{Pb}/^{206}\text{Pb}$ plot of the six analyses yields an initial $^{207}\text{Pb}/^{206}\text{Pb}$ composition of 0.818 ± 0.017 (95% cl.) and a lower intercept age of 26 ± 3 Ma (MSWD = 2.3, 95% cl., [Electronic annex Fig. 2](#)). The U–Pb intercept age although less precise, is identical to the weighted mean U–Pb age.

6.4. Berzona

Five allanite grains from BER1 meta-granite were analysed in situ from polished thin section (Fig. 8a). In thin section, allanite is unzoned, with the exception of a single, large ($\sim 500\ \mu\text{m}$) grain comprised of a core (av. REE + Th = 0.65 cpfu) and overgrowth (av. REE + Th > 0.4 cpfu) (Fig. 8a). The high-BSE intensity core (Fig. 8b) has high LREE contents (av. $\text{La}_\text{N}/\text{Lu}_\text{N} = 1090$) relative to the low-BSE intensity overgrowth and other analysed grains (av. $\text{La}_\text{N}/\text{Lu}_\text{N} \sim 518$ and ~ 157) (Table 3; Fig. 8c). The REE composition of the allanite core is also distinguished from the overgrowth by a large negative Eu anomaly (av. $\text{Eu}/\text{Eu}^* = 0.16$ for core and 0.62 for overgrowth) (Table 3). All allanite types in BER1 have low Th/U (Th/U = 14–18) (Table 3), in contrast to the high Th/U cores from previous samples. Thirty-one U–Th–Pb analyses of allanite were obtained by LA-ICPMS, including 6 core analyses and 25 overgrowth analyses ([Electronic annex Table 4](#)). The calculated proportion of radiogenic ^{206}Pb for each analysis is 24–54% of total ^{206}Pb ([Electronic annex Table 4](#)). Excluding the core analyses, the uncorrected data yield a Th–Pb isochron age of 25.0 ± 2.4 Ma (MSWD = 0.6) (Fig. 8d), which is considered a best estimate for the timing of Alpine allanite crystallization in this sample. The six core analyses lie off this isochron (Fig. 8d) and give an imprecise Th–Pb isochron age of 32 ± 34 Ma (MSWD = 0.2) ([Electronic annex Fig. 3](#)).

6.5. Age summary

High Th/U allanite cores in meta-tonalite, meta-granodiorite and meta-granite yield pre-Alpine $^{208}\text{Pb}/^{232}\text{Th}$ ages of 286 ± 5 Ma (VAM1), 297 ± 7 Ma (BEM1), 281 ± 5 Ma (GOL03) and 268 ± 10 Ma (GOL06). Notably, no pre-Alpine ages were reported from allanite in the leucosome samples. Alteration zones in allanite cores give low $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages (down to ~ 163 Ma) and may have low Th/U compositions and high non-radiogenic Pb contents compared to unaltered cores. In contrast, allanite overgrowths and weak oscillatory-zoned allanite in the meta-granitoids and leucosomes give a range of Alpine ages from 20 ± 5 Ma (BEL1) to 30 ± 4 Ma (VAM2). Whereas the $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages of pre-Alpine allanite generally agree within uncertainty, the Th–Pb and U–Pb age systems within allanite overgrowths differ in most samples (i.e. high $^{208}\text{Pb}/^{232}\text{Th}$ ages and low $^{206}\text{Pb}/^{238}\text{U}$ ages from the same analysis).

Table 4

Bulk rock major and trace elements determined by LA-ICP-MS and XRF.

	VAL1	VAL2	VAM2	VAM1
SiO_2	71.6	69.4	53.5	50.8
Al_2O_3	15.7	17.3	18.7	19.6
Fe_2O_3	2.30	1.49	8.05	9.33
CaO	4.52	5.22	6.94	7.41
MgO	0.80	0.69	4.30	3.54
MnO	0.04	0.03	0.13	0.15
Na_2O	3.08	4.68	3.53	3.28
K_2O	2.27	0.70	2.50	2.73
TiO_2	0.27	0.11	1.34	1.86
P_2O_5	0.10	0.06	0.26	0.62
F (ppm)	601	141	<1600	1830
Cl (ppm)	50	45	51	132
Total	100.7	99.7	99.5	99.7
Trace elements (average in ppm)				
	$n = 3$	$n = 3$	$n = 3$	$n = 3$
Sc	10	10	21	23
V	84	69	207	232
Cr	138	22	53	45
Rb	71	10	74	100
Sr	445	416	360	464
Y	4.8	5.2	23	37
Zr	56	33	171	342
Nb	2.6	1.4	14	24
Ba	404	164	512	700
La	6.4	4.0	24	56
Ce	13	8.1	49	110
Pr	1.5	0.98	6.2	13
Nd	6.3	4.0	26	52
Sm	1.3	0.90	5.3	10
Eu	0.35	0.40	1.5	2.3
Gd	1.3	0.90	4.9	8.8
Tb	0.16	0.14	0.70	1.2
Dy	0.95	1.0	4.5	7.3
Ho	0.19	0.19	0.88	1.4
Er	0.51	0.56	2.6	3.7
Tm	0.07	0.08	0.36	0.52
Yb	0.45	0.57	2.5	3.4
Lu	0.07	0.09	0.35	0.48
Hf	1.5	0.91	4.4	8.2
Ta	0.16	1.6	1.9	2.9
Pb	8.9	12	9.2	10
Th	1.6	0.95	4.3	11
U	0.26	0.30	0.92	1.3
Th/U	6.2	3.2	4.6	8.4

7. BULK-ROCK TRACE ELEMENT GEOCHEMISTRY

The bulk major and trace element compositions of two pairs of leucosome and meta-granitoid from Val d'Arbedo were investigated and are presented in Table 4. Leucosome samples VAL1 and VAL2 have major element compositions typical of granite. The REE patterns are enriched in LREE and flat for HREE (Fig. 9a). Sample VAL1 displays a small negative Eu-anomaly whereas VAL2 is characterised by a small positive Eu anomaly. The overall low LREE content together with low Zr content are in agreement with fluid-assisted melting at 650–700 °C as the main process for

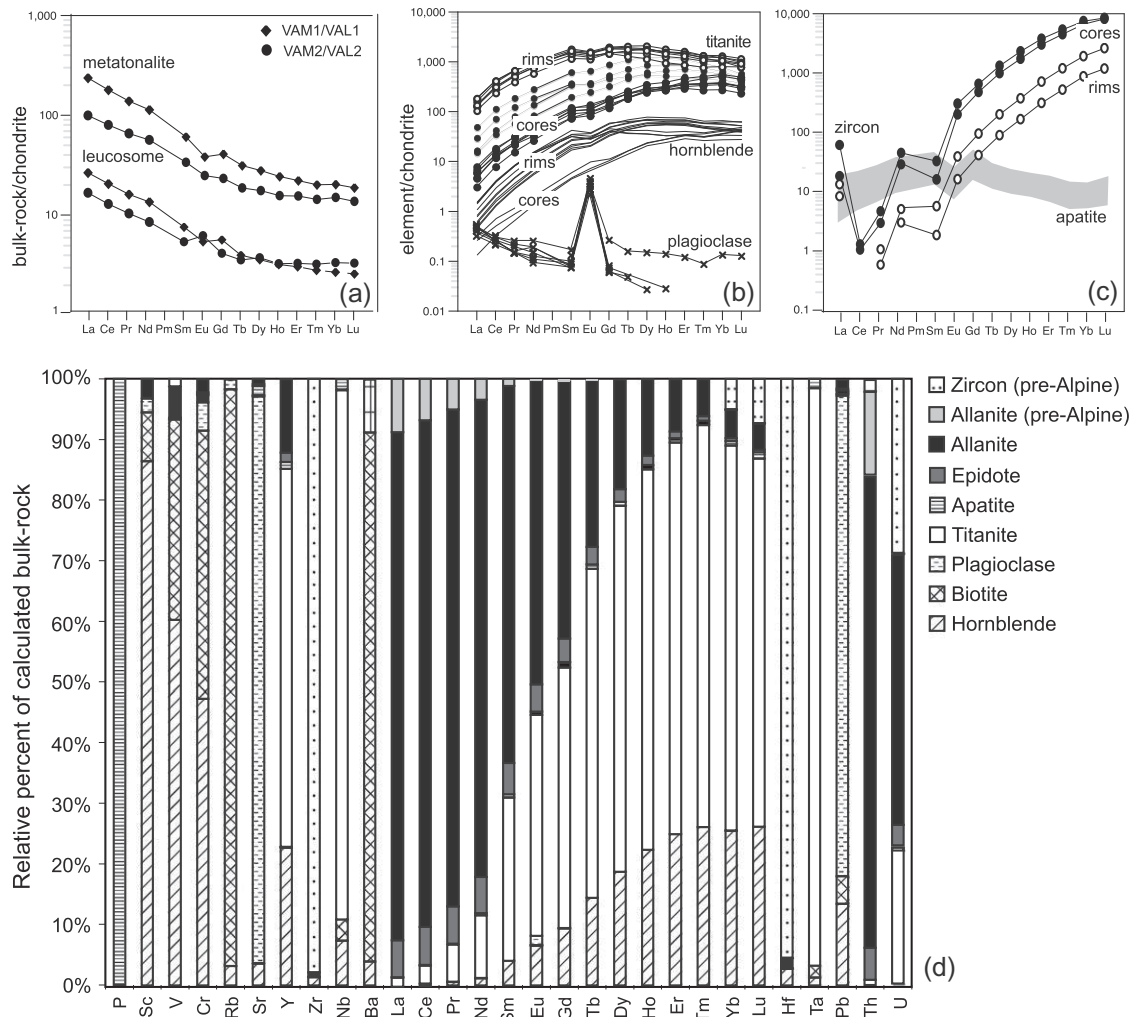


Fig. 9. Mineral and bulk rock trace element data determined by LA-ICPMS. (a) Chondrite-normalised REE-plots for country rock-leucosome pairs sampled at Val d'Arbedo (VAM1/VAL1 and VAM2/VAL2). (b) REE patterns of titanite, hornblende and plagioclase from sample VAM1. Note the very low LREE content in plagioclase and small negative Eu anomalies in titanite and hornblende. (c) REE-plots for zircon (Rubatto et al., 2009) and apatite. (d) Trace element distribution or budget for sample VAM1 meta-tonalite; see text for details.

the formation of the leucosomes (Berger et al., 2008; Rubatto et al., 2009).

Meta-granitoid samples VAM1 and VAM2 have higher FeO and MgO contents than the leucosomes and have high total alkali contents (5–6 wt.%), suggesting tonalite as a possible protolith. However, the rocks show lower than expected SiO₂ content (51 and 53.5 wt.%), which is attributed to melt extraction from the orthogneiss during anatexis. REE contents are generally higher in meta-tonalite compared to leucosome (Fig. 9a), reflecting the higher amount of trace element-rich phases such as titanite, allanite, apatite and amphibole in this rock type (see Section 8).

8. MINERAL TRACE ELEMENT COMPOSITIONS IN META-TONALITE

Trace element compositions for silicate and accessory phases in VAM1 (Table 5) were obtained to examine the role of allanite as a trace element host during fluid-assisted partial

melting. Chondrite-normalised rare earth element (REE) plots of each mineral are shown in Fig. 9b and c. Major mineral chemistry is provided in the Electronic annex Table 6 and only the key trace element features of minerals are discussed here. Using the mineral and bulk rock compositions from VAM1, it is possible to perform a mass balance in order to evaluate the major hosts for trace elements in meta-tonalite. The methodology for the mass balance calculations is detailed in the Electronic annex supplement.

A key feature of the mineral trace element compositions in VAM1 is the LREE-depleted REE patterns of phases co-existing with allanite. Hornblende and titanite REE patterns are LREE-depleted with respect to M-HREE ($Gd_N/La_N = 36$ and 26, respectively), with a general increase in trace element concentration (including LREE) from core to rim (Fig. 9b). It is possible that some cores of titanite grains are of magmatic origin, but their trace element contents are significantly lower than that documented for igneous titanite in metaluminous granites (Table 5) (Bea, 1996).

Table 5

Average trace element compositions of VAM1 minerals determined by LA-ICP-MS.

	Hornblende		Plagioclase	Biotite	Titanite		Apatite	Zircon	
	Core	Rim	Core		Core	Rim		Core	Rim
Trace elements in ppm	<i>n</i> = 5	<i>n</i> = 4	<i>n</i> = 17	<i>n</i> = 13	<i>n</i> = 8	<i>n</i> = 7	<i>n</i> = 8	<i>n</i> = 2	<i>n</i> = 2
Li	17	15	0.16	85	0.46	0.84	0.89		
Be	3.2	3.2	3.3	0.16	0.02	0.05	0.05		
Sc	108	116	1.4	17	4.5	5.1	1.4		
V	499	493	1.4	457	564	694	7		
Cr	20	16	1.1	31	6.2	8.2	1.3		
Rb	8.5	7.7	2.5	429	0.15	5.5	0.50		
Sr	52	48	819	3.0	31	40	287	1.7	0.25
Y	45	20	0.04	0.12	504	2070	20	2840	400
Zr	18	17	<0.01	0.33	130	169	0.40	11	2.0
Nb	4.4	5.5	<0.02	3.5	772	880	5.5		
Cs	0.01	0.01	<0.03	9.0	0.01	0.15	0.02		
Ba	64	55	84	2400	0.20	29	2.2		
La	0.15	0.05	0.08	0.01	1.5	35	2.1		
Ce	0.93	0.24	0.14	0.01	10	207	7.8	24	6.0
Pr	0.27	0.06	0.02	<0.01	2.5	52	1.5	0.09	<0.01
Nd	2.4	0.49	0.07	0.01	20	380	10	1.5	0.21
Sm	2.0	0.44	<0.01	0.01	16	227	3.6	5.3	0.51
Eu	0.84	0.24	0.11	0.02	6.9	78	0.91	1.1	0.17
Gd	4.5	1.1	<0.01	0.06	34	345	5.2	41	4.5
Tb	1.0	0.29	<0.02	<0.01	8.7	62	0.61	17	2.0
Dy	7.7	2.8	<0.03	0.01	77	416	3.4	234	29
Ho	1.7	0.73	<0.04	<0.01	19	80	0.70	91	12
Er	5.0	2.6	<0.05	<0.02	63	215	1.9	448	67
Tm	0.67	0.39	<0.06	<0.03	10	28	0.23	101	17
Yb	4.2	2.7	<0.07	0.01	67	176	1.5	937	185
Lu	0.60	0.42	<0.08	<0.01	8.6	23	0.30	169	38
Hf	1.0	0.89	<0.09	0.05	8.5	11	0.05	10,400	1160
Ta	0.03	0.04	<0.10	0.08	81	39	0.47	5.7	2.5
Pb	6.6	6.1	23	3.8	1.9	2.6	3.6	16	2.0
Th	<0.01	<0.01	<0.01	<0.01	0.17	5	0.04	663	73
U	0.01	0.01	<0.01	0.01	2	29	0.38	2420	562
Eu/Eu*	0.85	1.1	–	–	0.91	0.86	0.64	0.16	0.22
Gd _N /La _N	36	29	–	–	26	12	3	–	–
Th/U	–	–	–	–	0.07	0.16	0.09	0.27	0.13

Apatite and plagioclase in VAM1 are also REE-depleted (e.g. subchondritic LREE in plagioclase, Fig. 9c) compared to REE contents of igneous plagioclase and apatite in metaluminous granites (Bea, 1996). The REE patterns of hornblende, titanite, allanite and zircon rims are characterised by small negative Eu anomalies (Fig. 9b and c, Table 5), despite their crystallization in a feldspar-bearing rock. The Th/U composition of titanite (av. Th/U <0.2) and apatite (av. Th/U <0.1) is notably low (Table 5). Similarly, zircon overgrowths in VAL1 leucosome and rare zircon rims in VAM1 are Th-depleted (Th/U <0.1–0.001, Rubatto et al., 2009) compared to inherited zircon cores in the meta-tonalite (Table 5).

The mass balance results for VAM1 are given in Fig. 9d, and the relative contribution of each mineral to the calculated bulk rock composition is shown. The diagram shows metamorphic allanite to be the principal host of LREE and Th in the meta-tonalite, in line with the observed LREE-depletions in mineral REE patterns. The contribution of allanite to the REE budget is reduced with increasing

atomic number of the REE. Titanite is the principal host of HREE and contributes to MREE, whereas amphibole hosts about 20% of the HREE. Although plagioclase REE patterns display an accentuated positive Eu anomaly (Fig. 9b), it contributes only 2% to the Eu budget of the bulk rock (Fig. 9d). Apatite and zircon budget P, and Zr and Hf, respectively, while Rb and Ba are primarily hosted in biotite.

9. DISCUSSION

9.1. Behaviour of initial Pb in allanite

Allanite may incorporate large and variable amounts of Pb into its structure on formation (“initial Pb”), effectively reducing the precision of U–Pb ages, and to a lesser degree, Th–Pb ages. The proportion of non-radiogenic ²⁰⁸Pb in pre-Alpine allanite is <3% of the total ²⁰⁸Pb. Consequently, the choice of initial Pb isotopic composition only had a slight effect on calculated Th–Pb ages and the use of a model composition (Stacey and Kramers, 1975) is considered appropriate.

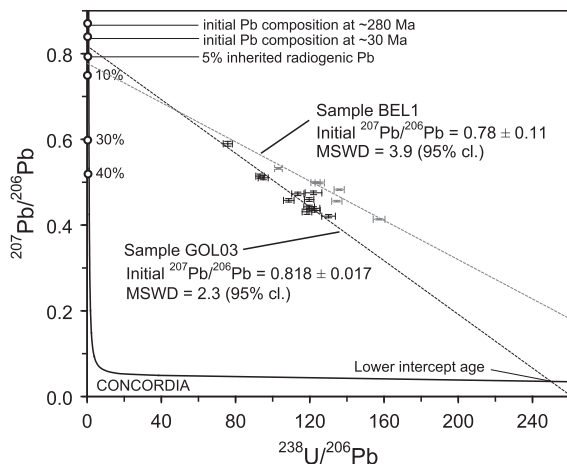


Fig. 10. Inverse Concordia plot of uncorrected U-Pb analyses for allanite overgrowths GOL03 and BEL1 and indicators showing the % effect of inherited radiogenic Pb from precursor allanite ($^{207}\text{Pb}/^{206}\text{Pb} = 0.05176$ at ~ 280 Ma, Stacey and Kramers, 1975) on the initial $^{207}\text{Pb}/^{206}\text{Pb}$ isotope composition of newly grown allanite. Error crosses are 1σ .

The proportion of non-radiogenic ^{208}Pb and ^{206}Pb in Alpine allanite ranges from 20% to 100%. The amount of non-radiogenic Pb changes with bulk rock composition: allanite overgrowths in meta-tonalite (e.g. VAM/L1, VAM/L2) have typically higher non-radiogenic Pb contents and lower Th/U than in meta-granodiorite (e.g. BEM/L1, GOL06) and meta-granite (e.g. GOL03, BER1). Protolith composition is thus an important consideration in sample selection for allanite dating. For allanites with such high non-radiogenic Pb contents, particularly those with $>50\%$ initial Pb, the suitability of a model Pb isotope composition must be based on independent evidence. The initial Pb can be considerably radiogenic relative to a bulk-crust model value (Stacey and Kramers, 1975) if allanite incorporates at formation radiogenic Pb from a Th- or U-bearing precursor mineral (Romer and Siegesmund, 2003). Such a situation may be favoured for solid-state and incomplete metamorphic reactions or mineral replacements because element transfer is limited to a local environment (Gabudianu et al., 2009). The measured isotopic composition of a coexisting low-U phase (K-feldspar) can be used to reduce such data but this assumes isotopic equilibration was achieved prior to closure of Pb diffusion in allanite, and in most complex metamorphic rocks this is likely to be problematic. In the investigated samples, two generations of epidote/allanite formed during metamorphism and it is unclear which one is in equilibrium with plagioclase. Additionally, feldspar Pb composition may re-equilibrate during retrograde, subsolidus metamorphism, whereas allanite is unaffected by low-grade overprints. Alternatively, concordia and isochron plots are useful as they avoid the need for choosing an initial Pb isotopic composition (Aleinikoff et al., 2002). A potential caveat is obtaining a sufficient spread of data to define a statistically meaningful regression (Ludwig, 2003).

Fig. 10 demonstrates that model Pb isotope compositions predicted by Stacey and Kramers (1975) change little

from the approximate time of granitoid intrusion (~ 280 Ma, $^{207}\text{Pb}/^{206}\text{Pb} = 0.864$) to high grade Alpine metamorphism (~ 30 Ma, $^{207}\text{Pb}/^{206}\text{Pb} = 0.838$). In contrast, in-take at growth of radiogenic Pb inherited from the precursor pre-Alpine allanite lowers the initial $^{207}\text{Pb}/^{206}\text{Pb}$ significantly (Fig. 10). In fact, only 5% of such “inherited radiogenic Pb” ($^{207}\text{Pb}/^{206}\text{Pb}$ at 280 Ma = 0.05176, Stacey and Kramers, 1975) lowers the initial $^{207}\text{Pb}/^{206}\text{Pb}$ to 0.80 (Fig. 10). The use of a model composition would underestimate the amount of non-radiogenic Pb in allanite and produce older apparent ages that increase with the proportion of initial Pb calculated (Gabudianu et al., 2009). For a radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ composition approximating that of magmatic allanite, the concordia method allows for detecting above 1% inherited radiogenic Pb in favourable cases (see data for sample VAM2, initial $^{207}\text{Pb}/^{206}\text{Pb} = 0.839 \pm 0.005$ 2σ , Fig. 5d). Independent estimates of initial $^{207}\text{Pb}/^{206}\text{Pb}$ from concordia intercepts ranged from 0.78 ± 0.11 (BEL1) to 0.86 ± 0.10 (VAM1) and agree, within error, with the model Pb isotope composition used (Figs. 4, 5 and 10). For some samples the $^{207}\text{Pb}/^{206}\text{Pb}$ intercept has a large uncertainty. The $^{207}\text{Pb}/^{206}\text{Pb}$ value of allanite in sample BEL1 indicates that more than 5% of inherited Variscan Pb is possible (Fig. 10). Application of the concordia $^{207}\text{Pb}/^{206}\text{Pb}$ value to calculate the amount of non-radiogenic Pb in BEL1 allanite lowers the single spot $^{206}\text{Pb}/^{238}\text{U}$ ages for the interpretation of allanite U–Pb data. For sample BER1, the Th–Pb isochron $^{208}\text{Pb}/^{206}\text{Pb}$ intercept at 2.58 ± 0.29 (2σ) is higher than the model Pb value ($^{208}\text{Pb}/^{206}\text{Pb}$ at ~ 30 Ma = 2.07, Stacey and Kramers, 1975). Given that most crustal rocks have ratios around 2.1 (Stacey and Kramers, 1975) the enhanced $^{208}\text{Pb}/^{206}\text{Pb}$ value may represent evidence for inheritance in this sample.

To assess the applicability of allanite dating in different geological settings, the non-radiogenic Pb contribution in allanite determined by ion microprobe was compiled for a range of magmatic, migmatitic and metamorphic rocks of Phanerozoic age (Fig. 11). In each case, the origin of allanite was inferred from P – T determinations, trace element compositions and petrography. The amount of non-radiogenic Pb, given in Fig. 11 as a proportion of the total measured thoranogenic Pb, is dependent on sample age and Th/U. The sample ages are ~ 12 – 290 Ma for magmatic allanite, ~ 30 – 550 Ma for migmatitic allanite and ~ 30 – 550 Ma for subsolidus metamorphic allanite (Fig. 11 and references therein). The allanite Th/U ratios are ~ 30 – 250 (magmatic), ~ 3 – 290 (migmatitic) and ~ 2 – 45 (metamorphic). The data in Fig. 11 show a relationship

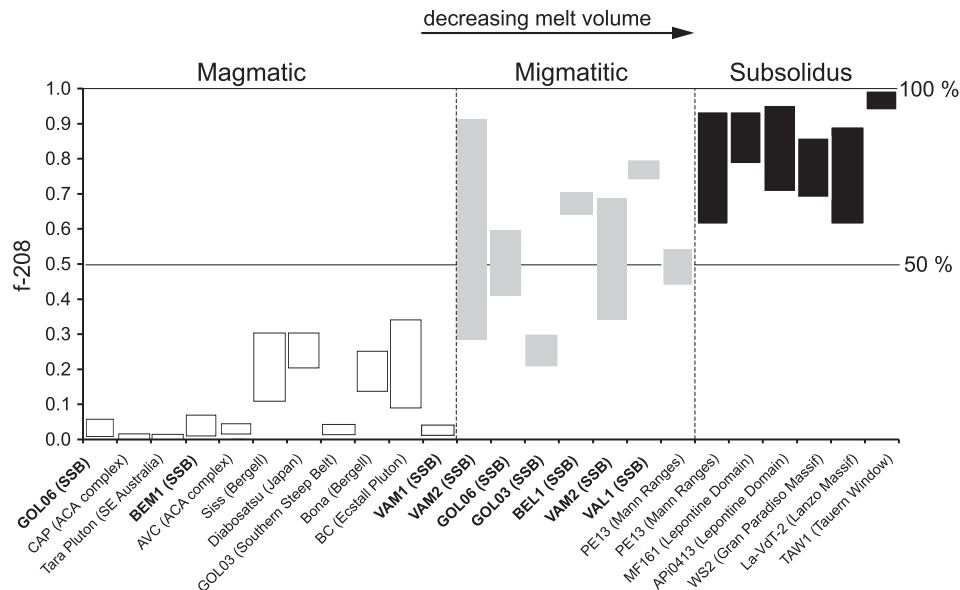


Fig. 11. Compilation of the fraction of non-radiogenic Pb of the total measured ^{208}Pb (f_{208}) in allanite from different geological settings. Samples analysed in this study are in bold. Other compositions are from allanite described in the literature. Magmatic samples: CAP allanite (276 Ma, ID-TIMS Th–Pb age, Barth et al., 1994); Tara allanite (415 Ma, SHRIMP Th–Pb age, Gregory et al., 2007); AVC allanite (276 Ma, ID-TIMS Th–Pb age, Barth et al., 1994); Siss (Bergell) allanite (31.5 Ma, ID-TIMS Th–Pb age, von Blanckenburg et al., 1992); Diabosatsu allanite (12 Ma, SHRIMP Th–Pb age, Gregory, 2009); Bona (Bergell) allanite (30.1 Ma, ID-TIMS Th–Pb age, von Blanckenburg et al., 1992); BC allanite (92 Ma, SHRIMP Th–Pb age, Gregory et al., 2007); PE13 allanite (550 Ma, SHRIMP Th–Pb age, Gregory et al., 2009a,b); PE13 allanite (559 Ma, SHRIMP Th–Pb age, Gregory et al., 2009a,b); MF161 allanite (29 Ma, SHRIMP Th–Pb age, Janots et al., 2009); APi0413 allanite (31 Ma, SHRIMP Th–Pb age, Janots et al., 2009); WS2 (31 Ma, SHRIMP U–Pb age, Gabudianu et al., 2009); La-VdT-2 allanite (47 Ma, SHRIMP Th–Pb age, Rubatto et al., 2008), TAW1 allanite (~30 Ma, SHRIMP U–Pb age, Gregory, 2009).

between allanite origin and non-radiogenic Pb content, irrespective of sample age.

Igneous allanites with high Th/U contain relatively small amounts of non-radiogenic ^{208}Pb (~1–35%). In comparison, allanites that form under subsolidus conditions have typically high non-radiogenic ^{208}Pb (>50%) and low Th/U. Certainly Th/U is responsible, in part, for the low non-radiogenic Pb contents in magmatic allanite and high non-radiogenic Pb contents in metamorphic allanite shown in Fig. 11. It is worth noting, however, that migmatitic allanite with high Th/U (e.g. ~60–290, sample VAM2) can contain much higher non-radiogenic ^{208}Pb contents (89–100%) than magmatic allanite of equivalent age and Th/U composition (e.g. the Bergell allanites). Thus, the amount of initial Pb may depend also on the process/reaction by which allanite formed.

Whilst non-radiogenic Pb is limiting for dating, particularly for metamorphic allanite containing relatively low Th and/or U, it may be useful as a petrological tool. Fig. 11 suggests that the amount of non-radiogenic Pb can be used as an indicator for subsolidus versus suprasolidus allanite. In addition, the composition of the initial Pb (e.g. presence of “inherited radiogenic Pb”) can potentially be used as a tracer for the recrystallization processes of allanite. The fact that no appreciable amount of “inherited radiogenic Pb” entered metamorphic allanite at formation indicates that the Pb isotope composition had been homogenised during the partial melting process. In this sense, metamorphic allanite may be used as a Pb isotope sensor.

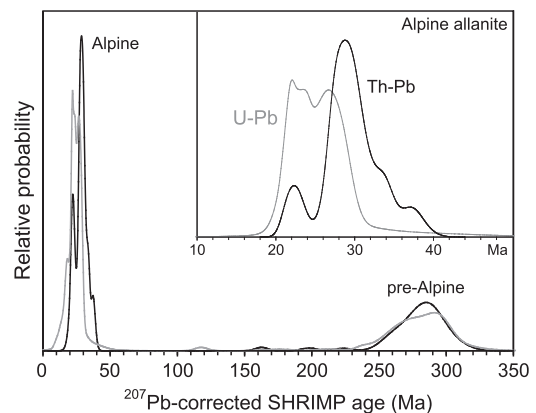


Fig. 12. Probability distribution diagram of single-spot $^{206}\text{Pb}/^{238}\text{Pb}$ ages (grey line) and $^{208}\text{Pb}/^{232}\text{Th}$ ages (black line) determined by SHRIMP for allanite samples VAM/L1, VAM/L2, BEM/L1, GOL03 and GOL06. Alpine ages are low Th/U allanite overgrowths and high Th/U weak oscillatory zoned allanite, and pre-Alpine ages are high Th/U allanite cores. Inset: enlargement of $^{206}\text{Pb}/^{238}\text{Pb}$ and $^{208}\text{Pb}/^{232}\text{Th}$ ages of allanite and REE-epidote overgrowths only.

9.2. U–Pb versus Th–Pb ages in allanite

A number of studies have demonstrated the importance of the Th–Pb system for accurate dating of Th-enriched minerals, such as allanite (von Blanckenburg et al., 1992; Barth et al., 1994; Oberli et al., 2004; Gregory et al.,

2007). The Th–Pb ages of high Th/U allanite are typically more precise and less sensitive to non-radiogenic Pb correction than U–Pb (^{208}Pb radiogenic contents exceed ^{206}Pb). Furthermore, the Th–Pb age is not affected by initial radioactive disequilibrium (excess ^{206}Pb from unsupported ^{230}Th), which may yield $^{206}\text{Pb}/^{238}\text{U}$ ages older than the $^{208}\text{Pb}/^{232}\text{Th}$ age on the same mineral (Oberli et al., 2004). We therefore prefer the Th–Pb system to date the high Th/U allanite cores. Excess ^{206}Pb contributions are not detected in pre-Alpine allanite: U–Pb and Th–Pb ages from the same grain are consistent at the level of precision of the dating technique ($\pm 2\text{--}3\%$, 1σ) (Fig. 12). The similar trace element compositions of the allanite samples and standards used to normalise ion microprobe data ($\text{LREE} + \text{Th} = 0.6\text{--}0.8$ cpfu; Gregory et al., 2007) minimized potential bias in $^{206}\text{Pb}^*/^{238}\text{U}^+$ and $^{208}\text{Pb}^*/^{232}\text{Th}^+$ caused by matrix mis-matching.

In contrast, allanite and REE-epidote overgrowths are low in Th and Th/U (Table 3) and may have equal amounts of radiogenic ^{208}Pb and ^{206}Pb (Electronic annex Tables 1 and 2). Valuable geochronological information may thus be gained from both the U–Pb and Th–Pb isotopic systems in low Th/U allanite. A comparison of the two geochronometers in Alpine allanite reveals that the U–Pb and Th–Pb ages on the same grain may differ by up to 25% with systematically low U–Pb ages compared to Th–Pb (Fig. 12). The decoupling of U–Pb and Th–Pb geochronometers in allanite may be explained by isotope systematics, such as initial isotopic heterogeneity of Pb (Romer and Siegesmund, 2003; Oberli et al., 2004) and isotopic resetting (Barth et al., 1994), or by analytical complications due to matrix effects (Catlos et al., 2000). We demonstrated above that only a small amount of “inherited radiogenic Pb” ($\leq 5\%$) is possible in the allanite overgrowths and would not account for the observed difference between U–Pb and Th–Pb ages. Excess ^{206}Pb is not relevant for low Th/U allanite, especially for the Val d’Arbedo and Bellinzona samples ($\text{Th}/\text{U} = 3\text{--}20$, av. 8), and if present, would produce older U–Pb ages, which are not observed.

SHRIMP dating is highly matrix dependent due to the effect of mineral chemistry on secondary ionisation efficiency (Williams, 1998). To achieve high accuracy in U–Th–Pb isotope analysis SHRIMP analyses must be calibrated against a matrix-matched standard (Stern and Berman, 2000; Fletcher et al., 2004, 2010). The Alpine overgrowths dated in this study have much lower trace element contents (REE-epidote $\text{LREE} + \text{Th} = 0.2$ cpfu, allanite $= >0.2\text{--}0.5$ cpfu) than pre-Alpine allanite and the standard CAP (Gregory et al., 2007). Such compositional differences produced a systematic offset in standard and sample ThO^+/Th^+ but did not noticeably affect UO^+/U^+ (see Electronic annex Tables 1–4). The offset in ThO^+/Th^+ is probably due to the different relative proportion of complex molecules produced by different allanite matrices during the sputtering process. The low oxide production of allanite and REE-epidote overgrowths (i.e. low ThO^+/Th^+) compared to that of CAP allanite can be explained by the different $\text{LREE} + \text{Th}$ contents of the standard and samples because REE + Th incorporation represents the primary element substitution in allanite (Gieré and Sorenson, 2004). This offset places a greater dependence on

the accuracy of the 2-dimensional calibration slope, thereby increasing the uncertainty on the standard calibration. Based on the good agreement of standard and sample UO^+/U^+ values we conclude that U–Pb (concordia) ages for low Th/U allanite are more robust than Th–Pb ages, in this case. It is clear that the apparent decoupling of U–Pb and Th–Pb ages in allanite, either by isotope systematics or by analytical effects, requires more systematic investigation of both geochronometers. The development of a low-REE–Th standard for the accurate calibration of ion microprobe $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ analyses is highly desirable for SHRIMP dating of young, metamorphic allanite.

9.3. Isotopic resetting in allanite

High spatial resolution dating isolated two main stages of allanite growth. The allanite cores from meta-granitoids have trace element compositions typical of magmatic allanite in tonalite and granodiorite (Gregory et al., 2009b): high La/Sm and Th/U and marked negative Eu anomalies (Fig. 13a–b). The ages of allanite cores (from 268 ± 10 to 297 ± 7 Ma) are consistent with the ages of inherited zircon (Rubatto et al., 2009) and the timing of Permian granitoid intrusion in the Lepontine Domain (Romer et al., 1996; Schaltegger and Gebauer, 1999). We conclude that the allanite cores are inherited from the igneous protolith. A later

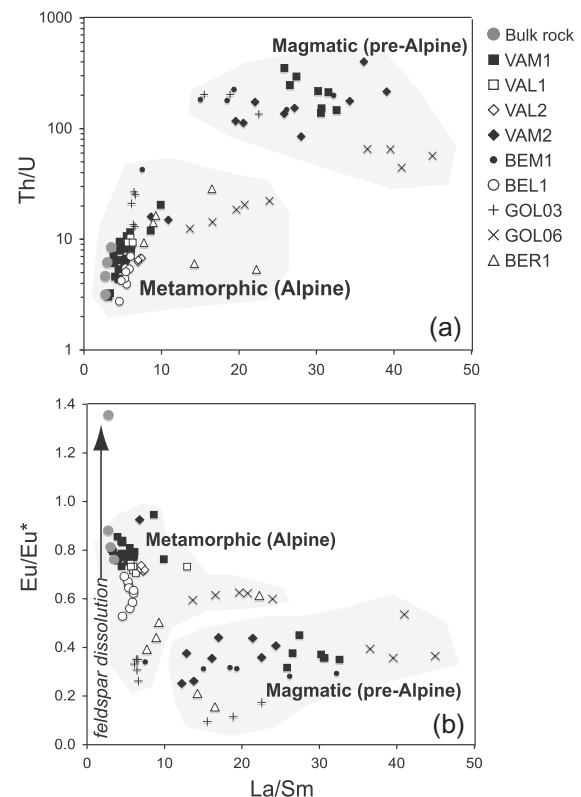


Fig. 13. (a) La/Sm versus Th/U plot for allanite and bulk rock samples. (b) La/Sm versus Eu/Eu^* plot for allanite and bulk rock samples.

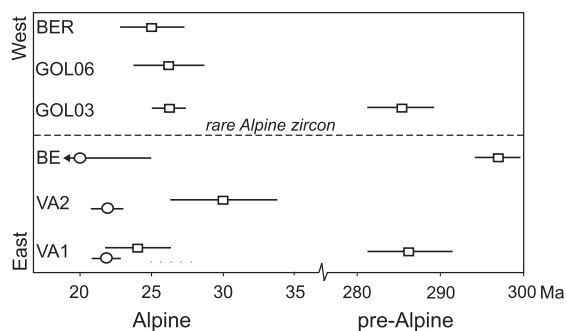


Fig. 14. Summary of allanite ages for each sample (including 1σ uncertainties): white squares = allanite in country rock (meta-granitoid); white circles = allanite in leucosome. Ages given for samples VAL1, VAL2 and GOL06 are weighted mean U–Pb ages, sample ages for VAM1, VAM2, BEL1 and GOL03 are U–Pb intercept ages and sample BER1 is a Th–Pb isochron age. Pre-Alpine ages are weighted mean Th–Pb ages.

generation of allanite overgrowths and new grains in meta-granitoids and leucosomes are characterised by low La/Lu and Th/U and small negative Eu anomalies (Fig. 13a–b). These yield a range of ages from 30 ± 4 to 20 ± 5 Ma (Fig. 14), which fall within the period recorded for Alpine collisional orogeny (Romer et al., 1996; Berger et al., 2005; Janots et al., 2009), and also for anatectic zircons in the same area (Rubatto et al., 2009).

The detection of inherited cores in composite grains has implications for isotopic resetting of allanite in high-grade rocks. Given the low solubilities of LREE and Th in hydrous granitic melts (Montel, 1993), it is predicted that high LREE and Th allanite will remain as a residual phase during incipient partial melting. This prediction is consistent with the preservation of inherited cores in meta-granitoids and indicates that the conditions of partial melting ($T = 620\text{--}700$ °C from Ti-in-zircon thermometry, Rubatto et al., 2009) were insufficient to completely dissolve protolith allanite. Instead, protolith allanite preserves a substantial memory of its initial age in spite of upper amphibolite facies re-working, which places strong constraints on closure temperature. For allanite grains >100 μm (typical grain size of inherited cores) the closure temperature of Pb diffusion is above that of the wet granite solidus (i.e. $T > 630$ °C). The robustness of allanite is even more significant in samples from Bellinzona and Val d'Arbedo where there is good evidence of prolonged high temperatures from zircon dating and Ti-in-zircon thermometry (Rubatto et al., 2009). This observation is consistent with, and improves on other empirical estimates of Pb closure temperature in allanite from high-grade gneisses (~ 650 °C, Heaman and Parrish, 1991; Parrish, 2001) and calc-alkaline igneous rocks (700–800 °C, von Blanckenburg et al., 1992; Oberli et al., 2004).

The low and scattered apparent ages (~ 280 to ~ 163 Ma) of alteration zones within inherited cores, however, indicate partial resetting of protolith allanite. Here, alteration is defined by irregular domains of patchy, low-BSE intensity zoning that proceed from fractures and core boundaries (Fig. 6b). The texture and U–Th–Pb isotopes points to partial

loss of (radiogenic) Pb from metamict zones, possibly facilitated by fluid along fracture pathways that lead to geologically meaningless ages. Some analyses with low Th/U, including the low Th/U allanite core in sample BER1, may reflect partial recrystallisation of protolith allanite at higher metamorphic temperatures, although similar features (i.e. low-BSE intensity, low Th contents and high non-radiogenic Pb) have also been described for the alteration of magmatic allanite at low temperatures (~ 200 °C, Poitrasson, 2002). The agreement of U–Pb and Th–Pb ages (within $\pm 1\sigma$) obtained from altered allanite suggests that the U–Pb and Th–Pb age systems in the analysed areas behaved similarly during secondary alteration, and were not significantly decoupled by secondary processes (e.g. Barth et al., 1994).

The identification of inherited cores partially replaced by new allanite overgrowths is of general importance for the interpretation of allanite ages in metamorphic rocks. The survival of igneous allanite grains to upper amphibolite facies and even anatexis coupled with the high reactivity of allanite during metamorphism suggests that allanite ages are likely to be reset by new mineral growth and recrystallization rather than by diffusion. The importance of mineral growth/recrystallization over diffusive resetting is supported by the fact that only Alpine ages were measured from newly-formed, low Th/U allanite, which indicates that growth/recrystallization processes were the dominant mechanism for new allanite ages in the migmatites.

9.4. REE distribution during incipient melting: constraints on allanite petrogenesis

Allanite is chemically complex, has a large stability field, and may form by several processes/reactions (Gieré and Sorenson, 2004). Trace element variations in allanite have proven valuable in relating this mineral to an evolving bulk silicate assemblage. For example, negligible Eu anomalies and high Sr content in allanite are proxies for its formation above the stability field of plagioclase in high pressure rocks (Rubatto et al., 2008), while changes in allanite HREE content have been used to infer the involvement of garnet (Gregory et al., 2009a).

In this study, the composition and origin of allanite are coupled. Magmatic allanite is characterised by higher Th and LREE contents than metamorphic allanite (Fig. 4b). As allanite is the main carrier of Th in these rocks (Fig. 9d), this distribution indicates that the modal abundance of allanite was smaller in the magmatic protholith than in the recrystallised meta-granitoid. Magmatic allanite has higher Th/U, generally displays a steeper LREE pattern (higher La/Sm) and has a more pronounced negative Eu anomaly (lower Eu/Eu*) than metamorphic allanite (Fig. 10a–b). These changes are best explained by a change in trace element budgets in the coexisting magmatic and metamorphic phases. Gregory et al. (2009b) showed that in the Bergell tonalite magmatic titanite has high trace element contents with normalized MREE $\geq$ LREE. Higher modal abundance of titanite with respect to allanite results in a LREE pattern of allanite that is steeper than that of the

bulk rock. In such magmatic rocks, plagioclase is the most important host of Eu and thus crystallization of plagioclase produces a negative Eu anomaly in all co-existing minerals. These trends are observed in the magmatic allanite studied here. The La/Sm of allanite is higher than the measured bulk rock whereas Eu/Eu* is smaller (Fig. 10a–b). The situation is significantly different during the metamorphic growth or recrystallization. Allanite is the main host for LREE and Sm and thus the La/Sm of allanite will be determined by the bulk composition. This is confirmed for the Val d'Arbedo samples (Fig. 10b). Interestingly, our mass balance shows that although plagioclase is the most abundant phase in the meta-granitoid, it hosts only 2% of the Eu (Fig. 9d) and thus is not able to impose a significant negative Eu anomaly in the coexisting phases. However, metamorphic allanite influences the trace element patterns of other metamorphic phases. The LREE depletion of amphibole and titanite (Fig. 8b) as well as the very low Th/U of metamorphic zircon and titanite are likely related to coexisting allanite.

The anomalous HREE-depletions in weakly oscillatory-zoned allanite from VAM2 meta-tonalite compared to unzoned overgrowths in the same sample (Fig. 5b), indicates that the weakly zoned allanite formed in the presence of stable phase that sequestered HREE, such as garnet or zircon. Early (~32 Ma) metamorphic zircon in leucosome VAL2 is also HREE-depleted (Rubatto et al., 2009). Titanite and hornblende contain significant HREE but they would additionally result in MREE depletion (Fig. 8d). Whilst garnet is not observed in samples VAM2 and VAL2, it is documented as a residual phase in migmatites from Val d'Arbedo and Bellinzona (Berger et al., 2008; Rubatto et al., 2009). Mineral equilibria modelling of Berger et al. (2008) shows that garnet can form at *P–T* conditions appropriate to the studied samples (i.e. between 650 and 750 °C at 0.8 GPa) in an average migmatite composition, and even small changes in pressure or bulk rock composition (e.g. Ca content) may render garnet metastable. Therefore, we suggest that garnet was likely stable in the sample when early, low HREE allanite formed at ~30 Ma.

9.5. Behaviour of mineral chronometers during incipient melting

Zircon is most commonly used chronometer to date migmatites (Vavra et al., 1996; Rubatto et al., 2001; Hokada and Harley, 2004), whereas allanite and titanite are more likely to record low- to medium-grade events in metamorphic rocks (Aleinikoff et al., 2002; Janots et al., 2009). Here we compare the behaviour of allanite, titanite and zircon (Rubatto et al., 2009) in the migmatites to assess their role as chronometers of incipient partial melting.

New zircon growth in migmatites occurred almost exclusively in leucosomes and was triggered by repeated injections of melt into the system (Rubatto et al., 2009). Zircon in country rocks (meta-granitoids) either failed to re-equilibrate (e.g. sample VAM1) or produced rare Alpine overgrowths (e.g. samples VAM2 and BEM1), probably owing to efficient melt segregation (Rubatto et al., 2009). Even in migmatites containing moderate amounts of leucosome

(sample GOL03, Fig. 2d), metamorphic zircon is scarce. As a result, zircon dating was not attempted for similar migmatites at Berzona (sample BER1, Fig. 2e). The occurrence of mainly inherited zircon in country rocks indicates that metamorphic zircon growth during Barrovian metamorphism in the Central Alps was limited to areas of intense migmatization (Val d'Arbedo–Bellinzona, Rubatto et al., 2009), where hydrate-breakdown melting was additionally reported in muscovite-bearing rocks (Fig. 1) (Burri et al., 2005).

In contrast, metamorphic allanite and titanite are more reactive and may form by different processes to metamorphic zircon. Alpine allanite formed in country rocks containing small leucosome volumes, and in segregated leucosomes with zircon (Fig. 14). Similarly, titanite with low trace element contents (interpreted as metamorphic titanite) occurred in both country rocks and leucosomes (Table 1). Berger et al. (2008) interpreted allanite textures in migmatite at Bellinzona to have formed by partial resorption of epidote (either prograde or magmatic) during incongruent melting followed by the precipitation of allanite overgrowths (+hornblende and accessory phases) from a melt (Mogk, 1992). Irregular core-rim boundaries of some allanite grains (Figs. 4–8) however, make it difficult to distinguish between new growth on magmatic cores or recrystallization of the outpart of a magmatic core. Newly grown allanite is abundant in migmatites that contain limited or rare metamorphic zircon, such as at Golino and Berzona, and is the principal U–Pb chronometer in these rocks (Fig. 14). The comparison of allanite and zircon in country rock–leucosome pairs in this study and in Rubatto et al. (2009) highlights the difficulty of dating amphibolite facies anatectic rocks using only zircon. Whereas new zircon may form in leucosomes, allanite (and titanite) could be better chronometers in the country rock (restite).

Allanite and titanite are found in many metamorphosed granitic rocks and are abundant in metaluminous rocks of intermediate composition, such as the meta-tonalites and meta-granodiorites investigated in this study. They are stable in metamorphic rocks to amphibolite facies, and the closure temperatures of Pb diffusion in both minerals lie at the upper limit of amphibolite facies, or possibly higher ($T > 650–700$ °C, this study, Aleinikoff et al., 2002). Allanite and titanite are therefore key minerals for dating medium to high temperature metamorphism. The utility of these chronometers may be limited by low U (and Th) contents, particularly for titanite, and high non-radiogenic Pb contents in metamorphic grains (Fig. 11) (Aleinikoff et al., 2002). The extremely low U and Th contents in titanite (from core to rim: 2–30 ppm U and 0.1–5 ppm Th) in the studied migmatites made it unsuitable for ion microprobe dating.

9.6. Implications of allanite ages for the Central Alps

New dating shows that allanite in meta-granitoids and leucosomes recorded different partial melt events during the Barrovian cycle between 30 ± 4 and 20 ± 5 Ma (Fig. 14). The distribution of allanite ages in different samples is in line with the episodic melt model of Rubatto et al.

(2009), whereby fluid-assisted melting and new mineral growth in the migmatites is intermittent and heterogeneously distributed, due to the availability of localised fluids (Berger et al., 2008). The timing of allanite growth in migmatites at Golino and Berzona (25.0 ± 2.4 and 26 ± 3 Ma) compared to allanite ages from Val d'Arbedo and Bellinzona (from 20 ± 5 to 30 ± 4 Ma) suggests that melting ceased earlier in rocks away from the areas of intense migmatization (Fig. 14).

Incipient partial melting in the Southern Steep Belt is contemporaneous with peak magmatism in the Central Alps, with the emplacement of the Bergell intrusive suite between 33 and 28 Ma (Oberli et al., 2004) and intrusion of the Novate leucogranite at 25 Ma (Liatì et al., 2000). In addition, the widespread formation of late to post-kinematic ~ 29 –25 Ma leucocratic dykes in the western part of the SSB (Romer et al., 1996; Schärer et al., 1996) and the ages of monazite growth in similar migmatites at 28 and 30 Ma (Berger et al., 2009) indicate that crustal melting was occurring over a period of time until the late Oligocene. Repeated allanite formation from around 30 to 20 Ma in migmatites across the SSB is consistent with the age pattern of anatectic zircons in the same rocks (32–22 Ma at Val d'Arbedo–Bellinzona, Rubatto et al., 2009). The allanite U–Pb ages therefore support the fast exhumation and cooling history (100 ± 20 °C/Ma) of the migmatite belt proposed by Rubatto et al. (2009).

10. CONCLUSIONS

Migmatites of the Central Alps provide an excellent example of allanite chronology in amphibolite facies rocks. The complex history of allanite in the investigated samples demonstrates the value of microanalysis and the additional information which may be gained from this mineral using such a technique. Allanite was present in the migmatites as an igneous accessory and as a product of subsequent metamorphism and melting. The texture, chemistry and U–Th–Pb isotopes within allanite indicate that metamorphic overgrowths did not inherit appreciable amounts ($\leq 5\%$) of radiogenic Pb from precursor magmatic allanite. Although protolith allanite underwent varying degrees of post-magmatic alteration, this study demonstrates that igneous allanite grains can survive to upper amphibolite facies and even anatexis and still retain a substantial component of the original age. Thus, in addition to its formation at lower metamorphic temperatures, allanite may provide robust metamorphic ages to at least upper amphibolite facies. The presence of non-radiogenic Pb in allanite, however, may limit dating applications in certain cases, particularly in low grade metamorphic rocks. The apparent decoupling of U–Pb and Th–Pb chronometers within low Th/U allanite requires further systematic investigation of allanite U–Pb and Th–Pb isotope systematics and the development of a low-Th-REE standard for ion microprobe analysis. In migmatite samples that lacked metamorphic zircon, allanite readily recorded the Alpine event. U–Th–Pb isotopes in allanite therefore present a complementary approach to zircon for dating incipient partial melting.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2012.01.020](https://doi.org/10.1016/j.gca.2012.01.020).

REFERENCES

- Aleinikoff J. N., Wintsch R. P., Fanning C. M. and Dorais M. J. (2002) U–Pb geochronology of zircon and polygenetic titanite from the Glastonbury Complex, Connecticut, USA: an integrated SEM EMPA, TIMS and SHRIMP study. *Chem. Geol.* **188**, 125–147.
- Barth S., Oberli F. and Meier M. (1994) Th–Pb versus U–Pb isotope systematics in allanite from co-genetic rhyolite and granodiorite: implications for geochronology. *Earth Planet. Sci. Lett.* **124**, 149–159.
- Bea F. (1996) Residence of REE, Y, Th and U in granites and crustal protoliths; implications for the chemistry of crustal melts. *J. Petrol.* **37**, 521–552.
- Berger A., Rosenberg C. and Schmid S. M. (1996) Ascent, emplacement and exhumation of the Bergell pluton within the Southern Steep Belt of the Central Alps. *Schweiz. Mineral. Petrogr. Mitt.* **72**, 357–382.
- Berger A., Mercogli I. and Engi M. (2005) The Lepontine Alps: notes accompanying the tectonic and petrographic map sheet Sopra Ceneri (1:100,000). *Schweiz. Mineral. Petrogr. Mitt.* **85**, 109–146.
- Berger A., Burri T., Alt-Epping P. and Engi M. (2008) Tectonically controlled fluid flow and water-assisted melting in the middle crust: an example from the Central Alps. *Lithos* **102**, 598–615.
- Berger A., Rosenberg C. and Schaltegger U. (2009) Stability and isotopic dating of monazite and allanite in partially molten rocks: examples from the Central Alps. *Swiss J. Geosci.* **102**, 15–29.
- Burri T., Berger A. and Engi M. (2005) Tertiary migmatites in the Central Alps: regional distribution, field relations, conditions of formation and tectonic implication. *Schweiz. Mineral. Petrogr. Mitt.* **85**, 215–232.
- Butler R. F., Gehrels G. E. and Baldwin S. L. (2002) Palaeomagnetism and geochronology of the Ecstall Pluton in the Coast Mountains of British Columbia: evidence for local deformation rather than large-scale transport. *J. Geophys. Res.* **107**, EPM3-1–13.
- Carlos E. J., Sorensen S. S. and Harrison T. M. (2000) Th–Pb ion-microprobe dating of allanite. *Am. Mineral.* **85**, 633–648.
- Cox R. A., Wilton D. H. C. and Kösler J. (2003) Laser-ablation U–Th–Pb in situ dating of zircon and allanite: an example from the October Harbour Granite, central Coast Labrador, Canada. *Can. Mineral.* **41**, 273–291.
- Eggins S. M., Rudnick R. L. and McDonough W. F. (1998) The composition of peridotites and their minerals: a laser ablation ICP-MS study. *Earth Planet. Sci. Lett.* **154**, 53–71.

- Engi M., Todd C. S. and Schmatz D. R. (1995) Tertiary metamorphic conditions in the eastern Lepontine Alps. *Schweiz. Mineral. Petrogr. Mitt.* **75**, 346–369.
- Engi M., Berger B. and Roselle G. (2001) The role of the tectonic accretion channel in collisional orogeny. *Geology* **29**, 1143–1146.
- Engi M., Bousquet R. and Berger A. (2004) Explanatory notes of the map: metamorphic Structure of the Alps. Central Alps. *Mitt. Öster. Min. Ges.* **149**, 53–69.
- Finger F., Broska I., Roberts M. P. and Schermaier A. (1998) Replacement of primary monazite by apatite-allanite-epidote coronas in amphibolite facies granite gneiss from the eastern Alps. *Am. Mineral.* **83**, 248–258.
- Fletcher I. R., Mc Naughton N. J., Aleinikoff J. A., Rasmussen B. and Kamo S. L. (2004) Improved calibration procedures and new standards for U–Pb and Th–Pb dating of Phanerozoic xenotime by ion microprobe. *Chem. Geol.* **209**, 295–314.
- Fletcher I. R., McNaughton N. J., Davis W. J. and Rasmussen B. (2010) Matrix effects and calibration limitations in ion probe U–Pb and Th–Pb dating of monazite. *Chem. Geol.* **207**, 31–44.
- Gabudianu I., Rubatto D., Gregory C. and Compagnoni R. (2009) The age of HP metamorphism in the Gran Paradiso Massif, Western Alps: a petrologic and geochronologic study of a “silvery micaschist”. *Lithos* **110**, 98–108.
- Gebauer D. (1996) A P–T–t path for an (ultra)high-pressure ultramafic/mafic rock-association and its felsic country-rocks based on SHRIMP-dating of magmatic and metamorphic zircon domains. Example: Alpe Arami (Central Swiss Alps). In *Earth Processes: Reading the Isotopic Code* (eds. A. Basu and S. R. Hart). American Geophysical Union, Washington, DC, pp. 309–328.
- Gieré R., Sorenson S. (2004) Allanite and other REE-rich epidote-group minerals. In *Epidotes* (eds. F. Axel, F. Gerhard). *Reviews in Mineralogy and Geochemistry* **56**, pp. 431–493.
- Gregory C. J. (2009) Allanite chemistry and U–Th–Pb geochronology. Ph. D. thesis, Research School of Earth Sciences, The Australian National University Canberra, p. 271.
- Gregory C. J., Rubatto D., Allen C., Williams I. S., Hermann J. and Ireland T. (2007) Allanite micro-geochronology: a LA-ICPMS and SHRIMP U–Th–Pb study. *Chem. Geol.* **245**, 162–182.
- Gregory C. J., Buick I. S., Hermann J. and Rubatto D. (2009a) Mineral-scale trace element and U–Th–Pb age constraints on metamorphism and melting during the Petermann Orogeny (central Australia). *J. Petrol.* **50**, 251–287.
- Gregory C., McFarlane C., Hermann J. and Rubatto D. (2009b) Tracing the evolution of calc-alkaline magmas: in-situ Sm–Nd isotope studies of accessory minerals in the Bergell Igneous Complex, Italy. *Chem. Geol.* **260**, 73–86.
- Gromet P. L. and Silver L. T. (1983) Rare earth element distributions among minerals in a granodiorite and their petrographic implications. *Geochim. Cosmochim. Acta* **47**, 925–939.
- Heaman L., Parrish R. R. (1991) U–Pb geochronology of accessory minerals. In *Applications of radiogenic isotope systems to problems in geology* (eds. L. Heaman, J. Ludden). *Mineral Assoc Can Short-course Handbook* **19**, 59–102.
- Hermann J. (2002) Allanite: thorium and light rare earth element carrier in subducted crust. *Chem. Geol.* **192**, 289–306.
- Hokada T. and Harley S. L. (2004) Zircon growth in UHT leucosome: constraints from zircon-garnet rare earth element (REE) relations in Napier Complex, East Antarctica. *J. Mineral. Petrol. Sci.* **99**, 180–190.
- Janots E., Negro F., Brunet F., Goffe B. and Engi M. (2006) Evolution of the REE mineralogy in HP-LT metapelites of the Sebide complex, Rif, Morocco: monazite stability and geochronology. *Lithos* **87**, 214–234.
- Janots E., Engi M., Berger A., Allaz J., Schwarz J.-O. and Spandler C. (2008) Prograde metamorphic sequence of REE minerals in pelitic rocks of the Central Alps: implications for allanite–monazite–xenotime phase relations from 250 to 610 °C. *J. Metamorph. Geol.* **26**, 509–526.
- Janots E., Engi M., Rubatto D., Berger A., Gregory C. and Rahn M. (2009) Metamorphic rates in collisional orogeny from in situ allanite and monazite dating. *Geology* **37**, 11–14.
- Krenn E. and Finger F. (2009) Formation of monazite and rhodophane at the expense of allanite during Alpine low temperature retrogression of metapelitic basement rocks from Crete, Greece: microprobe data and geochronological implications. *Lithos* **95**, 130–147.
- Liat A., Gebauer D. and Fanning M. (2000) U–Pb SHRIMP dating of zircon from the Novate granite (Bergell, Central Alps): evidence for Oligocene–Miocene magmatism, Jurassic/Cretaceous continental rifting and opening of the Valais trough. *Schweiz. Mineral. Petrogr. Mitt.* **80**, 305–316.
- Ludwig K. R. (2003). *Isoplot/Ex version 3. 0. A geochronological toolkit for Microsoft Excel*. Berkeley Geochronological Centre Spec. Pub., Berkeley, p. 70.
- Ludwig K. R. (2009). *SQUID 2 (rev. 2.50), A User's Manual*. Berkeley Geochronology Ctr. Special Publication vol. 5, p. 104.
- Mogk D. W. (1992) Ductile shearing and migmatization at mid crustal levels in an Archaean high grade gneiss belt, northern Gallatin range, Montana, USA. *J. Metamorph. Geol.* **10**, 427–438.
- Montel J.-M. (1993) A model for monazite/melt equilibrium and application to the generation of granitic magmas. *Chem. Geol.* **119**, 127–146.
- Oberli F., Meier M., Berger A., Rosenberg C. L. and Gieré R. (2004) U–Th–Pb and $^{230}\text{Th}/^{238}\text{U}$ disequilibrium isotope systematics: precise accessory mineral chronology and melt evolution tracing in the Alpine Bergell intrusion. *Geochim. Cosmochim. Acta* **68**, 2543–2560.
- Parrish R. R. (2001) The response of mineral chronometers to metamorphism and deformation in orogenic belts. In *Continental Reactivation and Reworking*, 184 (eds. J. A. Miller, R. E. Holdsworth, I. S. Buick and M. Hand). Geol Soc Lon Spec Pub, Publishing house located in Bath, United Kingdom, pp. 289–301.
- Parrish R. R., Gough S. J., Searle M. P. and Waters D. J. (2006) Plate velocity exhumation of ultrahigh-pressure eclogites in the Pakistan Himalaya. *Geology* **34**, 989–992.
- Petrík I., Broska I., Lipka J. and Siman P. (1995) Granitoid allanite-(Ce) substitution relations, redox conditions and REE distributions (on example of I-type granitoids, Western Carpathians, Slovakia). *Geol. Carpathica* **46**, 79–94.
- Poitras F. (2002) In situ investigations of allanite hydrothermal alteration: examples from calc-alkaline and anorogenic granites of Corsica (southeast France). *Contrib. Mineral. Petrol.* **142**, 485–500.
- Rasmussen B. and Muhling J. (2009) Reactions destroying detrital monazite in greenschist-facies sandstones from the Witwatersrand basin, South Africa. *Chem. Geol.* **264**, 311–327.
- Romer R. L. and Siegesmund S. (2003) Why allanite may swindle about its true age. *Contrib. Mineral. Petrol.* **146**, 297–307.
- Romer R. L., Schärer U. and Steck A. (1996) Alpine and pre-Alpine magmatism in the root zone of the western Central Alps. *Contrib. Mineral. Petrol.* **123**, 138–158.
- Rubatto D., Williams I. S. and Buick I. S. (2001) Zircon and monazite response to prograde metamorphism in the Reynolds Range, central Australia. *Contrib. Mineral. Petrol.* **140**, 458–468.
- Rubatto D., Muntener O., Barnhoorn A. and Gregory C. (2008) Dissolution-reprecipitation of zircon at low-temperature,

- high-pressure conditions (Lanzo Massif, Italy). *American Mineralogist* **93**, 1519–1529.
- Rubatto D., Hermann J., Berger A. and Engi M. (2009) Protracted fluid-assisted melting during Barrovian metamorphism in the Central Alps. *Contrib. Mineral. Petrol.* **158**, 703–722.
- Schaltegger U. and Gebauer D. (1999) Pre-Alpine geochronology of the Central, Western and Southern Alps. *Schweiz. Mineral. Petrogr. Mitt.* **79**, 79–87.
- Schärer U., Cosca M., Steck A. and Hunziker J. (1996) Termination of major ductile strike-slip shear and differential cooling along the Insubric line (Central Alps): U–Pb, Rb–Sr and $^{40}\text{Ar}/^{39}\text{Ar}$ ages of cross-cutting pegmatites. *Earth Planet. Sci. Lett.* **142**, 331–351.
- Schmid S. M., Aebli H. R., Heller F. and Zingg A. (1989) The role of the Periadriatic line in the tectonic evolution of the Alps. In *Alpine Tectonics*, 45 (eds. D. Dietrich and M. P. Coward). Geol Soc London Spec Pub, pp. 153–171.
- Schmid S. M., Pfiffner A., Froitzheim N., Schönborn G. and Kissling N. (1996) Geophysical-geological transect and tectonic evolution of the Swiss-Italian Alps. *Tectonic* **15**, 1036–1064.
- Smith H. A. and Barreiro B. (1990) Monazite U–Pb dating of staurolite grade metamorphism in pelitic schists. *Contrib. Mineral. Petrol.* **105**, 602–615.
- Spandler C., Hermann J., Arculus R. and Mavrogenes J. (2003) Redistribution of trace elements during prograde metamorphism from lawsonite blueschist to eclogite facies; implications for deep subduction-zone processes. *Contrib. Mineral. Petrol.* **146**, 205–222.
- Stacey J. S. and Kramers J. D. (1975) Approximation of terrestrial lead evolution by a two-stage model. *Earth Planet. Sci. Lett.* **26**, 207–221.
- Stern R. A. and Berman R. G. (2000) Monazite U–Pb and Th–Pb geochronology by ion microprobe, with an application to in situ dating of an Archean metasedimentary rock. *Chem. Geol.* **172**, 113–130.
- Todd C. S. and Engi M. (1997) Metamorphic field gradients in the Central Alps. *J. Metamorph. Geol.* **15**, 513–530.
- Tribuzio R., Messiga B., Vannucci R. and Bottazzi P. (1996) Rare earth element redistribution during high-pressure-low-temperature metamorphism in ophiolitic Fe-gabbros (Liguria, north-western Italy): Implications for light REE mobility in subduction zones. *Geology* **24**, 711–714.
- Vance D. and O'Nions R. K. (1992) Prograde and retrograde thermal histories from the central Swiss Alps. *Earth Planet. Sci. Lett.* **114**, 113–129.
- Vavra G., Gebauer D., Schmidt R. and Compston W. (1996) Multiple zircon growth and recrystallization during polyphase Late Carboniferous to Triassic metamorphism in granulites of the Ivrea Zone (Southern Alps): an ion microprobe (SHRIMP) study. *Contrib. Mineral. Petrol.* **122**, 337–358.
- von Blanckenburg F., Frueh-Green G., Diethelm K. and Stille P. (1992) Nd-, Sr-, O-isotopic and chemical evidence for a two-stage contamination history of mantle magma in the Central-Alpine Bergell intrusion. *Contrib. Mineral. Petrol.* **110**, 33–45.
- Williams I. S. (1998) U–Th–Pb geochronology by ion microprobe. In: Applications of microanalytical techniques to understanding mineralizing processes. (eds. M.A. McKibben, W.C. Shanks III, W.I. Ridley). *Reviews in Economic Geology* **7**, pp 1–35.
- Wing B. A., Ferry J. M. and Harrison T. M. (2003) Prograde destruction and formation of monazite and allanite during contact and regional metamorphism of pelites: petrology and geochronology. *Contrib. Mineral. Petrol.* **145**, 228–250.

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