

Allanite micro-geochronology: A LA-ICP-MS and SHRIMP U–Th–Pb study

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Abstract

The accessory mineral allanite occurs in a wide range of igneous and metamorphic rocks and contains appreciable amounts of trace elements including the REEs, Sr, Th and U. The high degree of compositional substitution and the variable incorporation of common Pb into the allanite crystal structure, however, have limited its use for U–Th–Pb dating. Procedures have now been developed for the isotopic dating of allanite using Laser Ablation ICP-MS and the Sensitive High Resolution Ion Microprobe (SHRIMP). The accuracy of those procedures has been demonstrated by dating six Phanerozoic allanite samples of known age and with different FeO, REE and Th contents. Both analytical techniques require normalising factors for the measurement of $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$, necessitating the use of external matrix-matched standards. The wide range of Th/U in allanite from single samples makes it possible to use multiple LA-ICP-MS analyses to construct Th–Pb isochrons from which ages can be calculated with a precision of 1.4–5.8% (95% confidence level) at a spatial resolution of $32 \times 32 \times 20\mu\text{m}$. A ^{207}Pb -based correction is used to estimate the fraction of common Pb in individual LA-ICP-MS analyses with a precision of 0.3–2%. Accurate (± 1 –3%) and precise (1–2%, 95% confidence level) SHRIMP $^{208}\text{Pb}/^{232}\text{Th}$ ages can be measured directly on allanite samples with $\text{REE} + \text{Th} > 0.5$ atoms per formula unit, without additional matrix corrections at a spatial resolution of $17 \times 21 \times 2\mu\text{m}$. LA-ICP-MS is an efficient technique for dating melt-precipitated allanite (e.g., from igneous or migmatitic rocks). SHRIMP analysis is preferable for samples that have a relatively small grain size, are isotopically complex or have relatively large common Pb contents (e.g., metamorphic allanite).

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1. Introduction

The accessory mineral allanite $[(\text{Ca}, \text{REE}, \text{Th})_2(\text{Fe}^{2+}, \text{Al})_3\text{Si}_3\text{O}_{12}(\text{OH})]$ is a prime target for dating geological processes because it plays a key role in the storage and

mobility of geochemically important trace elements including the rare earth elements (REE), strontium and thorium. Allanite occurs in a wide range of rock types, but is most commonly reported as an accessory phase in metaluminous granites to tonalites and pegmatites (Exley, 1980; Schmidt and Thompson, 1996; Giere et al., 1999) and in regional Barrovian metamorphic terranes (Smith and Barreiro, 1990; Wing et al., 2003). Of particular interest is the occurrence of allanite in mafic to intermediate

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metamorphic rocks, and its crystallisation under (upper)-amphibolite grade subsolidus or melt-present conditions (Sorensen and Grossman, 1989; Gieré, 1996; Finger et al., 1998). Allanite may also form as a product of prograde mineral reactions during (ultra) high-pressure metamorphism (Franz et al., 1986; Tribuzio et al., 1996; Hermann, 2002; Spandler et al., 2003). In both situations, allanite is stabilised, relative to epidote, by the incorporation of trace elements, including LREE and Th (Hermann, 2002).

Allanite forms part of the epidote solid solution series via the charge-balanced coupled substitution: $\text{REE}^{3+} + \text{Fe}^{2+} \Leftrightarrow \text{Ca}^{2+} + \text{Fe}^{3+}$ (Dollase, 1971), although it can contain minor to trace amounts of other elements including: Th^{4+} , U^{4+} , Sr^{2+} , Mn^{2+} , Mg^{2+} , P^{5+} , Ti^{4+} (Table 1), and Zr^{4+} , Cr^{3+} , Pb^{2+} , Ba^{2+} (Deer et al., 1986). The relative abundance of these elements is determined by the allanite crystal structure, which is dependent on a number of factors including pressure (P), temperature (T), oxygen fugacity, hydrogen fugacity, and bulk-rock/melt/fluid composition (Affholter, 1987; Sorensen, 1991; Bingen et al., 1996; Gieré et al., 1999; Wing et al., 2003). Here we define allanite as having a REE + Th content ≥ 0.5 atoms per formula unit (apfu), or

$< 20\text{wt.}\% \text{ CaO}$, as classified by Gieré and Sorensen (2004). Allanite incorporates Th in preference to U (typically 0.05–3wt.% and 10–3000ppm, respectively; Gieré and Sorensen, 2004). Thorium (and U) may be incorporated through substitution for the REEs: $\text{Th}^{4+} + \text{Ca}^{2+} \Leftrightarrow 2\text{REE}^{3+}$ (Gromet and Silver, 1983) or changes in oxidation state: $\text{Th}^{4+} + \text{Fe}^{2+} \Leftrightarrow \text{REE}^{3+} + \text{Fe}^{3+}$ (Gieré et al., 1999).

Uranium–Th–Pb dating of metamorphism is most commonly attempted using accessory zircon and monazite. In some cases, however, factors such as unsuitable bulk-rock composition (Smith and Barreiro, 1990; Broska and Siman, 1998) and relatively low metamorphic temperatures ($< 700^\circ\text{C}$) (e.g., Gebauer et al., 1997), can impede (re)-crystallisation and/or isotopic homogenisation of these phases in response to metamorphism, and therefore their usefulness as geochronometers. Allanite may crystallize in response to a wider range of metamorphic P – T conditions than zircon, or even monazite, mainly due to the solid solution between allanite and epidote (Janots et al., 2006a,b) and the propensity of allanite to incorporate a high concentration of trace elements into its crystal structure (Hermann,

Table 1
Composition of allanite used in this study determined by electron microprobe

	AVC			CAP			Siss			Tara			BC			Bona		
	iBSE	hBSE	hBSE	iBSE	hBSE	iBSE	hBSE	iBSE	IBSE	hBSE	iBSE	Altered zone	hBSE	iBSE	IBSE	hBSE	iBSE	IBSE
SiO ₂	31.0	31.4	31.5	32.2	31.3	31.8	31.8	33.9	35.2	31.5	32.2	33.1	32.7	34.1	34.9	31.1	31.7	32.1
Al ₂ O ₃	14.2	13.5	13.8	15.5	14.6	15.9	16.5	18.2	22.2	14.3	15.7	18.0	16.0	18.4	19.5	14.0	15.7	16.5
MgO	0.94	0.23	0.83	1.65	1.64	1.23	1.95	0.88	0.35	1.75	1.52	0.71	0.87	0.67	0.93	1.51	1.18	0.80
FeO	16.3	17.3	17.0	12.4	13.2	12.5	13.9	13.6	11.8	14.8	13.7	12.9	14.5	13.6	13.3	15.0	14.6	14.5
MnO	0.94	0.75	0.61	0.27	0.37	0.38	0.27	0.41	0.29	0.57	0.76	0.64	0.52	0.57	0.52	0.47	0.46	0.50
CaO	9.35	8.43	8.93	10.3	9.8	10.3	12.5	14.9	19.0	10.2	10.4	13.1	12.7	13.8	16.2	12.0	14.0	15.0
Y ₂ O ₃	0.21	0.58	0.47	0.12	0.15	0.12	0.03	0.04	0.01	0.17	0.12	0.18	0.03	0.03	0.05	0.07	0.11	0.14
ThO ₂	0.76	1.48	1.57	1.22	1.28	1.22	3.06	2.46	1.60	1.10	1.04	0.55	0.71	0.37	0.26	1.77	2.47	1.82
TiO ₂	1.57	0.88	1.05	1.29	1.76	0.89	0.58	0.40	0.13	0.97	1.09	0.61	0.69	0.24	0.34	0.88	0.61	0.57
La ₂ O ₃	5.85	4.95	5.08	6.60	7.07	6.43	5.93	3.65	1.81	6.47	6.08	4.65	5.05	3.46	2.93	6.42	4.21	4.31
Ce ₂ O ₃	11.7	11.3	11.2	11.8	11.7	11.9	9.04	7.12	3.93	11.7	11.3	8.72	9.95	9.26	6.66	10.7	8.22	7.69
Pr ₂ O ₃	1.15	1.30	1.28	1.04	1.22	1.07	0.66	0.54	0.35	1.01	1.04	0.88	0.88	1.04	0.67	1.11	1.00	0.90
Nd ₂ O ₃	3.98	5.34	4.88	3.39	3.85	3.59	1.58	1.90	1.21	3.18	3.00	2.44	2.87	3.27	2.57	3.03	3.09	2.67
Sm ₂ O ₃	0.54	0.80	0.69	0.14	0.23	0.34	0.15	0.12	0.10	0.41	0.19	0.29	0.15	0.40	0.22	0.18	0.31	0.28
Gd ₂ O ₃	0.17	0.55	0.40	0.21	0.21	0.25	0.14	0.08	0.08	0.08	0.03	0.10	0.18	0.22	0.17	0.08	0.09	0.13
U ₂ O ₃	bdl	bdl	0.02	0.00	0.03	0.01	0.05	0.07	0.07	bdl	bdl	0.01	0.01	bdl	0.01	0.06	0.07	0.04
P ₂ O ₅	bdl	0.05	0.01	bdl ^a	bdl	0.02	bdl	0.01	bdl	bdl	0.32	bdl	0.05	0.01	bdl	bdl	bdl	bdl
SrO	0.03	0.09	bdl	bdl	0.04	bdl	bdl	bdl	bdl	0.06	0.06	0.02	bdl	bdl	0.13	bdl	0.13	bdl
Total ^b	98.1	98.9	99.2	98.3	98.2	98.0	98.2	98.1	98.1	98.3	98.2	96.9	97.9	99.4	99.3	98.1	97.9	98.0
REE + Th ^c	0.86	0.91	0.87	0.83	0.89	0.85	0.68	0.49	0.29	0.84	0.76	0.60	0.65	0.59	0.42	0.75	0.59	0.54
Fe ³⁺ /Fe _{total} ^d	0.26	0.11	0.14	0.13	0.15	0.06	0.37	0.44	0.65	0.22	0.28	0.63	0.30	0.40	0.61	0.26	0.34	0.42

hBSE = high emission Back-Scatter Electrons, IBSE = low emission BSE, iBSE = intermediate emission BSE.

^a Below detection limit.

^b Totals do not include water, which is likely to be 1–2wt.%.

^c Atoms per formula unit.

^d Fe³⁺/Fe_{total} calculated by charge balance on the basis of 8 cations and 12.5 oxygens.

2002; Spandler et al., 2003). Allanite is often larger ($> 100\mu\text{m}$) than zircon and monazite, and may preserve internal textural, chemical, and isotopic zoning. Just as the REE composition of zircon reflects the growth of associated accessory and major minerals (Rubatto, 2002; Rubatto and Hermann, 2003), allanite preserves distinctive REE patterns characteristic of different parageneses (see Gieré and Sørensen, 2004), making it an effective chemical recorder of metamorphic processes.

Allanite dating can potentially be used to address important geological questions such as the timing of eclogite-facies metamorphism, emplacement of calc-alkaline magmas and partial melting associated with

convergent margins. U–Th–Pb dating of allanite remains largely unexploited however, because of the high and variable levels of substitution of trace elements, including initial Pb, into its crystal structure and its tendency to become metamict (Poitrasson, 2002; Romer and Siegesmund, 2003). Consequently, little is known about the behaviour of the U–Th–Pb isotopic system in allanite and there are no widely available allanite standards. Thus most previous U–Th–Pb dating of allanite employed isotope dilution TIMS methods (von Blanckenburg, 1992; Barth et al., 1994; Oberli et al., 2004).

Allanite is so chemically and texturally complex that ideally it should be dated by spot analysis. In this way

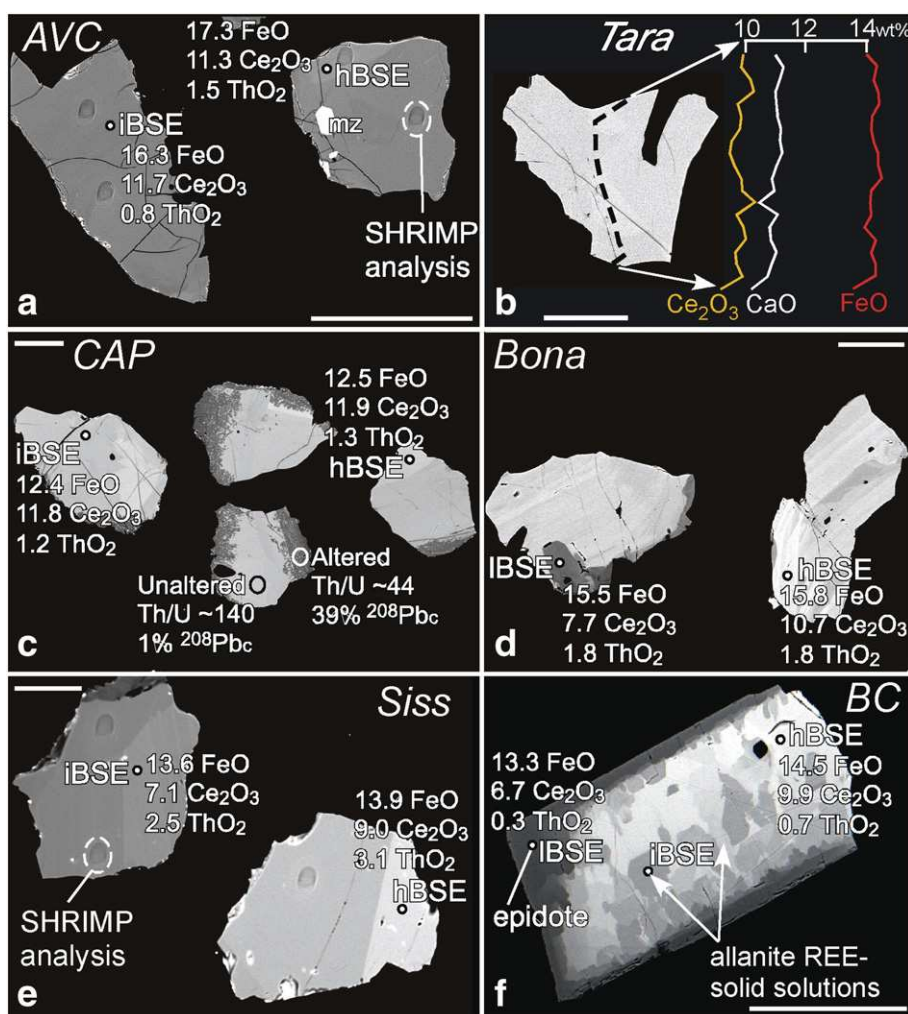


Fig. 1. Backscattered electron images of the allanite samples. BSE contrast is maximised for all samples, hBSE = high emission Back-Scatter Electrons, iBSE = intermediate emission Back-Scatter Electrons, IBSE = low emission Back-Scatter Electrons. Compositional information is taken from Table 1 for each sample and is shown as wt.% concentrations. Pits in 'a' and 'e' are SHRIMP analyses. Small bright spots in 'b' are EMP analysis sites. FeO, Ce_2O_3 and CaO traverse of Tara in 'b' demonstrate a lack of significant zoning. Alteration at grain boundaries of CAP in 'c' is promoted by network fractures that acted as fluid pathways. Scale bars are $100\mu\text{m}$. Mz = monazite.

chemical and isotopic mineral domains can be distinguished and either selectively avoided (e.g., alteration, partial isotopic resetting) or targeted (e.g. multiple age domains, chemical zones). The development of high-mass resolution ion microprobes, such as SHRIMP (Compston et al., 1984) makes it possible to sample grains at a spatial resolution of $\sim 100\mu\text{m}^3$ with a precision that allows the isotopic characterisation of individual crystal domains. The pioneering study of allanite by Catlos et al. (2000) that used a Cameca 1270 ion microprobe, however, discovered severe matrix effects apparently related to differences in the FeO contents of their samples. The in situ capabilities and precision of Laser Ablation ICP-MS intra-grain isotopic analysis for geochronology have also developed rapidly over recent years (e.g., Storey et al., 2004) and now enable the study of complex matrices that have compromised the use of SIMS techniques in the past. Routine U–Th–Pb LA-ICP-MS dating of allanite has previously been limited mainly by a lack of suitable standards and of information on the ablation characteristics of other actinide-rich minerals.

The present paper investigates the allanite U–Th–Pb geochronometer through comparative analyses of six igneous allanite samples using newly developed Laser Ablation Quadrupole ICP-MS and Sensitive High Resolution Ion MicroProbe (SHRIMP) procedures. The accuracy and precision of the analytical techniques are demonstrated by comparing the Th–Pb and U–Pb ages measured in situ with those measured by isotope dilution thermal ionisation mass spectrometry (ID-TIMS). In the two cases where TIMS analyses are not available, previous dating results and/or co-existing zircon U–Pb ages are used for reference. Normalisation factors used to correct for instrument-induced inter-elemental fractionation in both cases have been calibrated using external allanite mineral standards. Possible matrix effects on the SHRIMP analyses related to Fe and/or REE contents have been assessed using samples with a range of compositions. The accurate correction of allanite analyses for common Pb is a major focus of this study.

2. Allanite samples

2.1. AVC and CAP

The Atesina Volcanic Complex (AVC) rhyolite ($46^\circ 34'$ N, $11^\circ 40'$ E) and Cima D'Asta Pluton (CAP) granodiorite ($46^\circ 07'$ N, $11^\circ 29'$ E) are from a co-genetic igneous suite located in the Southern Alpine Domain, northern Italy (Barth et al., 1994). Both AVC and CAP contain accessory allanite + apatite + zircon $\pm$ titanite. The AVC and CAP

allanite grains are euhedral to subhedral, 200–400 μm diameter, dark brown and vitreous. Both samples show some compositional variation and grain-scale fracturing (Table 1, Fig. 1a and c). The AVC and CAP grains have REE + Th contents that range from 0.86 to 0.91 and 0.83 to 0.89 apfu, respectively. Two single allanite crystals from AVC and four from CAP gave mean isotope dilution Th–Pb ages of $276.3 \pm 2.2\text{Ma}$ and $275.5 \pm 1.5\text{Ma}$, respectively (Table 2; Barth et al., 1994). Despite a later overprinting hydrothermal event, Barth et al. (1994) reported no Pb loss from the Th–Pb system. Whole rock REE and Sm–Nd isotopic signatures were also unaffected. The ID-TIMS $^{208}\text{Pb}/^{232}\text{Th}$ ages have been reproduced within error by ion microprobe (Catlos et al., 2000) and LA-ICP-MS (Cox et al., 2003). Alteration observed at the grain margins of some CAP allanites (Fig. 1c), is associated with a decrease in Th/U and gain of ^{204}Pb and such zones have been avoided (Table BD4).

2.2. Siss and Bona

The Siss3 (Siss) tonalite ($46^\circ 18'$ N, $9^\circ 45'$ E) and Bona1 (Bona) granodiorite ($46^\circ 19'$ N, $9^\circ 45'$ E) samples are from the Central-Alpine Bergell intrusion, northern Italy. The samples are those analysed by von Blanckenburg (1992) using ID-TIMS. The tonalite and granodiorite contain accessory allanite, apatite, zircon and titanite. The Siss allanite grains are $\leq 150\mu\text{m}$ diameter and have more pronounced compositional zoning from a REE + Th of 0.29 apfu (epidote-rich) to 0.68 (allanite-rich) (Table 1). Zoning is visible in BSE images (Fig. 1e) and optically the grains have dark brown–black cores and (light) brown rims. The Bona allanite grains are 100–300 μm diameter, are more compositionally homogeneous in REE, Th and U, and contain fewer inclusions than the Siss allanites (Fig. 1d). The U–Pb and Th–Pb systems show no evidence of post-emplacement Pb loss (von Blanckenburg, 1992; Oberli et al., 2004), and Sm–Nd isotopes indicate an absence of inherited components in allanite (von Blanckenburg, 1992). Bulk analysis of eleven Siss3 allanite grains and five Bona1 grains yielded Th–Pb ages of $31.5 \pm 0.4\text{Ma}$ and $30.1 \pm 0.3\text{Ma}$, respectively (Table 2; von Blanckenburg, 1992). Zircons from Siss3 yielded a $^{206}\text{Pb}/^{238}\text{U}$ age of $31.9 \pm 0.1\text{Ma}$, in close agreement with the allanite $^{208}\text{Pb}/^{232}\text{Th}$ age, whereas zircon from Bona1 contained inheritance (von Blanckenburg, 1992).

2.3. BC

The Ecstall Pluton (BC) ($54^\circ 8'$ N, $130^\circ 0'$ W) is located adjacent to the Prince Rupert shear zone, British

Table 2

Compositional variation of samples and summary of SHRIMP and LA-ICP-MS age results

	ThO ₂ (ppm)	Reference age	SHRIMP	% ²⁰⁸ Pb _c ²	SHRIMP	% ²⁰⁶ Pb _c	Std	LA-ICP-MS isochron age	LA-ICP-MS single-spot mean age	Std
	U ₂ O ₃ (ppm)									
	sum REE ₂ O ₃ (wt.%)	(Ma) ³	Pb/Th age ¹		Pb/U age					
AVC	8000–18,000	276.3 (2.2) ⁴	280.0 (2.1)	0.9–1.4	289.6 (5.6)	16–30	CAP	274.0 (7.0)	274.9 (1.2)	CAP
	20–200		MSWD = 0.71		MSWD = 0.5			MSWD = 0.2	MSWD = 0.7	
	23		N = 24/26		N = 24/26			N = 29/30	N = 30/30	
CAP	8000–15,000	275.5 (1.5) ⁴	276.9 (2.2)	0.7–1.0	275.0 (4.7)	13–21	Tara	277.7 (5.0)	277.9 (1.0)	AVC
	40–200		MSWD = 0.5		MSWD = 0.9			MSWD = 0.9	MSWD = 1.5	
	22		N = 25/27		N = 23/26			N = 43/49	N = 44/49	
Siss	900–30,000	31.5 (0.4) ⁵	31.4 (0.3)	12–25	35.5 (1.6)	55–88	CAP	NA.	NA.	NA.
	50–700		MSWD = 1.1		MSWD = 2.5					
	10–18		N = 14/14		N = 13/14					
Bona	9000–25,000	30.1 (0.3) ⁵	30.5 (0.4)	14–22	36.5 (2.0)	65–85	CAP	31.1 (1.8)	30.9 (0.2)	AVC
	40–700		MSWD = 0.8		MSWD = 1.0			MSWD = 0.2	MSWD = 0.4	
	20		N = 10/11		N = 10/11			N = 42/42	N = 40/42	
BC	2000–8000	90.8 (1.0) ⁶	92.4 (2.1)	9.0–24	96.5 (5.3)	55–75	CAP	88.6 (1.5)	89.4 (0.8)	AVC
	50–500		MSWD = 1.6		MSWD = 0.6			MSWD = 0.3	MSWD = 0.31	
	13–19		N = 8/10		N = 8/10			N = 23/23	N = 23/23	
Tara	9000–12,000	412.0 (1.4) ⁷	414.9 (3.3)	0.5–1.0	419.3 (7.7)	12–25	CAP	414.4 (6.2)	417.5 (1.4)	AVC
	20–150		MSWD = 0.8		MSWD = 0.9			MSWD = 0.3	MSWD = 0.3	
	22		N = 26/28		N = 24/28			N = 69/69	N = 63/69	

¹All ages are calculated at the 95% confidence level, on the basis of 1σ error.²% of common ²⁰⁸Pb in sample.³Reference ages are ²⁰⁸Pb/²³²Th ages, with the exception of BC (U–Pb zircon) and Tara (Rb–Sr).⁴Barth et al. (1994), ⁵von Blanckenburg (1992), ⁶Butler et al. (2002), ⁷Williams et al. (1983). NA = not analysed.

Columbia. The granodiorite sample (98-19) kindly provided by L. Hollister is from the interior of the pluton. ID-TIMS analyses of four zircon fractions by Butler et al. (2002), yielded a concordant U–Pb age of 90.8 ± 1.0 Ma (Table 2). In the absence of previous allanite ages, the zircon U–Pb age is used for reference. The BC allanite grains (50–150 μm diameter) are complexly zoned and typically consist of REE-rich allanite solid solution core (REE + Th of 0.59–0.65 apfu), surrounded by an epidote rim (REE + Th of 0.42 apfu; Table 1, Fig. 1f).

2.4. Tara

The Tara granodiorite (36° 50' S, 148° 50' E) is from the Berridale Batholith, southeast Australia. It contains accessory zircon, titanite, apatite and allanite. The allanite grains are 100–300 μm diameter, dark brown, vitreous, and have conchoidal fractures. Fig. 1b shows a traverse of FeO, CaO and Ce₂O₃ for a typical Tara allanite, indicating only small compositional variations. The allanite grains are inclusion-poor, lack complex internal zoning and show only rare alteration features, which reflects the shallow emplacement and relatively rapid cooling of the pluton (Williams et al., 1983). The

Tara allanite REE + Th composition varies from 0.77 to 0.84 apfu, whereas altered zones have lower REE + Th contents of ~ 0.60 apfu (Table 1, Fig. 1b). No ID-TIMS U–Th–Pb data are available. Zircon U–Pb data obtained by isotope dilution is discordant due to inheritance and post-emplacement Pb loss (Williams et al., 1983). Twenty SHRIMP analyses of zircon also produced a spread of ²⁰⁶Pb/²³⁸U ages from 320 to 458 Ma with a cluster of ages ca. 417 Ma (Gregory, unpublished). A preliminary SHRIMP U–Pb age of ca. 417 Ma was recently determined for Tara zircon (R. Ickert, pers. comm.). Based on biotite Rb–Sr and K–Ar ages reported by Williams et al. (1982) and hornblende K–Ar and Ar–Ar ages measured by Tetley (in press), Williams et al. (1982) concluded that the pluton was emplaced at 412 ± 1.4 Ma (Table 2).

3. Analytical protocols

3.1. Electron microprobe analysis and compositional imaging

Allanite grains were imaged by backscattered electrons (BSE) using the Cambridge S360 SEM at the ANU Electron Microscopy Unit (2 nA, 15 kV and 15 mm w.d.),

prior to isotopic analysis. High-resolution BSE images revealed mineral domains defined by zoning in the heavier (high atomic number) REEs and to a lesser extent in Th and U (Fig. 1), the abundances of which were typically correlated with elemental substitutions involving Ca and Fe (e.g., Siss and BC in Table 1). Wavelength dispersive electron microprobe (EMP) analysis was subsequently used for an independent chemical characterisation of the allanite samples, in order to (1) assess the effects of compositional differences on ion microprobe analyses, (2) calibrate LA-ICP-MS geochemical data (CaO as internal standard), (3) cross-check ion microprobe Th/U measurements and (4) help avoid dating of altered or chemically anomalous domains. The analyses were made using the Cameca SX100 at RSES, ANU with working conditions of 15kV, 20nA and a defocused electron beam (5µm) to avoid crystal damage. Background noise and interference effects were minimised through careful selection of background and REE peak positions, and choice of crystal spectrometer for optimum resolution (Table BD2, Williams, 1996). Synthetic REEPO₄, UO₂ and ThO₂ standards from the Chinese Ceramic Society were used for initial calibrations. Internal consistency was monitored by analysing in-house silicate mineral standards and the Tara allanite. On-line ZAF procedures corrected for dead time and background. Allanite EMP analyses were normalised to 8 cations and 12.5 oxygens. Fe³⁺/Fe²⁺ was estimated on the basis of cation charge balance.

3.2. Laser Ablation ICP-MS

LA-ICP-MS Pb/Th and compositional analyses of allanite crystal domains were carried out using an ArF Excimer laser system (193nm wavelength) coupled to a quadrupole ICP-MS (Agilent 7500S) at RSES, ANU. The instrumental set-up followed that described by Eggins et al. (1998) and Eggins and Shelley (2002). The signal response of the analyte and the precision of the time-dependent isotope signals were optimised by ablating into a He–Ar carrier gas (mixed 1:3) above the sampling site for injection into a signal smoothing manifold and then plasma (Eggins et al., 1998). Depending on the target, the laser was focused to produce an ablation pit ranging in diameter from 32 to 54µm, using a laser pulse rate of 5Hz and a laser irradiance of approximately 10–12J/cm². Rare earth element (REE) concentrations were determined by LA-ICP-MS using similar working conditions and a spot size of 32µm diameter. Data acquisition for each element during a single analysis included a total of 70 to 80 mass spectrometer sweeps, comprising a gas background of

20–25 sweeps. During the time-resolved analysis, contamination or alteration was detected by monitoring several elements and only the relevant part of the signal was integrated. A synthetic glass (NIST 612) was used as standard material, assuming the trace element concentrations from Pearce et al. (1997). The internal standard was CaO previously analysed by electron microprobe. Each isotopic analysis took about 65s in time-resolved (peak hopping) analysis mode, 40s of ablation and 25s measuring the gas blank. The approximate hole depth for 40s ablation was 20µm. Dwell times were set to 0.01s for ²⁸Si, ³¹P, ⁴³Ca (internal standard), ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁶³Dy, ¹⁷⁵Lu, and 0.04s for the Pb isotopes, ²³²Th and ²³⁸U, enabling ~ 100 mass sweeps per analysis. ²⁰⁴Pb was not measured because systemic ²⁰⁴Hg swamped the ²⁰⁴Pb signal (see Section 4.3.1).

At the start of each analytical session, torch position and lens tunings were adjusted to maximize sensitivity for the appropriate masses (Pb isotopes, Th and U) and stability, while minimizing the production of molecular compounds as monitored by ThO⁺/Th⁺, a readily produced, post-plasma oxide. The maximum allowed ThO⁺/Th⁺ was 0.5%, and interferences from all other species were assumed to be this, or less. Lead hydride interferences were checked on a pure Pb sample, and assuming a maximum PbH/Pb of 0.5% (extreme), the effect on the ²⁰⁸Pb/²³²Th for Tertiary grains was to increase the age by less than 0.5Ma. Peak centering was checked and the ETP electron multiplier voltage was optimised using Agilent software. Dead time was set on installation and checked annually. Cross-calibration of the two counting modes provided in this detector to expand dynamic range (pulse and analogue) was conducted at session commencement by providing a ~ 2 × 10⁶cps signal to the electron multiplier. RF power was set at 1200W. All other torch, gas flows and lens settings changed daily, but typically torch distance from cones was 5.6mm, and gas flow was 1.2L/min. This produced a sensitivity of 1000cps/ppm for ²⁰⁸Pb and 1400cps/ppm for ²³²Th for NIST 610 glass from surface scans using a 32µm spot.

Signal intensity and elemental ratios evolved during each analysis. Raw data were processed off-line using a macro-based EXCEL spreadsheet, which enabled selective integration of isotope signals prior to data reduction in order to avoid heterogeneities such as inclusions. Each analysis was corrected for background gas blank and inter-elemental fractionation (see Section 4.2). Unknowns were referenced directly to NIST 610 glass (for ²³²Th/²³⁸U, Si, P, Ca and REE ratios) and AVC allanite (U–Th–Pb isotope ratios). These materials were re-analysed once after every 5 unknowns. Data sets for

standard allanites were vetted for outliers (those deviating by > 2% from the mean $^{208}\text{Pb}/^{232}\text{Th}$).

3.3. SHRIMP

Allanite was analysed for U–Th–Pb isotopes using the SHRIMP II and Reverse Geometry (RG) ion microprobes at RSES, ANU. Epoxy-mounted grains of allanite were analysed with a 3–4 nA, 10 kV primary O_2^- beam focussed to a $\sim 20\mu\text{m}$ diameter spot. The analytical procedure was broadly similar to that for zircon (Williams, 1998), except that the reference peak was $^{139}\text{La}^{28}\text{Si}^{16}\text{O}_2$ (mass 198.873 amu) and ^{232}Th was measured in addition to ThO for calibration purposes (Table 3). Each analysis consisted of six scans through the masses. The CAP standard was analysed after three unknowns and all samples, except BC and Bona, were cast in the same grain mount. At mass resolution ~ 5500 the Pb, Th and U isotopes were resolved from all major interferences. Energy filtering was not required, but the retardation lens on SHRIMP II was used to suppress scattered ions. Background count rates averaged 0.05 cps/nA primary O_2^- . As allanite is a hydrous mineral there is the potential for hydride interferences. There was no significant peak at mass 209 (^{208}PbH), however, indicating that Pb hydrides were negligible. SHRIMP $^{208}\text{Pb}^+/^{206}\text{Pb}^+$ secondary ion ratios measured on the CAP and AVC allanites were equal within error ($\sim 1\%$) to the respective ID-TIMS values, indicating no significant mass fractionation of the Pb isotopic compositions (e.g., Stern and Sanborn, 1997). Th/U ratios for allanite were estimated from a $f_{\text{ThO}^+/\text{UO}^+}$ value (0.83–0.89) derived from the measured ThO^+/UO^+ vs. $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ values (Williams et al., 1996) and the U contents were obtained by electron microprobe. Data were reduced using ANU Prawn/Lead 6.5 software (1996) written by the RSES Ion Probe Group and ages calculated using Isoplot/Ex (Ludwig, 2003).

Table 3

Typical run table for allanite U–Th–Pb SHRIMP analysis of the allanite samples presented here

Mass station	Isotope	Mass (amu)	Time (s)	Delay (s)
1	$^{199}\text{LaSiO}_2$	198.875	2.0	4.0
2	^{204}Pb	203.948	10.0	1.0
3	bkgd	203.998	10.0	1.0
4	^{206}Pb	205.939	30.0	2.0
5	^{207}Pb	206.931	30.0	1.0
6	^{208}Pb	207.929	5.0	1.0
7	^{232}Th	232.007	5.0	1.0
8	^{238}U	238.063	10.0	2.0
9	^{248}ThO	248.054	2.0	2.0
10	^{254}UO	254.044	2.0	2.0

4. Standardisation and matrix corrections

The magnitude of elemental fractionation observed during in situ analysis is significantly greater than that encountered for ID-TIMS. The two techniques presented here provide a complementary view of U–Th–Pb behaviour. SHRIMP isotope analysis displays good down-hole behaviour, but has a strong matrix dependency, where some of the fractionation is probably due to changing the relative proportion of complex molecules. For SHRIMP analysis of zircon, enrichment of Pb^+ over U^+ can be as much as a factor of three. In contrast, LA-ICP-MS shows significant Pb/U and Pb/Th down-hole fractionation on the order of 10's % (e.g., Black et al., 2004; see Section 4.2). The effect of compositional variation on the sample ionisation efficiency is small relative to SHRIMP, however, due to ionisation taking place removed from the sample surface (e.g., Eggins et al., 1998; Mason and Mank, 2001). This effectively minimises the production of complex molecular interferences, notably oxides that are readily produced during ion microprobe sputtering.

Previous studies have demonstrated that to achieve high accuracy, ion microprobe analyses must be calibrated against a matrix-matched standard (Compston et al., 1984; Catlos et al., 2000; Stern and Berman, 2000; Black et al., 2004; Fletcher, 2004). Conversely, it has recently been claimed that the standards used for LA-ICP-MS isotopic analyses of titanite and allanite need not be matrix-matched (Storey et al., 2004). Any matrix effect needs to be evaluated at two stages of the dating process. Firstly when choosing a standard material, glass or mineral (i.e., structural), for the isotopic measurement. Secondly, when using that standard to analyse a mineral of variable composition (i.e., chemical). Matrix effects due to compositional variations are particularly important for allanite, because compared to other accessory minerals commonly used for U–Th–Pb dating, it has a much greater range of elemental substitution. This is demonstrated clearly by electron-backscatter imaging (Fig. 1), which shows the intra-crystal variation in mean atomic number, determined by heavy (high Z) elements REE and Th.

The range of allanite compositions used to test our procedures is listed in Tables 1 and 2. The REE composition of each sample, determined by LA-ICP-MS, is displayed in Fig. 2 (Table BD1). REE patterns were normalised to chondritic values (McDonough and Sun, 1995). All of the samples have fractionated LREE-enriched patterns (note the HREE content varies by seven fold), and negative Eu anomalies that are typical of igneous allanite (Giere and Sorensen, 2004). Significant

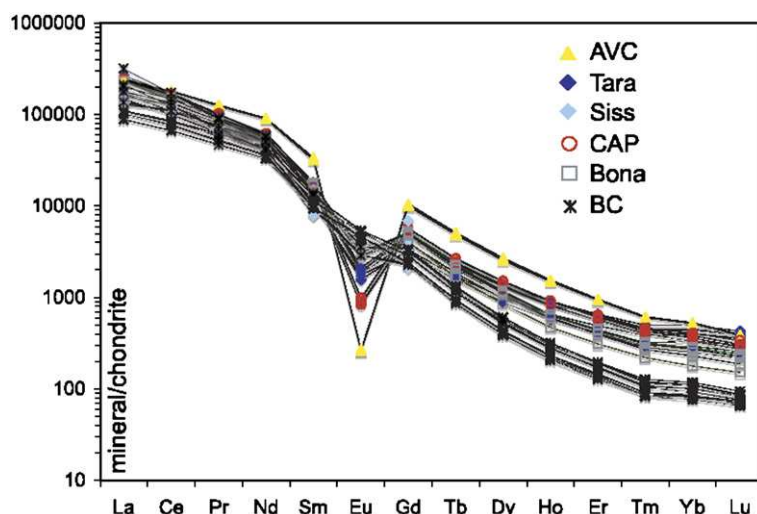


Fig. 2. Chondrite-normalised REE patterns for the allanite samples used for this study. REE patterns are averages of multiple LA-ICP-MS trace element analyses (see Table BD1).

compositional differences (> 1wt.%) between the test samples are shown in Table 1. Notably, AVC has the largest total FeO content of 16.3–17.3wt.%, CAP has the lowest FeO content of 12.4–13.2wt.%, both Siss and BC grains have the lowest Ce₂O₃ content of 3.9–9.0wt.% and 6.7–9.9wt.%, respectively, BC has the lowest concentration of ThO₂ at 0.3–0.7wt.%, and Siss contains the most ThO₂ at 1.6–3.1wt.%. Tara displays intermediate compositions.

4.1. SHRIMP calibration

The energy distributions of sputtered Pb⁺, Th⁺ and U⁺ secondary ions and ion-oxides from allanite are similar to those observed for zircon and monazite, and a linear relationship is observed between $\ln(\text{ThO}^+/\text{Th}^+)$ and $\ln(^{208}\text{Pb}^+/\text{Th}^+)$, and $\ln(\text{UO}^+/\text{U}^+)$ and $\ln(^{206}\text{Pb}^+/\text{U}^+)$ (Fig. 3). A calibration approach analogous to that for zircon was therefore used to correct for inter-elemental fractionation (Williams, 1998). Correction factors were derived from analyses of the standard allanite using an empirical power law relationship (Claoue-Long et al., 1995):

$$\ln[^{208}\text{Pb}^*/^{232}\text{Th}^+] = b \times \ln[^{248}\text{ThO}^+ / ^{232}\text{Th}^+] \quad (1)$$

where b is the slope of the linear regression, (for allanite $b \approx 1.85$). ThO^+/Th^+ is the measured ratio and $^{208}\text{Pb}^*/\text{Th}^+$ is the measured ratio corrected for common Pb. Due to the high Th/U in allanite, $^{208}\text{Pb}/^{232}\text{Th}$ was calculated directly from the $^{208}\text{Pb}^+ / ^{232}\text{Th}^+$, $^{248}\text{ThO}^+ / ^{254}\text{UO}^+$ and $^{248}\text{ThO}^+ / ^{232}\text{Th}^+$ secondary ions, rather than a calibration based on UO^+/U^+ .

Four allanite samples AVC, CAP, Tara and Siss were tested by ion microprobe in a round-robin experiment. Calculated weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ ages of Tara and Siss are compatible when referenced to CAP, as is the Bona allanite, which was analysed separately against CAP. The AVC however, which contains up to 17.3wt.% FeO_{total} (up to 30% more than CAP), has a positive discrepancy of 2.4 ± 2.6 from its ID-TIMS age (Table 2). This discrepancy is not significant and Pb/Th ages for the CAP, Tara, Siss and AVC are statistically indistinguishable from their reference ages (Table 2). Similar observations for $^{206}\text{Pb}/^{238}\text{U}$ ages were limited by low measurement precision and the presence of excess ^{206}Pb (from decay of initial ^{230}Th). No additional bias related to REE content was observed from the comparison of results obtained from the Siss allanite (only 3.9–9.0wt.% Ce₂O₃) to the CAP, AVC and Tara allanites (Table 2, Fig. 4).

Stern and Berman (2000) have reported that SHRIMP U–Th–Pb ages measured on monazite are affected by its high ThO₂ content (up to 10wt.%). Allanite typically contains ≤ 3 wt.% ThO₂ (and even less U) so the matrix effects of Th (and U) may not be so important. They were tested by comparing analyses of the Siss and BC allanites, which have essentially the same composition except for ThO₂, with maximum contents of 3.4wt.% and 0.7wt.%, respectively (Table 1). The mean SHRIMP Pb–Th ages of the BC and Siss allanites are within analytical error of their reference ages (Table 2). The higher precision of the Siss allanite analysis is due in part to better ^{232}Th and ^{208}Pb counting statistics. Minor elements, such as Mg, Mn and Sr also substitute in allanite. These elements are present at low concentrations (< 2wt.%) in the samples

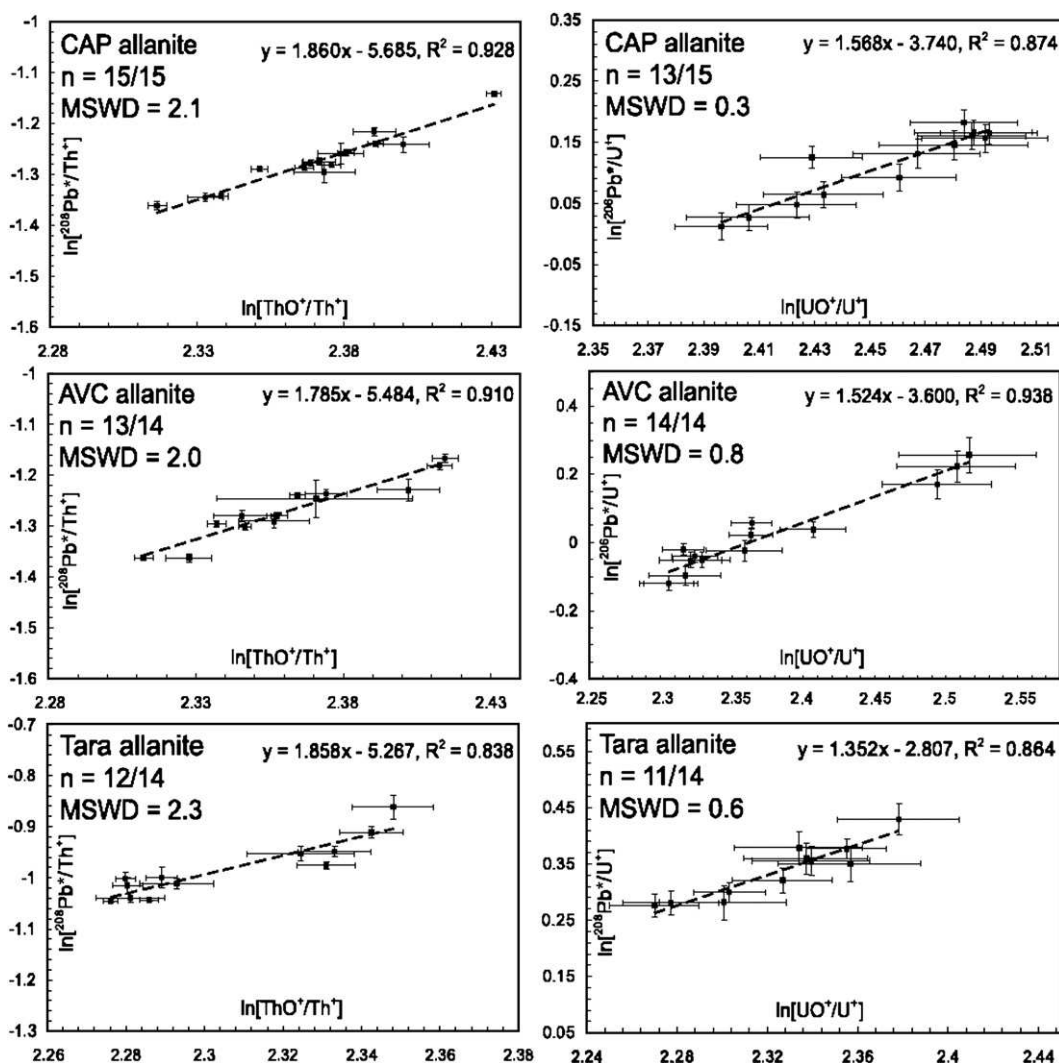


Fig. 3. $\ln[^{208}\text{Pb}^*/^{232}\text{Th}^+]$ vs. $\ln[\text{ThO}^+/\text{Th}^+]$ and $\ln[^{206}\text{Pb}^*/^{238}\text{U}^+]$ vs. $\ln[\text{UO}^+/\text{U}^+]$ calibration plots for the AVC, CAP and Tara allanites. The linear arrays are consistent with power law relationships between $^{208}\text{Pb}^*/^{232}\text{Th}^+$ and ThO^+/Th^+ , and $^{206}\text{Pb}^*/^{238}\text{U}^+$ and UO^+/U^+ respectively. Secondary ion ratios illustrated here were measured on SHRIMP II during a single analytical session. Error bars are 1σ .

analysed for the present study, however, and therefore exert negligible influence on the Pb^+ , Th^+ (U^+) ionisation efficiencies.

Despite matrix compositional variations of up to 30% for $\text{FeO}_{\text{total}}$, 66% for Ce_2O_3 and 80% for ThO_2 for the tested allanite samples (Table 1), the SHRIMP calibration method presented here allows the accurate standardisation of unknowns at the 95% confidence level. The lack of a strong correlation between age and composition is clearly demonstrated in Fig. 4 for Siss, which along with BC displays the most chemical heterogeneity (Table 1). EMP chemical compositions were acquired beside each SHRIMP spot for all samples and yield similar observations.

4.2. Matrix normalisation factors in LA-ICP-MS

Similar to the ion microprobe, we have implemented an external standardisation approach to monitor and correct measured LA-ICP-MS data for Pb/Th fractionation. Inter-elemental fractionation is a common feature of laser ablation (e.g., Longerich et al., 1996; Horn et al., 2000) and originates from processes at the sample site (Fryer et al., 1993; Eggins et al., 1998; Mason and Mank, 2001), due to factors including (1) the strength of atomic bonding of the material (2) the relative behaviour and transport of volatile and refractory elements and (3) the rate of ablation.

Elemental fractionation is strongly depth dependent. Consequently, a matrix normalisation factor (F) was

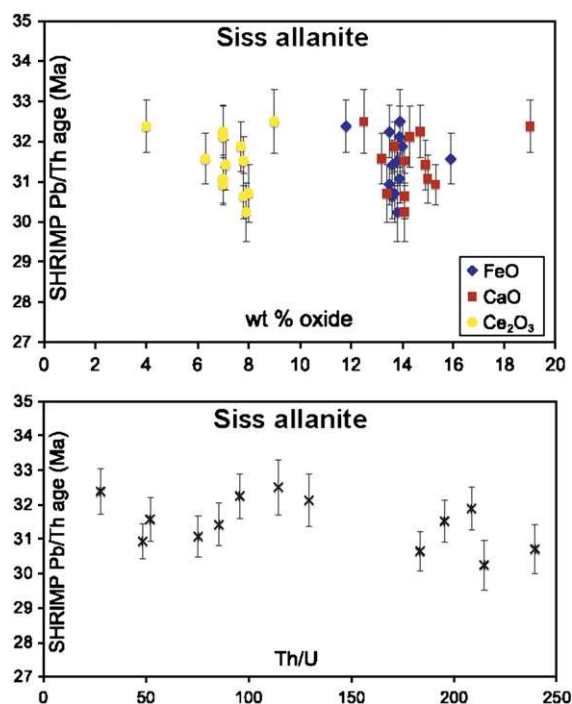


Fig. 4. SHRIMP Pb/Th age versus composition diagrams for Siss (CAP standard), one of the more chemically heterogeneous samples (Table 1). No clear relationship is observed between age and composition, despite a range of REE + Th contents. Error bars are 1σ .

determined during each analytical session from the average of replicate standard measurements for each data report during the drilling process (depth) and applied to the unknown for the same depth interval:

$$F = \frac{{}^{208}\text{Pb}/{}^{232}\text{Th}_{\text{known}}}{{}^{208}\text{Pb}/{}^{232}\text{Th}_{\text{measured}}} \quad (2)$$

where ${}^{208}\text{Pb}/{}^{232}\text{Th}_{\text{known}}$ is the ID-TIMS reference value. F_{MS} is the F calculated for the same mass sweep (depth interval) down an ablation pit, whereas F_{AVG} is the average of a group of the above. For allanite F is relatively constant during a single analytical session and the uncertainty of F_{MS} determined from each standard analysis is propagated to the final F_{MS} error as applied to the unknowns.

Four potential standard materials were assessed. The NIST SRM 610 glass currently the most widely available standard for LA-ICP-MS analysis, GSC SHRIMP monazite standard Thompson Mine Monazite (TMM at 1766Ma), the most Th and trace element-rich material next to allanite, GA SHRIMP zircon standard Temora (417Ma), and CAP, Tara and AVC allanites.

Accurate standardisation is dependent on how a material ablates during drilling, i.e., how F changes with depth, and whether that behaviour can be reasonably

applied to an unknown. Instrument stability is the next most significant factor. The potential standard materials were analysed with ablation pits of 32, 40, 54 and 70 μm diameter, during a single analytical session and under constant operating conditions. Fig. 5 demonstrates that, apart from a change in counting statistics (${}^{208}\text{Pb}$ counts increased by nearly a factor of 3 from 32 μm to 70 μm for Tara), the general evolution of the isotope ratio with depth remained constant. To quantify the rate of Pb/Th fractionation with spot size we used a slope of regression through the signal (Fig. BD6, Tiepolo, 2003). A gradual increase in Pb/Th fractionation (s^{-1}) with decreasing spot size was observed for all materials (Fig. 5). Notably,

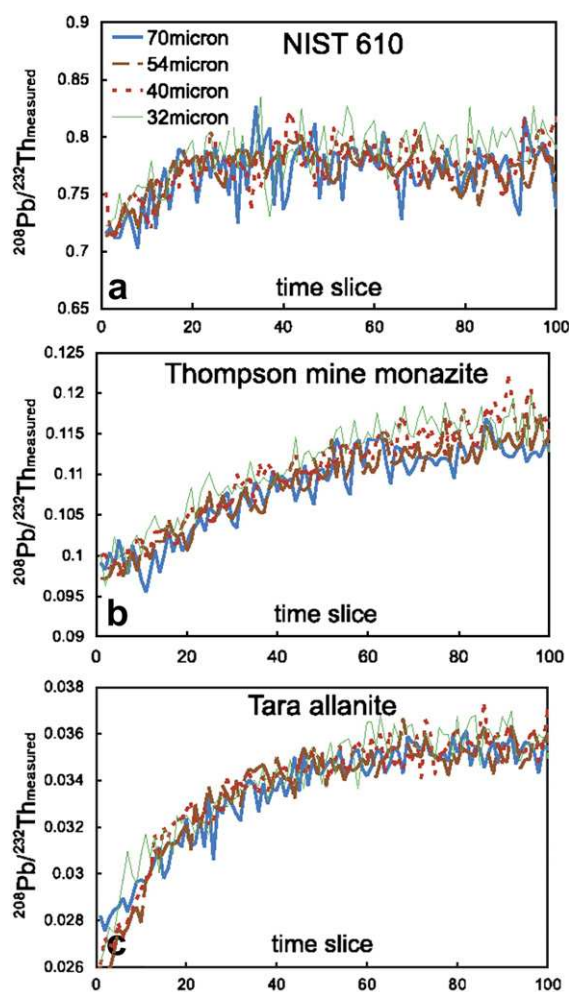


Fig. 5. LA-ICP-MS time-resolved Pb/Th isotope ratio signals measured using 32, 40, 54 and 70 μm spot sizes on synthetic glass NIST 610 (a), Thompson Mine monazite (TMM), Australia (b) and from Tara allanite (c). The analyses were conducted during a single analytical session under the same instrumental conditions. The isotope ratio signal was similar for all spot sizes, although the rate of inter-element fractionation changed earlier for smaller spot sizes.

the rate for NIST 610 ($\sim 0.04\%$ at $70\mu\text{m}$ to $\sim 0.06\%$ at $32\mu\text{m}$) is significantly slower than that of the two LREE, Th-rich minerals allanite ($\sim 0.18\%$ at $70\mu\text{m}$ to $\sim 0.23\%$ at $32\mu\text{m}$) and monazite. This indicates that the NIST glass is not a suitable standard for allanite $^{208}\text{Pb}/^{232}\text{Th}$ analysis. By using a short ablation time ($\sim 40\text{s}$), the observed fractionation was minimised and vertical (down-hole) spatial resolution was optimised.

To further assess matrix effects, F_{AVG} was determined for the series of potential standards. The results plotted in Fig. 6, show that different materials produce characteristic F_{AVG} values for $^{208}\text{Pb}/^{232}\text{Th}$. For a $54\mu\text{m}$ spot diameter, F is 0.72 for NIST 610, 0.91 for TMM and 0.69 for allanite (Table BD3). External standardisation of allanite with NIST 610 and TMM would therefore result in $^{208}\text{Pb}/^{232}\text{Th}$ ages in excess of their reference TIMS ages by $\sim 4\%$ and $\sim 25\%$, respectively. Considering the matrix dependence of F therefore, the evaluation of external standard efficiency of different matrices by residual error based on slope alone is not sufficient. F_{AVG} may vary from 0.61 to 0.69 between analytical sessions for an arbitrarily selected mass sweep (depth) due to instrumental factors. These include variations in laser fluence, torch position, carrier gas flow, ICP lens settings, and pit diameter.

The internal reproducibility of $^{208}\text{Pb}/^{232}\text{Th}$ (and therefore F_{AVG}) in AVC is 0.3–0.4% (% SE) compared to 0.2–0.3% in NIST 610, the most widely used standard material in LA-ICP-MS. This error is mainly related to standard homogeneity rather than instrumental drift; the

latter would be observed as a linear change in F_{AVG} with time and is corrected for prior to external standardisation. Standard uncertainty is propagated to the final single-spot or isochron ages. It is clear, based on the matrix dependency of F , that the allanite and monazite signals are sufficiently different to indicate that matrix-matched standards are highly desirable.

4.3. Common Pb correction

Unlike most zircon and monazite, allanite can have large initial common Pb contents, which makes the calculated Pb/Th and Pb/U ages sensitive to errors in estimating the fraction of initial Pb in an analysis. The allanite samples investigated vary in radiogenic ^{208}Pb ($^{208}\text{Pb}^*$) from $> 98\%$ (Tara, CAP, AVC; REE + Th $> 0.8\text{apfu}$) to $\sim 80\%$ (BC, Siss, Bona; REE + Th = $0.42\text{--}0.65\text{apfu}$), as shown in Table 2. As a high Th/U phase, the Th–Pb system in allanite contains the lowest fraction of common Pb and was targeted for allanite.

4.3.1. Single-spot correction method

To estimate common ^{208}Pb , two methods for single-spot corrections are suitable for Phanerozoic, high Th/U minerals; one based on the measured $^{204}\text{Pb}/^{206}\text{Pb}$ and the other using $^{207}\text{Pb}/^{206}\text{Pb}$ (Compston et al., 1984; Williams, 1998). Both have been tested in the course of this study. The two methods give the same result when used to correct SHRIMP Pb/Th measurements (Table BD4). The ^{204}Pb correction is less precise, however, because the counting error on ^{204}Pb is larger than on the more abundant ^{207}Pb . ^{204}Pb is also more susceptible to measurement error due to isobaric interferences. For relatively young samples where it is valid to assume near concordance, the ^{207}Pb -based common Pb correction is therefore preferred. There is no correlation between common Pb content and the ^{207}Pb -corrected $^{208}\text{Pb}/^{232}\text{Th}$ or $^{206}\text{Pb}/^{238}\text{U}$, indicating that the assumption of concordance for calculating the percentage of common ^{207}Pb has no significant bearing on the final Pb correction.

Correction of LA-ICP-MS isotope analyses for common Pb is more problematic because the presence of ^{204}Hg in the carrier gas precludes the accurate measurement of ^{204}Pb . Mercury backgrounds are more than an order of magnitude greater than Pb backgrounds, which compromises accurate peak stripping. Andersen (2002) has proposed an alternative three-dimensional numerical correction, but it is designed primarily for U-rich phases (e.g. zircon) with relatively small common Pb contents and so is not fully applicable here. The obvious alternative approach is to extrapolate data to the U–Pb Concordia (e.g., Storey et al., 2004), which, unfortunately, is not

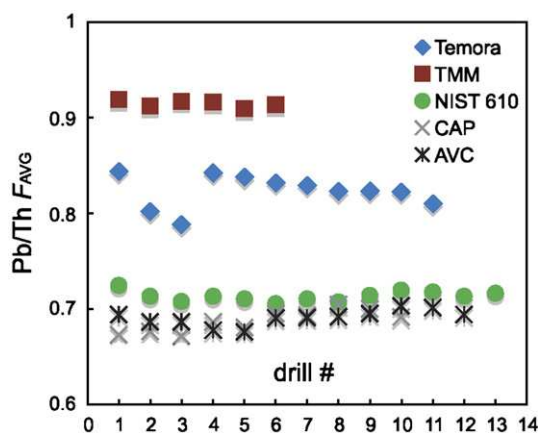


Fig. 6. Pb/Th normalisation factors (F_{AVG}) calculated from different materials during a single LA-ICP-MS session using a $54\mu\text{m}$ spot size. The F values presented here are bulk averages of each ablation, and not the individual F values calculated for each time slice (~ 100) from the start to the end of a single drill, which are used to correct for fractionation in unknown. The allanite analyses are taken from several grains and indicate a consistent intra- and inter-sample behaviour. The bulk F values and the range of F values (from the start to end of a single drill) are given in Table BD3.

possible for the Th–Pb system. Consequently, we use the ^{207}Pb -based correction, as for SHRIMP isotope ratios. In the case of allanite, the relatively poor counting statistics of the U–Pb system, coupled with a moderate to high fraction of common ^{206}Pb , places an unacceptable uncertainty on the F value and age for useful standardisation.

Use of ^{204}Pb to correct allanite SHRIMP U–Pb data is hampered by the presence of a mass 204 isobar. ^{204}Pb -corrected $^{206}\text{Pb}/^{238}\text{U}$ ages measured on allanite were found to be systematically lower than ^{207}Pb -corrected $^{206}\text{Pb}/^{238}\text{U}$ ages by up to 7% for young (< 50 Ma) samples. Unresolved isobaric interferences at mass 204 have been noted previously for monazite (Stern and Berman, 2000). Unlike monazite, however, no relationship was observed in allanite between ThO_2 content and apparent ^{204}Pb counts. Energy filtering to remove/suppress the interference (Rubatto et al., 2001) is a trade-off between increasing the accuracy of the ^{204}Pb -based common lead correction and loss of precision in measuring the ^{206}Pb and ^{207}Pb isotopes. For analyses of Phanerozoic allanites such a loss of precision is unacceptable, so the ^{207}Pb -based correction was used (Fig. 7).

The amount of common ^{206}Pb contributing to an analysis is calculated from the ^{207}Pb by assuming concordancy between the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ages. This correction is most applicable to Phanerozoic samples for which the range of potential $^{207}\text{Pb}/^{206}\text{Pb}^*$ is small, they are known or expected to be concordant, and the target is to estimate (in this case) radiogenic $^{208}\text{Pb}/^{232}\text{Th}$ (Williams, 1998).

$$f206 = \frac{^{206}\text{Pb}_c}{^{206}\text{Pb}_{\text{TOTAL}}} = \frac{^{207}\text{Pb}/^{206}\text{Pb}_m - ^{207}\text{Pb}/^{206}\text{Pb}^*}{^{207}\text{Pb}/^{206}\text{Pb}_c - ^{207}\text{Pb}/^{206}\text{Pb}^*} \quad (3)$$

where $f206$ is the amount of common ^{206}Pb expressed as a fraction of the total ^{206}Pb , $^{207}\text{Pb}/^{206}\text{Pb}_m$ is the measured ratio, $^{207}\text{Pb}/^{206}\text{Pb}^*$ is the expected radiogenic ratio for the inferred age and $^{207}\text{Pb}/^{206}\text{Pb}_c$ is the common Pb composition. The number of atoms of common ^{206}Pb is usually

calculated based on a projection from Cumming and Richards (1975) model Pb composition to concordia. The number of ^{207}Pb and ^{208}Pb atoms can be calculated by ratios from the same model. Radiogenic $^{206}\text{Pb}/^{238}\text{U}$ is calculated from:

$$^{206}\text{Pb}^*/^{238}\text{U} = (1 - f206) \times ^{206}\text{Pb}/^{238}\text{U}_m \quad (4)$$

For the Th–Pb system $f208$ is calculated from:

$$f208 = f206 \times \frac{^{208}\text{Pb}/^{206}\text{Pb}_c}{^{208}\text{Pb}/^{206}\text{Pb}_m} \quad (5)$$

where $^{208}\text{Pb}/^{206}\text{Pb}_c$ is the model common Pb composition (Cumming and Richards, 1975) and $^{208}\text{Pb}/^{206}\text{Pb}_m$ is the measured ratio. This does require the assumption however, that Th/U in the area of interest has remained undisturbed. Radiogenic $^{208}\text{Pb}/^{232}\text{Th}$ is then calculated using a Pb/Th equivalent of Eq. (4).

When the initial $^{207}\text{Pb}/^{206}\text{Pb}$ corresponds to a model Pb composition (e.g. Cumming and Richards, 1975), the single-spot correction method is applicable. Romer and Siegesmund (2003) demonstrated, however, that the potential incorporation of unsupported radiogenic Pb in allanite, originating from a precursor mineral, results in a mixed initial Pb composition. In this instance, either a direct measurement (i.e., from co-existing Pb-rich phase) or a free regression of uncorrected data is required to obtain the sample's initial Pb composition. For example, initial $^{207}\text{Pb}/^{206}\text{Pb}$ can be estimated by regressing uncorrected $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{238}\text{U}/^{206}\text{Pb}$. Alternatively, an isochron approach can be used to treat uncorrected Th–Pb data.

4.3.2. Isochron correction method

Th–Pb ages can be calculated from LA-ICP-MS analyses using 2D isochron plots (Fig. 8). This method is well suited to less radiogenic samples ($f208 > 0.4$), for which the accurate determination of the common Pb contribution is particularly crucial. Isochrons can be

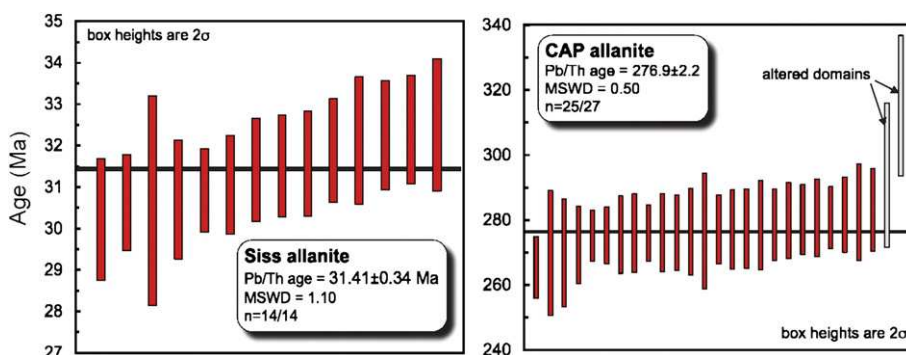


Fig. 7. SHRIMP single-spot corrected Pb/Th ages for CAP (Tara standard) and Siss (CAP standard). Analyses that were not included in the age calculation (e.g., altered domains, statistical outliers) are marked as grey. Ages are given at the 95% confidence level.

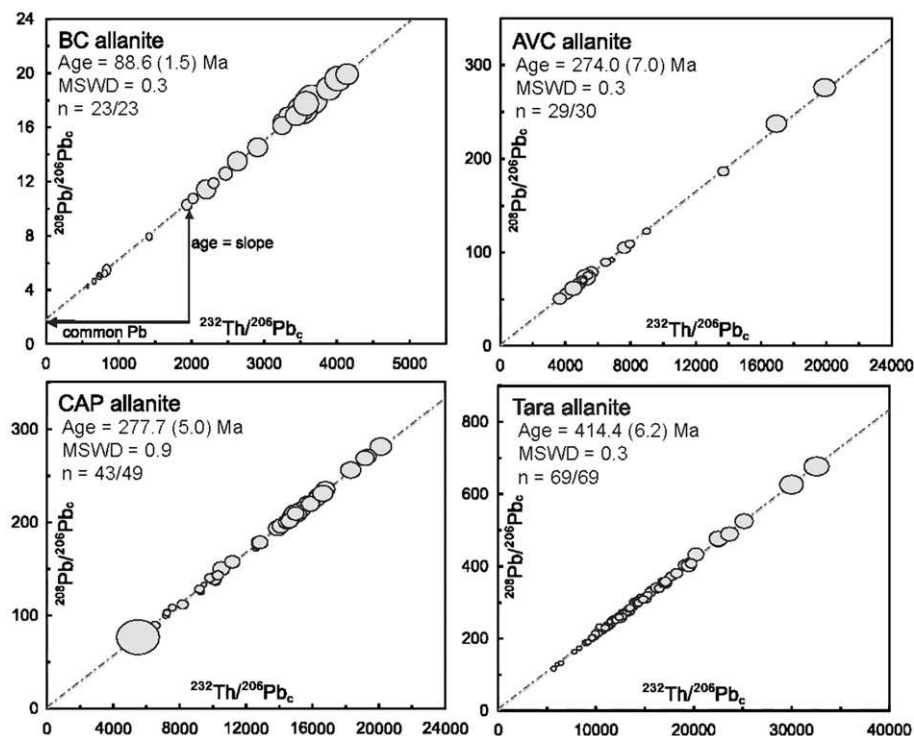


Fig. 8. LA-ICP-MS Th–Pb isochrons of the allanite samples. The AVC was used as standard for BC, CAP and Tara allanites and the CAP as standard for the AVC allanite. Error ellipses are 2σ and ages are given at the 95% confidence level. Note the denominators are the common Pb portion of the total measured ^{206}Pb , whereas the numerator of the y axis is total measured ^{208}Pb .

constructed from multiple LA-ICP-MS analyses (≥ 30) of a single allanite grain or multiple grains from the same rock, providing that all analysed spots are the same age, remained closed systems and have identical initial Pb isotopic compositions. The benefit of this method is that the age and suitability of the sample for dating is assessed from a regression of all the analyses, as opposed to interpreting individually corrected ages. In this way, Pb/Th data are assessed statistically for population homogeneity and/or isotopic disturbance based on the fit of the statistical regression (MSWD). This is particularly useful for young (Phanerozoic) rocks where common Pb, and not Pb loss, is the likely source of discordance, and for which uncertainty in the assumed initial $^{207}\text{Pb}/^{206}\text{Pb}$ is negligible. Furthermore, the initial $^{208}\text{Pb}/^{206}\text{Pb}$ can be determined from the intercept of the isochron (Fig. 8a). The isochrons are constructed with common ^{206}Pb ($^{206}\text{Pb}_c$) as the reference stable isotope. Common ^{206}Pb or f_{206} is determined from Eq. (3) and measured $^{232}\text{Th}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ are adjusted accordingly:

$$^{232}\text{Th}/^{206}\text{Pb}_c = \frac{^{232}\text{Th}/^{206}\text{Pb}_m}{f_{206}} \quad (6)$$

The uncertainty in the calculated fraction of common Pb is given by:

$$\pm f_{206} = f_{206} \times \frac{\sqrt{\pm^{207}\text{Pb}/^{206}\text{Pb}_m^2 \times (1 + f_{206}^2)}}{^{207}\text{Pb}/^{206}\text{Pb}_m - ^{207}\text{Pb}/^{206}\text{Pb}^*} \quad (7)$$

as referenced from RSES Lead 6.5 data reduction program. The corresponding errors for corrected $^{232}\text{Th}/^{206}\text{Pb}_c$ and $^{208}\text{Pb}/^{206}\text{Pb}_c$ include the uncertainty on the measured ratios and the common lead correction and are added in quadrature (Ludwig, 1980). For the samples investigated, the calculation of f_{206} is only weakly dependent on the assumption of common Pb composition. Changing the Cumming and Richards (1975) model age by 1Ga did not alter the Th–Pb isochron age significantly (i.e., < 1Ma difference). Standard uncertainty was added in quadrature through the final calculated isotope ratios (Ludwig, 1980). The Pb/Th isochrons were constructed using Isoplot/Ex software (Ludwig, 2003).

4.3.3. Effect of excess ^{206}Pb on the estimate of common lead

The presence of excess ^{206}Pb from the decay of initial ^{230}Th incorporated into a Th-bearing mineral at the time of

crystallisation is particularly important in young minerals where the excess ^{206}Pb is not diluted by radiogenic ^{206}Pb (Schaerer, 1984). We modelled the effect of excess ^{206}Pb on the $^{207}\text{Pb}/^{206}\text{Pb}$ -based correction for both LA-ICP-MS and SHRIMP ion microprobe procedures by systematically varying the amount of common lead and excess ^{206}Pb . For a young (45Ma), Th-rich ($\text{Th}/\text{U} = 35$) sample containing 60–90% common ^{208}Pb , the effect of excess ^{206}Pb is negligible, with a 30% ^{206}Pb excess resulting in a calculated f_{206} only 0.15% lower than the case of no ^{206}Pb excess. This variation is within the statistical error of f_{206} propagated onto the corrected isotope ratios (1–4% for LA-ICP-MS). Intuitively, the larger the common Pb content, the smaller the effect.

5. Ages

A summary of the U–Th–Pb results is given in Table 2 and Fig. 10. LA-ICP-MS results are given in Table BD5 and SHRIMP results are given in Table BD4. Uncertainties in the tables are given as 1σ and ages were calculated at the 95% confidence level ($t \times \text{sigma}$; Ludwig, 2003), using the constants recommended by the IUGS Subcommittee in Geochronology (Steiger and Jaeger, 1977). SHRIMP data for the CAP, AVC, Tara and Siss samples were collected over 2 sessions, by alternating analyses. BC and Bona were run during a separate analytical session. LA-ICP-MS data for all samples were compiled from 9 analytical sessions over the course of 18 months. The data were obtained with different laser spot sizes of 24, 32 and 54 μm .

5.1. CAP

A weighted mean SHRIMP $^{208}\text{Pb}/^{232}\text{Th}$ age of $276.9 \pm 2.2\text{Ma}$ from 25 analyses and a $^{206}\text{Pb}/^{238}\text{U}$ age of $275.0 \pm 4.7\text{Ma}$ from 23 analyses were measured using the Tara as standard (at 416Ma). Both ages are within error of their respective ID-TIMS ages of $275.6 \pm 1.5\text{Ma}$ (Table 2) and $274.0 \pm 0.6\text{Ma}$ (Barth et al., 1994). As a SHRIMP standard, CAP single-spot Pb/Th ages were reproduced with a precision of ± 0.1 –2.5% (excluding 3 outliers) over the 3 sessions. A sufficient spread was obtained from 43 LA-ICP-MS analyses to give a Th–Pb isochron age of $277.7 \pm 5.0\text{Ma}$ (Fig. 8). The weighted mean LA-ICP-MS $^{208}\text{Pb}/^{232}\text{Th}$ age of $277.9 \pm 1.2\text{Ma}$ from 47 analyses is in close agreement with the isochron age using AVC as standard (Table 2).

5.2. AVC

Using the CAP allanite as standard, 24 SHRIMP analyses yielded a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of

$280.0 \pm 2.1\text{Ma}$, that is 1.4% higher but within error of its ID-TIMS $^{208}\text{Pb}/^{232}\text{Th}$ age of $276.3 \pm 2.2\text{Ma}$ (Table 2, Fig. 10). The SHRIMP $^{206}\text{Pb}/^{238}\text{U}$ age of $289.6 \pm 5.6\text{Ma}$ is 3.5% in excess of the ID-TIMS $^{206}\text{Pb}/^{238}\text{U}$ age ($279.0 \pm 0.5\text{Ma}$; Barth et al., 1994). Fig. 7 shows that 29 LA-ICP-MS analyses of the AVC allanite produce a Th–Pb isochron of $274.0 \pm 7.0\text{Ma}$. The majority of the analyses fall within a similar range of parent/daughter ratios. This closely matches with the weighted mean LA-ICP-MS age of $274.9 \pm 1.2\text{Ma}$ from 30 single-spot corrected analyses (Table 2).

5.3. Siss and Bona

A weighted mean SHRIMP $^{208}\text{Pb}/^{232}\text{Th}$ age of $31.4 \pm 0.3\text{Ma}$ from 14 analyses of the Siss allanite and a $^{206}\text{Pb}/^{238}\text{U}$ age of $35.5 \pm 1.6\text{Ma}$ from 13 analyses were obtained with the CAP allanite as standard (Table 2, Figs. 7 and 10). Both ages are within error of their respective ID-TIMS ages of $31.5 \pm 0.4\text{Ma}$ (Table 2) and $36.5 \pm 0.5\text{Ma}$ (von Blanckenburg, 1992). The Bona allanite gave a weighted mean SHRIMP $^{208}\text{Pb}/^{232}\text{Th}$ age of $30.5 \pm 0.4\text{Ma}$ and a $^{206}\text{Pb}/^{238}\text{U}$ age of $36.5 \pm 2.0\text{Ma}$ from 10 analyses. These agree with their corresponding ID-TIMS ages of $30.1 \pm 0.3\text{Ma}$ and $36.5 \pm 0.6\text{Ma}$ (von Blanckenburg, 1992). The discrepancy in Pb/Th and Pb/U ages (11.2% for Siss and 17.5% for Bona) is primarily related to (uncorrected for) excess ^{206}Pb in the U– ^{206}Pb system (von Blanckenburg, 1992; Oberli et al., 2004), on the basis that the $^{208}\text{Pb}/^{232}\text{Th}$ age is accurate. Forty LA-ICP-MS analyses of the Bona allanite gave a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of $30.9 \pm 0.2\text{Ma}$. The same analyses plotted as a Th–Pb isochron yield an age of $31.1 \pm 1.8\text{Ma}$,

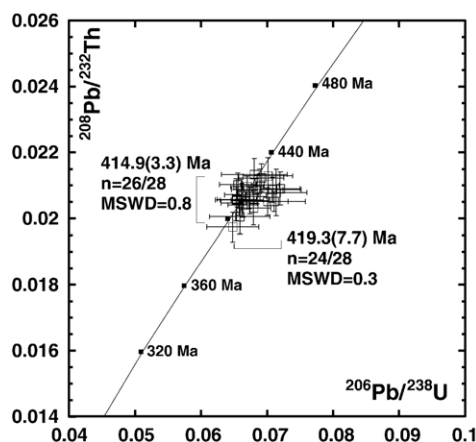


Fig. 9. Th–Pb vs. U–Pb concordia diagram for the Tara allanite SHRIMP analyses, using the CAP allanite as the standard. Error bars are 1σ and ages are calculated at the 95% confidence level.

within error of the ID-TIMS age of 30.1 ± 0.3 Ma (Table 2).

5.4. BC

A weighted mean SHRIMP $^{208}\text{Pb}/^{232}\text{Th}$ age of 92.4 ± 2.1 Ma and a $^{206}\text{Pb}/^{238}\text{U}$ age of 96.5 ± 5.3 Ma from 8 analyses were obtained with the CAP as standard during one SHRIMP II session (Table 2, Fig. 10). The Th–Pb age is within error of the reference U–Pb zircon age of 90.8 ± 0.8 Ma. The elevated U–Pb age (5.9%) could be explained in part, by excess ^{206}Pb , as demonstrated for the Siss allanite (see Section 6.2). Twenty-three LA-ICP-MS analyses formed a Th–Pb isochron with an age of 88.6 ± 1.5 Ma (Fig. 8). The same analyses gave a single-spot corrected mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 89.4 ± 0.8 Ma.

5.5. Tara

From SHRIMP II and RG, 24 analyses of the Tara allanite were broadly concordant and show no evidence of inherited radiogenic Pb or significant Pb loss (Fig. 9). Both the SHRIMP Pb/Th age of 414.9 ± 3.3 Ma and the LA-ICP-MS ages are 3–4 Ma older than the Rb–Sr age of 412.0 ± 1.4 Ma (Fig. 10, Table 2). Fig. 10 shows the LA-ICP-MS Th–Pb single-spot corrected age data of the Tara allanite over the course of 7 analytical sessions, with a cumulative age of 417.5 ± 1.4 Ma. A slightly younger weighted mean LA-ICP-MS isochron age of 414.4 ± 6.2 Ma was obtained from 63 analyses (Fig. 8, Table 2), although the results from the two methods are within error.

6. Discussion

6.1. Matrix chemical variability

For accurate LA-ICP-MS isotopic analysis the down-hole fractionation of Pb and Th must be correctly monitored (Fig. 5). Based on reproducible monazite F values (Fig. 6), the use of a monazite standard would underestimate the fractionation of $^{208}\text{Pb}/^{232}\text{Th}$ measured on allanite by nearly a factor of three. It follows that neither the NIST glass, the most commonly available LA-ICP-MS standard, nor monazite, the U–Th mineral that most closely approaches the allanite matrix, are suitable standards for allanite Pb–Th ages by LA-ICP-MS. Furthermore, in most cases of mineral matching, the targeted isotopes for standard and unknown are measured in the same detector mode (pulse or analogue). Therefore we conclude that there is good reason to mineral match if the best accuracy is sought. From the evaluation of matrix effects, AVC was chosen as the primary Pb/Th standard as it demonstrated consistent ablation behaviour and $^{208}\text{Pb}/^{232}\text{Th}$ reproducibility due to a homogeneous composition and common Pb content, and therefore consistent F values for each down-hole mass sweep (Fig. 6).

For SHRIMP isotopic analysis, the evaluation of matrix effects focuses on the differences in composition between standard and unknown. The ion microprobe Th–Pb ages of the allanite samples in this study remain within error of their reference ages even when FeO content ranges from 11.8 to 17.3 wt.% (Table 1, Fig. 10). Furthermore, no matrix effect due to REE content was observed for the samples tested. Our findings are based on, and therefore may be reliably applied to, allanite compositions of $\text{Th} + \text{LREE} \geq 0.5$ cations per formula unit. In this study we have used the Sensitive High Resolution Ion

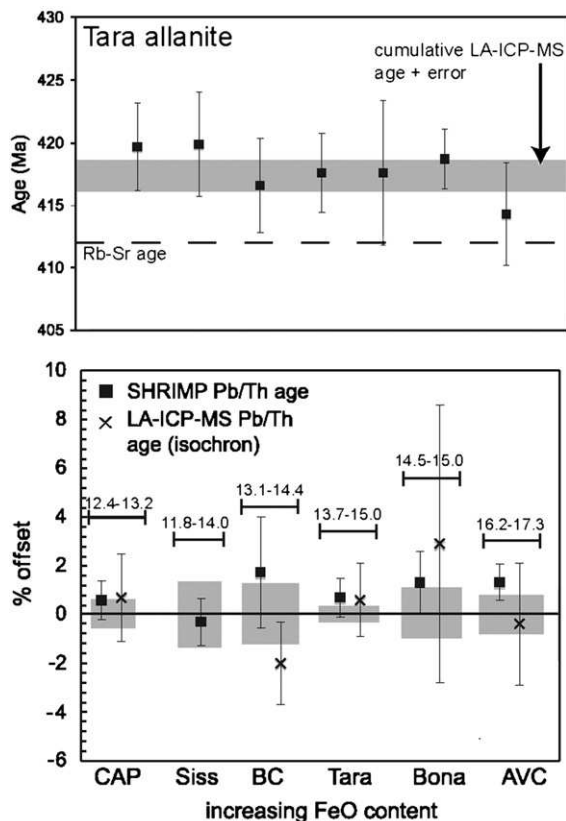


Fig. 10. (Above) Reproducibility of LA-ICP-MS *single-spot* ^{207}Pb -corrected Pb/Th ages for the Tara allanite over 7 sessions using AVC allanite for standardisation. Error bars are calculated at the 95% confidence level. The grey box represents the cumulative age and uncertainty. The Rb–Sr age (Williams et al., 1983) is indicated by the dashed line. (Below) Summary of age data for each sample as % offset from their reference ages. Error on reference ages shown in grey. Values displayed above ages are the range of total FeO contents in wt.%.

Microprobe (SHRIMP) instrument, which have quite a different ion optic design from the Cameca 1270 used by Catlos et al. (2000). Catlos et al. (2000) discovered severe matrix effects during analysis of AVC and CAP and for a 2D calibration plot similar to ours obtained a Pb/Th age of 137 ± 10 Ma (MSWD = 2.6) for the AVC, 50% lower than the 276 Ma TIMS age, using the CAP as standard. The fact that our findings somewhat contradict those of Catlos et al. (2000) despite both analysing CAP and AVC, may be attributed to the use of ion microprobes with of different secondary ion extraction optics.

SHRIMP analysis of a sample of epidote (REE + Th < 0.15) was attempted as a ‘worst case scenario’ using the CAP allanite as standard. The elevated initial Pb component in epidote (95% $^{208}\text{Pb}_c$) precluded any sensible age determination, however we can extract useful information regarding the ionisation efficiency of Pb^+ , Th^+ and U^+ sputtered from epidote relative to allanite. Aside from a greater scatter about the calibration line due to poor counting statistics, the significant epidote component reduced the ionisation efficiency of sputtered lower energy ThO^+ molecules relative to higher energy Th^+ atoms. This caused an offset of the epidote mean $\text{ThO}^+/\text{Th}^+ = 6$ relative to the CAP allanite mean $\text{ThO}^+/\text{Th}^+ = 11$ that placed a substantial uncertainty on the accurate extrapolation of the standard calibration line. Although an extreme case, because the epidote end-member can have ≥ 10 wt.% differences in LREE, Fe and Ca (and Al) contents, it is pertinent to evaluate the compositional limits of the allanite–epidote solid solution relationship.

The CAP allanite was routinely used as the SHRIMP Th–Pb standard based on reproducible Pb/Th and Pb/U calibrations. It is more radiogenic and displays less chemical variation than either the Siss or BC allanites. The AVC allanite, which is the chosen ICP-MS standard for its chemical homogeneity, was not used as the SHRIMP standard because it has the highest total FeO content and allanite component (REE + Th > 0.86 apfu) and thus has a potentially restricted applicability to allanite that contains < 12 wt.% FeO or REE + Th < 0.5. Considering the differences between the two instruments, different external standards were chosen in order to optimise accuracy and reproducibility: a standard of intermediate composition (CAP) was used for SHRIMP but the material with the best homogeneity (AVC) was used for LA-ICP-MS. The Tara allanite also is a promising and readily available standard material, being chemically and apparently isotopically homogeneous. The absolute age for the Tara allanite (and potentially zircon), however, needs to be better determined via ID-TIMS, which is work currently in progress.

6.2. Th–Pb versus U–Pb ages

The importance of the Th–Pb system for the accurate dating of allanite has been demonstrated previously (e.g., von Blanckenburg, 1992; Barth et al., 1994; Oberli et al., 2004). Fundamentally, because allanite is a Th-rich mineral, precise Pb/Th ages are easier to obtain than Pb/U ages for two reasons: (1) counting statistics on ^{232}Th and ^{208}Pb are better, and (2) the relative amount of common ^{208}Pb is less than common ^{206}Pb . Furthermore, the use of $^{208}\text{Pb}/^{232}\text{Th}$ ages avoids the problem of excess ^{206}Pb resulting from the decay of ^{230}Th in Th-bearing minerals (e.g. Schaerer, 1984).

The superiority of the Pb/Th system over the Pb/U system in allanite is highlighted in the present study by the relative accuracy of SHRIMP Pb/Th ages (accurate to ± 1 –3%) as compared to Pb/U ages (accurate to ± 2 –7%; Table 2). As a result, for the samples analysed here, the U–Pb system is used only as a measure of concordance (e.g., Cox et al., 2003), and for additional information on geological processes such as the presence of excess ^{206}Pb (see Oberli et al., 2004 for applications to isotopic tracing of melt evolution). For example, SHRIMP U–Pb analyses of the Siss and Bona allanites identified the same amount of excess ^{206}Pb as reported by von Blanckenburg (1992). The elevated Pb/U age for the BC allanite could be attributed in part to excess ^{206}Pb , although in this case, the low precision of the U–Pb system (5.4%, Table 2), limited the observations.

6.3. SHRIMP versus LA-ICP-MS

The two micro-analytical techniques measure different sample volumes using different analytical approaches so they are not directly comparable. Nevertheless a comment on technique precision and long-term reproducibility is useful for future applications. SHRIMP reproducibility is not within the scope of this paper, however as LA-ICP-MS is a relatively young technique we have shown a plot of Tara LA-ICP-MS ages as a demonstration of reproducibility over an 18-month period using the AVC as standard (Fig. 10). Tara ages for each analytical session (10–20 analyses) are statistically indistinguishable ($\sim 1\%$ at 95% confidence) but are systematically older than the Rb–Sr age. AVC and Tara were analysed twice by SHRIMP with identical results. A summary of all age data for each sample is also given in Fig. 10, along with their relevant FeO contents, in order to demonstrate the absence of a significant correlation between composition and age (offset from the reference). The within-session precision for the Th–Pb isochron method suffers from the uncertainty (0.4–10%) contributed by the estimate of the

common ^{206}Pb contribution, compared to the single-spot method. Isochron precision was also dependent on a sufficient spread of parent-daughter ratios. Consequently, LA-ICP-MS dating required a larger number of analyses (i.e., > 30) compared to SHRIMP in order to achieve similar precision. Precision of single-spot LA-ICP-MS analyses was slightly better than SHRIMP analyses (Tables BD4 and BD5). This is attributed to the larger volume sampled by LA-ICP-MS leading to better counting statistics; uncertainty on raw Pb/Th data is 0.3–0.5% (1σ) for drilling compared to 0.2–1.2% for SHRIMP sampling. The spatial resolution of SHRIMP analyses however, provides better textural control compared to LA-ICP-MS, for which drilling through a zoned grain is possible for all accessory phases analysed by this method.

6.4. Accuracy, reproducibility and versatility

The accuracy and precision of LA-ICP-MS and SHRIMP Th–Pb isotope ratios are reliant on the absolute age of standards being correctly known, good reproducibility of standard calibration (procedure reliability), and correct estimation of common Pb content. Spatial resolution influences the counting statistics (Section 4.2) and therefore precision of measured data, however we have not observed a noticeable gain in overall precision with increasing spot size, as the main contributors are the common Pb contribution and standard homogeneity. The short drill time employed also helps to minimise the effect of pit aspect ratio on accuracy. For LA-ICP-MS analysis, within-session uncertainty of the AVC allanite $^{208}\text{Pb}/^{232}\text{Th}$ F_{AVG} was $\sim 1.0\%$ (1σ). Uncorrected LA-ICP-MS $^{208}\text{Pb}/^{232}\text{Th}$ ratios were measured with a precision of $\sim 0.25\%$ (1σ), however analysis of minerals with a moderate common Pb component is problematic. The isochron approach presented here provided an alternative statistical assessment of the measured Pb/Th data and sample isotopic homogeneity. Allanite Th–Pb isochron ages were calculated with an accuracy of 0.6–3.3% and a precision of 1.4–5.8% at the 95% confidence level. The single-spot ^{207}Pb -based method yielded $^{208}\text{Pb}^*/^{232}\text{Th}$ ratios with an uncertainty of ~ 1.2 –3.5% (1σ) and Pb/Th weighted mean ages accurate to 0.5–3%. However we suggest that for Th–Pb analysis of less radiogenic samples ($f_{208} > 0.4$) the isochron approach is preferable because the age determination is based on the best-fit regression of all the sample data that is only weakly dependent on an assumption of the common ^{206}Pb composition as the reference stable isotope. Isochrons however, are based on the assumption of sample age homogeneity; if grains show complex internal age structure then the isochron method is

not applicable. Thus, in the case of high common Pb, the preferable approach must be evaluated case by case.

The potential range of REE + Th content in allanite does not limit the LA-ICP-MS technique. In fact igneous and metamorphic grains of varying major and minor elemental composition show comparable $^{208}\text{Pb}/^{232}\text{Th}$ fractionation with depth. The LA-ICP-MS technique presented here for allanite provides useful age information from > 30 spot analyses; each analysis lasting ~ 1 min. For relatively large grains that are igneous or migmatitic in origin, it provides an important tool that allows the investigation of sample isotopic heterogeneity, textural and spatial association (inclusion versus matrix grains) and inheritance within a single thin section. LA-ICP-MS analysis can also provide complimentary trace element characterisation within the time frame of the U, Th–Pb study.

For SHRIMP analysis, within-session uncertainty of the CAP allanite Pb/Th age is 1.5–2% (1σ). Weighted mean SHRIMP Pb/Th ages were calculated to be within error of their reference ages at the 95% confidence level at 1–2% precision. The agreement of SHRIMP and ID-TIMS Th–Pb ages indicates that, with the exception of ^{204}Pb , Pb isotopes measured from allanite by ion microprobe are free from significant isobaric interferences. The presence of common Pb introduces comparatively (to zircon) large within-spot uncertainties on corrected Th–Pb ages (1.5–2.5%, 1σ).

The high resolution, minute sample volume and attainable precision of individual spots analysed by SHRIMP ion microprobe facilitates the investigation of samples where grain size is relatively small and populations are complex with respect to intra and inter-grain isotopic and chemical heterogeneity. The accuracy of the in situ technique has been demonstrated for Pb/Th in allanite (± 1 –3% accuracy; Table 2), which exhibits compositional variation in Fe, REEs and Th. This said, the samples are igneous and contain a significant allanite component (REE + Th of 0.4–0.9). SIMS analysis of allanite with a larger epidote component (e.g. REE + Th < 0.4) due to higher CaO contents and therefore fewer coupled substitutions involving REE, Th and Fe^{2+} , is planned to further examine the compositional limits of the ion microprobe calibration technique (i.e., difference between the ThO^+/Th^+ position of the standard and unknown calibration) and the suitability of the CAP allanite standard.

6.5. Potential of allanite dating

The use of allanite U, Th–Pb dating is restricted relative to zircon and monazite, primarily due to the incorporation of common lead and the susceptibility of allanite to alteration. However the method reported here

allows the investigation of many types of geological problems, some of which are inaccessible to monazite and zircon dating.

6.5.1. Igneous allanite

Primary allanite is common in many metaluminous granitoid rocks (e.g. [Zen and Hammarstrom, 1984](#); [Broška et al., 2000](#)). It commonly forms the cores of epidote grains and may be stable to higher temperatures than epidote ([Schmidt and Thompson, 1996](#)). After monazite, allanite is the most important LREE carrier in granitic rocks and can contain > 50% and 15–42% of the LREE and Th fraction, respectively, in metaluminous granites ([Bea, 1996](#); [Broška et al., 2000](#)), highlighting the importance of allanite in controlling the behaviour of REE in granitic magmas.

Zircon is the most commonly used geochronometer for the dating of igneous rocks. Zircon does not always yield coherent age information, however, and the Tara Granodiorite and Bona Granodiorite provide two relevant examples of this (see Section 2). The bulk-composition of both intrusions excludes monazite. Zircon displays open-system behaviour, and despite both being I-type granites, both zircon populations display a complex inheritance pattern ([Williams et al., 1983](#); [von Blanckenburg, 1992](#); Gregory, unpublished). In contrast, co-existing allanite yields a coherent age group (Table 2, Fig. 7). In the case of the Tara Granodiorite, the allanite Pb/Th system appears to be more resistant to later Pb loss than U–Pb in zircon. In addition, no indication of inheritance has been observed in allanite from the Tara Granodiorite or the Bona Granodiorite. Magmatic allanite also commonly forms larger grains than zircon and therefore can be dated more readily in thin section, which avoids the mineral separation process.

There is limited information on the Pb diffusion rates or closure temperature of allanite. Work by [von Blanckenburg \(1992\)](#) and [Oberli et al. \(2004\)](#) on the Bergell intrusion provides the most considered estimate of a Pb loss closure temperature of $\geq 700^\circ\text{C}$. [Oberli et al. \(2004\)](#) used single crystal U, Th–Pb ID-TIMS analyses of zircon, titanite and allanite fractions (from the Bergell tonalite), the preservation of primary trace and major element zoning and substantial excess ^{206}Pb in allanite, to quantitatively demonstrate that the Th–Pb and U–Pb systems in igneous allanite remained closed to Pb loss by volume diffusion under prolonged magmatic conditions. This also suggests that allanite Pb/Th ages in igneous systems represent crystallisation and not cooling ages. This is in line with the data obtained from the Tara Granodiorite for which the allanite age is older than the reported Rb–Sr age ([Williams et al., 1983](#)). Direct

evidence of allanite Pb inheritance has been observed in (upper)-amphibolite grade migmatites from the Central Alps, where migmatitic allanite contains dateable, inherited cores from the igneous protolith, despite experiencing prolonged metamorphic temperatures of up to 700°C (Gregory, unpublished).

6.5.2. Metamorphic allanite

Metamorphic allanite covers an important P – T range that is barely accessible with other phases and therefore shows potential for novel geochronology. The phase stability of allanite in metamorphic rocks is mainly derived from petrological analysis (e.g., [Bingen et al., 1996](#); [Finger et al., 1998](#); [Wing et al., 2003](#); [Bingen et al., 1996](#); [Janots et al., 2006a,b](#)). Petrological studies show that allanite is stable under a wider range of P – T conditions than epidote, as previously speculated by [Catlos et al. \(2002\)](#), although its presence may be restricted by bulk-rock composition or promoted by the presence of melt or fluids.

The most studied metamorphic reactions involving allanite are those occurring during the prograde evolution of regional Barrovian metamorphic terranes. Detailed petrographic observations of the prograde evolution of REE-minerals in pelites show that allanite crystallises at the expense of detrital monazite at the chloritoid–biotite isograd ($\sim 400^\circ\text{C}$, $\sim 4\text{ kbar}$) and then breaks down to form monazite at the garnet–staurolite isograd at $\sim 500^\circ\text{C}$ ([Smith and Barreiro, 1990](#); [Wing et al., 2003](#); [Janots et al., 2006a,b](#)). The existence of metamorphic allanite may therefore be linked to major silicate phases of known P – T stability. With the new in situ dating technique it is possible to date metamorphic reactions in thin section, in textural context, with minimal preparation. The estimated closure temperature for allanite suggests that the allanite U–Th–Pb system will not be easily reset during subsequent temperature increases compared to the $^{40}\text{Ar}/^{39}\text{Ar}$ system traditionally used to date low temperature paths in polymetamorphic terranes.

Metamorphic allanite may also form at relatively low metamorphic temperatures ($\leq 700^\circ\text{C}$) in migmatitic (e.g., [Sorensen and Grossman, 1989](#); [Scrimgeour and Close, 1999](#)) and high-pressure rocks, which have proved more difficult to date by other mineral phases due to factors such as unfavourable bulk-rock composition and limited isotopic homogenisation (e.g., [Gebauer et al., 1997](#)). In particular, growing evidence of the stability of allanite under eclogite-facies conditions in mafic and pelitic rocks has come from recent petrological and experimental studies of (ultra) high-pressure terranes ([Franz et al., 1986](#); [Tribuzio et al., 1996](#); [Hermann, 2002](#); [Spandler et al., 2003](#); [Janots et al., 2006a,b](#)). Accessory allanite is

stabilised at high-pressure and temperature conditions due to the incorporation of “impurities” such as LREE, Sr, Pb, Th and U into an increasingly distorted epidote crystal structure (e.g., Affholter, 1987). During subduction metamorphism, the breakdown of the major mineral (clino)-zoisite to form accessory allanite has been observed in (mafic) blueschist and eclogitic rocks (Tribuzio et al., 1996; Spandler et al., 2003). There is the potential, therefore, to date prograde and peak metamorphic allanite in (U)HP rocks, particularly if their evolution was fast and below the estimated Pb loss closure temperature of allanite. As the principal sink for LREE and Th in metabasites and HP/LT metasedimentary rocks, allanite crystallisation has an important influence on governing the (LREE, Th) trace element budget of subducted rocks (Hermann, 2002). Dating metamorphic allanite should be applied with some caution in regard to common Pb correction, however, as it has been frequently observed that allanite formed by metamorphic processes contains 20–90% common Pb (Gregory, unpublished).

Finally, the REEs have been shown to be an important tool for linking zircon isotopic ages with the pressure-temperature conditions of zircon growth (e.g., Rubatto, 2002). Metamorphic allanite typically displays fractionated REE patterns (Fig. 1, see Giere and Sorensen, 2004 for a complete review). The enrichment of LREE relative to HREE is variable and in metamorphic systems it is primarily attributed to the competitive crystallisation of other REE-minerals, e.g. garnet and zircon (Tribuzio et al., 1996; Hermann, 2002). Additionally, the negative Eu anomaly commonly found in igneous allanite (Fig. 2; e.g., Bea, 1996; Poitrasson, 2002) is absent in allanite from HP metamorphic terranes (Tribuzio et al., 1996; Hermann, 2002; Spandler et al., 2003). Therefore, in a manner that zircon is currently used, the REE composition of allanite can potentially be used to provide P – T information. With the use of LA-ICP-MS for dating allanite, trace element patterns can be obtained simultaneously with age.

7. Conclusions

- (1) For Phanerozoic rocks, allanite Th–Pb isochron ages can be determined by LA-ICP-MS with a precision of 1.4–5.8% (95% confidence) and ^{207}Pb -corrected single-spot ages with a precision of 1.2–3.5%, using an external allanite standard. SHRIMP Th–Pb weighted mean ages can be obtained to a precision of 1–2.5% (95% confidence) and accuracy of ± 1 –3%.
- (2) The common lead correction is crucial for allanite dating. Here we successfully applied a single-spot correction using the ^{207}Pb -based method, and an

isochron regression method to uncorrected allanite U–Th–Pb data.

- (3) Five allanite samples analysed by SHRIMP, with a compositional range of REE + Th = 0.5 to 0.9 apfu (with up to 30% variation in FeO between samples), show no matrix-induced effects at the 95% confidence level, with all samples yielding Pb/Th ages within error of their reference ID-TIMS ages.
- (4) The relative fractionation of Pb and Th observed in an external allanite standard was used to accurately correct for instrumental inter-element fractionation of unknowns during both SHRIMP and LA-ICP-MS analysis.
- (5) The Tara Granodiorite provides an excellent example of the use of allanite U–Th–Pb dating of granitoids when the zircon U–Pb system is compromised by inheritance and post-emplacement lead loss.

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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.chemgeo.2007.07.029.

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