SHRIMP allanite U–Th–Pb dating of bimodal Triassic metamorphism of Neoproterozoic tonalitic gneisses, Daeijak Island, central Korea

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ABSTRACT: The microstructures, compositions and U–Th–Pb ages of allanite from tonalitic gneisses in a Neoproterozoic migmatite complex, Daeijak Island, central Korea, have been investigated. Allanite crystals up to ~300 µm in diameter occur with accessory apatite, ilmenite, magnetite and zircon primarily in the major foliation defined by aggregates of biotite and hornblende. The allanite is commonly rimmed by clinozoisite, and has a range of oscillatory to patchy compositional zoning. Its total LREE + Th content ranges from 0.58 to 0.83 atoms per 12.5 oxygens. The $^{208}\text{Pb}/^{232}\text{Th}$ isotopic ages of allanite from two tonalitic gneiss samples measured using the SHRIMP II ion microprobe show the same two age clusters, 229 ± 2 and 215 ± 4 Ma in sample DE28, and 227 ± 7 and 213 ± 4 Ma in sample DE43. The allanite $^{206}\text{Pb}/^{238}\text{U}$ ages from sample DE28 are similarly clustered, but those from sample DE43 are consistently younger, ~185 Ma. These results, indicating a bimodal Triassic metamorphic overprint, are in contrast to the Neoproterozoic age (~2.51 Ga) of thick zircon overgrowths in sample DE28. Allanite in both samples has retained its $^{208}\text{Pb}/^{232}\text{Th}$ crystallization age(s) through an event that caused major Pb loss from its U–Pb system, recording the later metamorphic history of a Neoproterozoic migmatite terrane.

Key words: allanite, U–Th–Pb dating, SHRIMP, tonalitic gneiss, Daeijak Island

1. INTRODUCTION

Allanite ($\text{CaREEAl}_2\text{Fe}^{2+}\text{Si}_3\text{O}_{12}(\text{OH})$) is a common accessory mineral in a wide variety of Ca-rich lithologies such as calcic granitoids, calcic pelites and mafic rocks. It incorporates relatively large amounts of a range of trace elements, including the rare earth elements (REEs), Sr, Th and U (Gieré and Sorensen, 2004). These petrological and geochemical features, together with its relatively high isotopic closure temperature (~700 °C: von Blanckenburg, 1992; Oberli et al., 2004; Gregory et al., 2009), potentially allow us to use allanite dating to help understand some important geological processes. For example, allanite forms in eclogites and metapelites as a product of prograde mineral reactions under greenschist- to amphibolite-facies conditions, and can therefore provide a temporal constraint on the subduction of

oceanic crust and the burial of pelitic sediments (e.g., Wing et al., 2003; Parrish et al., 2006; Janots et al., 2008; Kim et al., 2009). The emplacement and partial melting of some tonalites and granodiorites can be also dated with allanite (e.g., Romer and Siegesmund, 2003; Gregory et al., 2009).

The use of allanite for geochronology has been hampered, however, by its incorporation of relatively large amounts of initial Pb, and its common occurrence in a metamict state. Moreover, the high Th/U ratios in allanite make it difficult to measure its U–Pb ages with sufficient precision to assess their concordance with its Th–Pb age. In contrast, zircon is a popular chronometer because of its negligible initial Pb content, very low intracrystalline diffusion rates for U, Th and radiogenic Pb, and the common concordance of its $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ ages (Harley and Kelly, 2007). However, zircon rarely crystallises below upper amphibolite-facies conditions in the absence of melt (Williams, 2001; Rubatto et al., 2001). Although micro-zircon grains (up to 3 µm diameter) possibly can form in this temperature range (e.g., Dempster et al., 2008), it is presently technically difficult to measure their U–Th–Pb isotopic compositions with high precision. Instead, monazite has been extensively investigated for a decade because of its ability to record amphibolite-facies metamorphism (e.g., Williams, 2001; Rubatto et al., 2001). The chemical stability of monazite during metamorphism is sensitive to whole rock composition, however. In particular, elevated Ca and Al contents can destabilize monazite (e.g., Wing et al., 2003). Allanite is therefore an appropriate alternative to monazite for dating medium-grade metamorphism in Ca-rich lithologies.

Most dating studies of allanite, in spite of its complex internal structures, have used multi-grain samples, isotope dilution methods and thermal ionization mass spectrometry (TIMS) owing to the high and variable levels of substitution of trace elements, including initial Pb (Gieré and Sorensen, 2004). Some in-situ U–Th–Pb dating of allanite has been attempted using both isotopic and chemical techniques (e.g., Catlos et al., 2000; Cox et al., 2003; Suzuki et al.,

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2006; Gregory et al., 2007). The calibration and procedure for dating allanite using the sensitive high resolution ion microprobe (SHRIMP) were established by Gregory et al. (2007), who found that, for six different allanite reference materials, there was no significant matrix effect on the measured ages in the REE + Th range over 0.5 atoms per formula unit (apfu). Gregory et al. (2007) further suggested that both hydride interferences and mass fractionation of Pb isotopic compositions were negligible at the level of precision that could be achieved. Consequently, SHRIMP allanite dating can now be applied to solving a range of geological problems (e.g., Gregory et al., 2009; Janots et al., 2009).

In this study, we first report the internal and external resolution of U–Th–Pb dating of allanite using the SHRIMP II ion microprobe recently installed at the Korea Basic Science Institute (KBSI), and then the results of a study of the U–Th–Pb ages of allanite from tonalitic gneisses on Daeijak Island, central Korea. The study focused on a comparison between the Th–Pb and U–Pb isotopic systems in allanite to examine: (1) the robustness of Th–Pb ages during an event that caused severe ^{206}Pb loss; and (2) the different geochronological responses of allanite and zircon to metamorphism in a migmatite complex.

2. GEOLOGICAL BACKGROUND

Daeijak Island is situated in the Yellow Sea, west of central Korea. Geologically, it is contiguous with the Imjingang belt and the Gyeonggi massif (Fig. 1a). The Imjingang belt is an EW-trending fold-thrust belt that separates two Precambrian basement blocks, the Gyeonggi and Nangrim massifs (Fig. 1a). The belt consists mainly of sedimentary and volcanoclastic sequences with minor marble that were metamorphosed in the Permo-Triassic, at ~250 Ma (Cho et al., 2007). The depositional ages of the sequences are equivocal (Cho et al., 2007), but recent SHRIMP U–Pb ages from detrital zircon and intervening hornblende granite have constrained the deposition to be, at least in part, of Devonian age (Kee et al., 2008). The Gyeonggi massif to the South is a polymetamorphosed granulitic gneiss terrane consisting of Proterozoic continental basement and a Paleo-Mesoproterozoic supracrustal series (Lee et al., 2000, 2003). It also was subject to regional metamorphism during the Triassic (at ~230 Ma; e.g., Kim et al., 2006; Jeong et al., 2008; Kim et al., 2008). These lithotectonic units most likely represent the eastward extension of the Dabie-Sulu collisional belt in China (Cho et al., 2007; Ernst et al., 2007 and references

Fig. 1. (a) Major tectonic units of East Asia. Asterisk represents the location of Daeijak Island. (b) Simplified geological map of the study area with sample locations. Abbreviations: GM, Gyeonggi Massif; NM, Nangrim Massif; and YM, Yeongnam Massif.

therein). On the other hand, the Nangrim massif to the north is comparable to the North China craton, and includes Late Archean to Paleoproterozoic gneisses associated with younger metagneous and metasedimentary rocks (Zhao et al., 2005, 2006; Wu et al., 2007).

The Daeijak and nearby Soijak Islands are composed of a tonalitic-granodioritic migmatite complex overlain by metasedimentary cover (Fig. 1b). The migmatite complex has been divided into two different gneiss units (migmatitic gneisses to the west and tonalitic gneisses to the east) on the basis of apparent migmatization (Fig. 1b). The gneisses are intruded by leucocratic granite. Mafic xenoliths, or layers of dioritic to gabbroic amphibolite, commonly several meters in size, are enclosed in the tonalitic-granodioritic migmatite body (Cho et al., 2008). The timing of migmatization was recently constrained as late Archean on the basis of SHRIMP U–Pb zircon ages (Cho et al., 2008). The dated zircons consisted of a core with oscillatory zoning (~2.58 Ga) surrounded by a wide unzoned metamorphic overgrowth (~2.51 Ga). Despite its geographical proximity to the Gyeonggi massif, this Neoproterozoic migmatite might have a closer affinity to the Nangrim massif, which is comparable to the North China craton.

3. SAMPLE DESCRIPTIONS

The occurrence of allanite is mostly restricted to the tonalitic gneiss unit, but some tonalitic bodies within the migmatitic gneiss unit also contain a minor amount of allanite crystals (Fig. 1b). Two tonalitic gneiss samples, DE28 and DE43, one from each gneiss unit, were collected for allanite dating (Fig. 1b). The major mineral assemblage of the tonalitic gneisses includes biotite and hornblende coexisting in a felsic matrix primarily of oligoclase and quartz. The shape, size and modal proportion of biotite and hornblende differs from leucosomes to melanosomes. The major foliations are well defined by an aggregate of biotite and hornblende (Fig. 2a), but porphyritic hornblende is rarely present in the matrix. Kink bands and micro-folds have developed in the major foliations, with fold axes normal to the cleavage plane of biotite (Fig. 2b).

Allanite crystals, commonly rimmed by clinozoisite, are generally 100–300 µm in diameter, and are particularly common in the major foliations, together with accessory apatite, ilmenite, magnetite and zircon (Fig. 2a). These accessory minerals are aligned subparallel to the major foliations. The allanite crystals range in colour from medium brown to light brown, and have zonation patterns ranging from oscillatory to patchy (Fig. 2b). The zoning is also apparent in backscattered-electron images (Fig. 3). Apatite, quartz, and zircon are common inclusions in the allanite. At the outer rims of allanite bright layers, ~20 µm in width, are characterized by a high amount of Ce, Pb, and Th (Figs. 3a and d), and at the grain margin, thorium silicate and monazite rarely

Fig. 2. Photomicrographs showing the distribution and zonation of allanite crystals. (a) The distribution of accessory minerals subparallel to the major foliation defined by an aggregate of biotite and hornblende. (b) Allanite crystals of various zonation. Mineral abbreviations: Aln, allanite; Ap, apatite; Bt, biotite; Cz, clinozoisite; Hbl, hornblende; Ilm, ilmenite; and Zrn, zircon.

occur as minute inclusions together with cerium oxidic veinlets. The internal zonation of allanite is commonly disturbed, particularly in sample DE43, by clinozoisitic veinlets (Figs. 3j and k).

4. ANALYTICAL METHODS

Allanite grains were separated for isotopic analysis using conventional heavy liquid techniques, and were mounted in epoxy together with two reference allanites—Tara, from the Tara granodiorite in SE Australia, and CAP, from the Cima D'Asta Pluton granodiorite in northern Italy. The reference ages of the Tara and CAP allanites used in this study are 412 and 275.6 Ma, on the basis of the biotite Rb–Sr and TIMS $^{208}\text{Pb}/^{232}\text{Th}$ ages, respectively (Williams et al., 1982, 1983; Barth et al., 1994). After cleaning of the mount, com-

Fig. 3. Backscattered electron images of allanite. The sample and grain numbers used in Table 2 are shown in each image. White ellipses denote the analytical spots of ion probe, and white numbers represent the $^{208}\text{Pb}/^{232}\text{Th}$ age of the spot listed in Table 2. The ellipses without ages indicate the spot analyses incorporating more than 90% common ^{206}Pb and 10% common ^{208}Pb .

positional zonation of the allanite crystals was examined in low vacuum using a JEOL 6610LV scanning electron microscope at KBSI. Quantitative analyses were performed after isotopic analyses using a fully-automated JEOL 8900R electron microprobe at Seoul National University. The conditions and procedures for the analyses were after those of Kim et al. (2009), apart from the background positions for Fe and Sm, which were shifted owing to the proximity of peaks between Fe $K\alpha$ and Sm $L\beta_1$.

The U–Th–Pb isotopic compositions of the allanite were measured using the SHRIMP II ion microprobe at KBSI, Ochang campus. The analytical procedure was based upon that described by Gregory et al. (2007). Following the method, ^{232}Th was measured in addition to ThO for the independent U–Pb and Th–Pb calibration processes, using the linear relationship governed by equations:

$$\ln(^{206}\text{Pb}^+/^{238}\text{U}^+) = b \times \ln(^{238}\text{UO}^+/^{238}\text{U}^+) + c,$$

and

$$\ln(^{208}\text{Pb}^+/^{232}\text{Th}^+) = b \times \ln(^{232}\text{ThO}^+/^{232}\text{Th}^+) + c,$$

respectively, where b is the slope of the linear regression, and c is the y-intercept. The Th/U ratios of allanite were calculated from interelement fractionation between $^{232}\text{ThO}^+$ and $^{238}\text{UO}^+$, beginning with an equation (Williams et al., 1996),

$$^{232}\text{Th}/^{238}\text{U} = b \times ^{232}\text{ThO}^+/^{238}\text{UO}^+$$

where b is the fractionation factor (0.84 assumed here) and $^{232}\text{ThO}^+$ and $^{238}\text{UO}^+$ are the measured count rates. Epoxy-mounted grains of allanite were analyzed with a 3–5 nA, 10 kV primary O_2^- beam focused to a $\sim 20 \mu\text{m}$ diameter spot. The retardation lens on SHRIMP II was used to suppress scattered ions and minimize an isobaric interference with ^{204}Pb at ~ 5000 mass resolution. Each analysis consisted of five scans through the La, Pb, Th and U species of interest. Analytical uncertainties listed in Table 2 are one standard error precision estimates. All ages mentioned in the text, calculated using the constants recommended by the IUGS Sub-

commission on Geochronology (Steiger and Jäger, 1977), are cited with 95% confidence limits ($t\sigma$). Data reduction and age calculations were carried out using Prawn/Lead 6.5.5 software (T.R. Ireland, written communication, 1996) and Isoplot/Ex (Ludwig, 2003), respectively. Common Pb corrections were made using ^{207}Pb , assuming Pb/U concordance (Williams, 1998) and an assumed rock Pb composition at 230 Ma (Cumming and Richards, 1975). The common ^{208}Pb proportion (f_{208}) of allanite was calculated with the equation:

$$f_{208} = f_{206} \times \frac{(^{208}\text{Pb}/^{206}\text{Pb})_c}{(^{208}\text{Pb}/^{206}\text{Pb})_m}$$

where f_{206} is the common ^{206}Pb proportion in total ^{206}Pb , $(^{208}\text{Pb}/^{206}\text{Pb})_c$ is the model common Pb composition of Cumming and Richards (1975), and $(^{208}\text{Pb}/^{206}\text{Pb})_m$ is the measured ratio.

5. RESULTS

5.1. Standard Calibration

The ages of allanite were calculated from independent calibrations based upon the U–Pb and Th–Pb isotopic systems. Tara allanite was used as the primary standard, and CAP allanite as a secondary standard to estimate the accuracy of the calculated ages. The total REE + Th abundances of the two standards range from 0.77 to 0.84 apfu and 0.83 to 0.89 apfu, respectively (Gregory et al., 2007). Twenty-five spots on Tara allanite were analyzed in this study, and their common ^{206}Pb and ^{208}Pb abundances constitute 8–19% and up to 3% of total Pb, respectively. The U–Th–Pb isotopic compositions of Tara allanite, plotted in a ^{232}Th – ^{208}Pb vs. ^{238}U – ^{206}Pb concordia diagram (Fig. 4a), cluster around 412 Ma, mostly with less than 5% discordance. Omitting one analysis which was more than 10% discordant, the weighted mean $^{208}\text{Pb}/^{232}\text{Th}$

Fig. 4. ^{232}Th – ^{208}Pb vs. ^{238}U – ^{206}Pb concordia diagrams showing the spot analyses of allanite from (a) Tara, (b) CAP, (c) sample DE28, and (d) sample DE43, respectively. Open squares represent spot analyses excluded in the age calculations.

Fig. 5. Weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{Th}$ ages of (a) and (b) Tara allanite; and (c) and (d) CAP allanite, respectively. Ages are given at the 95% confidence limits (τ).

and $^{206}\text{Pb}/^{238}\text{U}$ ages of Tara allanite are 411.5 ± 2.6 Ma (τ , MSWD = 1.04) and 412.1 ± 9.0 Ma (τ ; MSWD = 0.33), respectively (Figs. 5a and b). These results suggest that allanite could be dated with an internal precision of $\sim 0.6\%$ and $\sim 2.2\%$ for each isotopic age. Fifteen spots on CAP allanite were dated during the analytical session of sample DE28. Plotted on a ^{232}Th – ^{208}Pb vs. ^{238}U – ^{206}Pb concordia diagram, the results show minor discordance due to a slight excess of ^{206}Pb (Fig. 4b). The weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of the CAP allanite is 274.4 ± 2.2 Ma (τ , MSWD = 1.16) (Fig. 5c), and the weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age is 279.5 ± 7.1 Ma (τ , MSWD = 0.40) (Fig. 5d). These data suggest that the accuracy of $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages in the analyses were measured within $\sim 0.4\%$ and $\sim 1.4\%$ error estimates, with respect to the reference age of CAP allanite (275.6 Ma), respectively.

5.2. Allanite Ages from Tonalitic Gneisses

The U–Th–Pb isotopic compositions of seventy-three

spots were measured on allanite from samples DE28 and DE43. The total LREE + Th abundances ranged from 0.58 to 0.83 apfu (Table 1), so no significant matrix effect is expected on the calculated ages (Gregory et al., 2007). Initial Pb contents are high, up to 99% and 94% of total ^{206}Pb and ^{208}Pb , respectively. Twenty-seven analyses with more than 90% common ^{206}Pb and 10% common ^{208}Pb were omitted from the age calculations. The remaining forty-six analyses are listed in Table 2. Analyses 5.1 and 5.2 of a single crystal from sample DE43 have a strong relative enrichment in ^{206}Pb (Table 2). It is not known whether the enrichment resulted from U-bearing micro-inclusions or from the incorporation of radiogenic ^{206}Pb inherited from a precursor (e.g., Romer and Siegesmund, 2003), but these two analyses were also omitted from the age calculations.

The U–Th–Pb isotopic compositions of forty-four spots are plotted in a ^{232}Th – ^{208}Pb vs. ^{238}U – ^{206}Pb concordia diagram (Figs. 4c and d). Twenty-one spots were analyzed from sample DE28, yielding two distinct age groups, with $^{208}\text{Pb}/^{232}\text{Th}$ ratios above and below 0.011, respectively (Fig. 4c).

Table 1. Representative compositions of allanite

Sample	DE28					DE43				
	Aln	Aln	Aln	Aln*	Aln	Aln	Aln*	Aln	Aln	Aln
SiO ₂	32.39	32.94	32.27	32.45	32.32	32.79	34.97	33.20	32.59	32.21
TiO ₂	0.80	0.53	0.60	0.75	1.03	0.76	0.94	0.71	0.88	0.82
Al ₂ O ₃	15.87	17.60	15.25	15.51	16.27	16.39	16.61	16.31	16.27	15.52
FeO	13.69	13.39	13.70	13.54	13.91	14.78	12.07	14.44	14.86	14.56
MgO	1.12	0.61	1.69	0.59	0.94	0.67	0.65	1.00	0.57	1.20
MnO	0.39	0.37	0.28	0.52	0.40	0.52	0.39	0.30	0.48	0.09
CaO	11.76	13.80	10.37	10.64	12.42	11.44	10.40	12.22	11.52	11.16
ThO ₂	0.89	0.75	1.05	3.62	0.39	0.84	2.68	0.85	0.56	0.67
F	0.08	0.11	0.05	0.08	0.08	0.44	0.22	0.30	-	0.09
Y ₂ O ₃	0.19	0.27	0.15	0.93	0.16	0.23	0.31	0.04	0.06	0.03
La ₂ O ₃	7.10	5.39	7.63	3.28	7.95	5.88	3.96	5.55	6.48	7.20
Ce ₂ O ₃	10.01	8.07	10.89	6.87	9.59	10.28	7.03	10.23	10.92	11.06
Pr ₂ O ₃	0.95	0.70	0.97	0.67	0.49	0.81	1.72	1.65	1.38	1.83
Nd ₂ O ₃	2.16	2.06	3.55	3.70	1.65	2.46	2.58	3.04	2.66	2.79
Sm ₂ O ₃	-	-	-	0.42	-	-	-	-	-	-
Gd ₂ O ₃	0.28	0.27	-	0.75	0.02	0.35	0.14	-	0.29	-
Total	97.65	96.81	98.42	94.27	97.56	98.46	94.55	99.70	99.59	99.17
Numbers of ions										
Si	3.066	3.055	3.078	3.151	3.040	3.062	3.274	3.066	3.038	3.047
Ti	0.057	0.037	0.043	0.055	0.073	0.053	0.066	0.050	0.061	0.058
Al	1.771	1.924	1.713	1.774	1.804	1.803	1.833	1.775	1.787	1.730
Fe + Mg + Mn	1.274	1.152	1.354	1.227	1.257	1.289	1.067	1.277	1.276	1.328
Ca	1.192	1.372	1.059	1.107	1.252	1.144	1.043	1.209	1.150	1.131
Th	0.019	0.016	0.023	0.080	0.008	0.018	0.057	0.018	0.012	0.014
Y	0.010	0.013	0.008	0.048	0.008	0.012	0.015	0.002	0.003	0.002
REEs	0.709	0.559	0.803	0.552	0.678	0.675	0.527	0.690	0.740	0.792

Notes: - = below the detection limits listed in Kim et al. (2009). Formulae were calculated on the basis of 12.5 oxygens per formula unit. Asterisk denotes the high-Th analyses possibly contaminated with thorium silicate.

Thirteen analyses that were mostly less than ~5% discordant clustered around ~230 Ma (Fig. 4c). Excluding one analysis with more than 20% discordance (analysis 14.1), their mean $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages were 228.5 ± 2.2 Ma (τ) and 222.7 ± 6.6 Ma (τ), respectively (Table 2). On the other hand, the remaining eight analyses had a mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 215.0 ± 3.6 Ma (τ) (Table 2). Apart from three analyses lying on a discordance line projecting towards ~190 Ma (analyses 3.1, 7.3, and 9.1), their mean $^{206}\text{Pb}/^{238}\text{U}$ age was 209.2 ± 15.8 Ma (τ) (Table 2).

Twenty-three spots were analyzed from sample DE43, showing a discordant pattern characterized by the systematic deviation of $^{206}\text{Pb}/^{238}\text{U}$ from the concordia at ~190 Ma (Fig. 4d). The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of twenty-one analyses, excluding two analyses whose $^{206}\text{Pb}/^{238}\text{U}$ ratios are greater than 0.033 (analyses 9.1 and 10.1), is 185.6 ± 9.0 Ma (τ , MSWD = 2.72) (Table 2). In contrast, their $^{208}\text{Pb}/^{232}\text{Th}$ compositions show a similar age pattern to that from sample DE28 (Fig. 6), although three analyses are displaced towards ~190 Ma (Fig. 4d). These three analyses (4.1, 8.1,

and 23.1 in Table 2) were omitted from the age calculations because they are possibly affected by the same event that reset the $^{206}\text{Pb}/^{238}\text{U}$ ages. When the same criterion used in sample DE28 was applied, eight spot analyses belong to an older age group and twelve to a younger one. After rejecting two analyses (10.1 and 11.1) to pass the *F*-test, the mean $^{208}\text{Pb}/^{232}\text{Th}$ age of the remaining six analyses was 227.1 ± 7.2 Ma (τ) (Table 2). On the other hand, the twelve analyses on the younger age group gave a $^{208}\text{Pb}/^{232}\text{Th}$ age of 213.2 ± 4.1 Ma (τ) (Table 2).

6. DISCUSSION

6.1. Robustness of Allanite Th–Pb Ages

The importance of the Th–Pb system for the accurate dating of allanite has previously been demonstrated (e.g., von Blanckenburg, 1992; Barth et al., 1994; Oberli et al., 2004; Gregory et al., 2007), and its superiority over the U–Pb system is largely based upon the better counting statistics

Table 2. U–Th–Pb isotope compositions of allanite

Label	Th/U	Common Pb (%)		$^{206}\text{Pb}^*/^{238}\text{U}$	$^{208}\text{Pb}^*/^{232}\text{Th}$	Apparent age (Ma)		Concordance (%)
		^{206}Pb	^{208}Pb			$^{206}\text{Pb}/^{238}\text{U}$	$^{208}\text{Pb}/^{232}\text{Th}$	
Sample DE28								
1.1	278	68	6	0.03430 ± 229	0.01090 ± 12	217 ± 16	219 ± 2	99.1
2.1	63	45	11	0.03408 ± 95	0.01126 ± 27	216 ± 6	226 ± 5	95.6
2.2	22	57	35	0.03393 ± 163	0.01137 ± 30	215 ± 10	228 ± 6	94.3
3.1	309	68	5	0.03059 ± 528	0.01179 ± 21	194 ± 33	237 ± 4	81.9
4.1	243	55	4	0.03441 ± 209	0.01131 ± 20	218 ± 13	227 ± 4	96.0
5.1	328	51	3	0.03625 ± 269	0.01151 ± 11	230 ± 17	231 ± 2	99.6
6.1	77	37	7	0.03555 ± 165	0.01129 ± 30	225 ± 10	227 ± 6	99.1
7.1	130	41	4	0.03567 ± 172	0.01124 ± 24	226 ± 11	226 ± 5	100.0
7.2	126	45	5	0.03524 ± 240	0.01155 ± 16	223 ± 15	232 ± 3	96.1
7.3	92	65	14	0.03086 ± 198	0.01092 ± 17	196 ± 12	219 ± 3	89.5
8.1	50	32	8	0.03607 ± 104	0.01134 ± 15	228 ± 6	228 ± 3	100.0
8.2	25	62	36	0.03222 ± 97	0.01081 ± 19	204 ± 6	217 ± 4	94.0
9.1	189	59	6	0.02943 ± 181	0.01063 ± 19	187 ± 11	214 ± 4	87.4
9.2	330	26	1	0.03271 ± 206	0.01045 ± 29	207 ± 13	210 ± 6	98.6
10.1	257	26	1	0.03312 ± 259	0.01074 ± 26	210 ± 16	216 ± 5	97.2
10.2	279	31	1	0.03258 ± 191	0.01029 ± 29	207 ± 12	207 ± 6	100.0
11.1	246	63	5	0.02993 ± 250	0.01081 ± 10	190 ± 16	217 ± 2	87.6
12.1	168	81	18	0.03180 ± 688	0.01131 ± 56	202 ± 43	227 ± 11	89.0
12.2	174	37	3	0.03573 ± 298	0.01124 ± 15	226 ± 19	226 ± 3	100.0
13.1	32	24	9	0.03658 ± 149	0.01115 ± 23	232 ± 9	224 ± 5	103.6
14.1	229	67	6	0.02688 ± 165	0.01115 ± 14	171 ± 10	224 ± 3	76.3
Sample DE43								
1.1	309	60	4	0.02976 ± 239	0.01136 ± 28	189 ± 15	228 ± 6	82.9
2.1	309	73	6	0.02323 ± 302	0.01058 ± 38	148 ± 19	213 ± 8	69.5
3.1	248	78	9	0.02483 ± 247	0.01059 ± 30	158 ± 16	213 ± 6	74.2
4.1	333	62	4	0.02591 ± 318	0.00961 ± 126	165 ± 20	193 ± 25	85.5
5.1	91	10	2	0.06184 ± 204	0.00947 ± 7	387 ± 12	190 ± 1	203.7
5.2	79	12	2	0.05122 ± 95	0.00892 ± 6	322 ± 6	179 ± 1	179.9
6.1	169	63	7	0.03146 ± 309	0.01129 ± 12	200 ± 19	227 ± 2	88.1
7.1	286	70	5	0.02855 ± 251	0.01133 ± 14	181 ± 16	228 ± 3	79.4
8.1	25	4	1	0.03002 ± 33	0.00952 ± 8	191 ± 2	191 ± 2	100.0
9.1	288	58	4	0.03678 ± 326	0.01091 ± 11	233 ± 20	219 ± 2	106.4
10.1	15	38	22	0.03354 ± 53	0.01205 ± 14	213 ± 3	242 ± 3	88.0
11.1	272	72	6	0.02795 ± 267	0.01190 ± 14	178 ± 17	239 ± 3	74.5
12.1	348	64	4	0.02587 ± 268	0.01143 ± 57	165 ± 17	230 ± 11	71.7
13.1	297	72	6	0.02153 ± 198	0.01062 ± 17	137 ± 12	214 ± 3	64.0
14.1	317	49	3	0.02752 ± 355	0.01109 ± 40	175 ± 22	223 ± 8	78.5
15.1	291	60	4	0.02280 ± 335	0.01061 ± 38	145 ± 21	213 ± 8	68.1
16.1	342	64	4	0.02296 ± 323	0.01097 ± 47	146 ± 20	220 ± 9	66.4
17.1	337	82	9	0.02995 ± 297	0.01128 ± 34	190 ± 19	227 ± 7	83.7
18.1	331	57	3	0.02682 ± 374	0.01064 ± 35	171 ± 24	214 ± 7	79.9
19.1	294	65	5	0.02718 ± 237	0.01062 ± 33	173 ± 15	214 ± 7	80.8
20.1	345	72	5	0.02707 ± 264	0.01030 ± 30	172 ± 17	207 ± 6	83.1
21.1	290	55	3	0.02189 ± 349	0.01058 ± 38	140 ± 22	213 ± 8	65.7
22.1	150	28	2	0.02844 ± 231	0.01036 ± 23	181 ± 14	208 ± 5	87.0
23.1	293	72	6	0.02642 ± 153	0.00943 ± 22	168 ± 10	190 ± 4	88.4
24.1	348	66	4	0.02348 ± 321	0.01109 ± 46	150 ± 20	223 ± 9	67.3

All the isotopic compositions and apparent ages were calculated on the basis of the ^{207}Pb correction methods (Williams, 1998), and the calculation of Th/U ratios was after the method described in Williams et al. (1996). The $^{208}\text{Pb}^*/^{232}\text{Th}$ ratio of 0.011 is used as a reference for the older and younger age groups.

Fig. 6. Distribution diagrams showing the $^{208}\text{Pb}/^{232}\text{Th}$ ages of allanite from (a) sample DE28 and (b) sample DE43. Five spot analyses in sample DE43 which were not involved in the age calculations are excluded (see the text for more details).

on ^{232}Th and ^{208}Pb due to the high Th/U ratio of allanite. This geochemical feature also means that the incorporation of common Pb has a much smaller effect on ^{208}Pb than on ^{206}Pb . Moreover, the $^{208}\text{Pb}/^{232}\text{Th}$ ages of allanite are free from the excess ^{206}Pb resulting from the decay of ^{230}Th (Schärer et al., 1984). As a consequence, the allanite $^{208}\text{Pb}/^{232}\text{Th}$ ages measured in this study are three times more precise than the $^{206}\text{Pb}/^{238}\text{U}$ ages, and also more accurate (Fig. 5). However, the Th–Pb age uses a single isotopic pair that cannot alone provide a measure of concordance. Assuming no loss or gain of U or Th, the degree of concordance can be assessed by comparing $^{208}\text{Pb}/^{232}\text{Th}$ ages with $^{206}\text{Pb}/^{238}\text{U}$ ages. Even this test is impeded, however, by the very high Th/U ratios in allanite, and the relatively large amounts of common Pb. Thus, the robustness of $^{208}\text{Pb}/^{232}\text{Th}$ ages of allanite has to be

demonstrated prior to the widespread use of allanite geochronology. In the present case, the excess or deficit of ^{206}Pb was variable enough to give complementary information for this test.

Although both the Tara and CAP allanite standards have a similar range of measured Th/U ratios (174–275 and 177–253, respectively), a slight excess of ^{206}Pb is apparent in the CAP (Fig. 4b). On the other hand, there is a systematic ^{206}Pb deficit in the sample DE43 allanite (Fig. 4d), but not in the allanite from sample DE28 (Fig. 4c). Nevertheless, the Th–Pb ages of the two allanite samples show the same bimodality (Fig. 6). The discordance between the $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages of allanite might be explicable either by incorporation of external U or by different responses of ^{206}Pb and ^{208}Pb to a Pb-loss event. The former is considered unlikely because kinetic studies on U–Th-rich minerals such as monazite and zircon, although not directly applicable to allanite, have shown that the intracrystalline diffusion rates for Th and U are slower than those for radiogenic Pb by several orders of magnitude (Cherniak and Watson, 2003; Cherniak et al., 2004; Cherniak and Pyle, 2008). Thus, if the bonding around tetravalent sites is loose enough to incorporate external U, no radiogenic Pb might survive in those sites.

On the other hand, discordance between $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ ages is common in zircon, particularly if the zircon is metamict. The differential losses of radiogenic ^{206}Pb and ^{208}Pb in zircon can be controlled by variable factors such as *P*, *T*, valence state of Pb, redox state, and α -recoiling (Kramers et al., 2009). Likewise, the discordance between the $^{208}\text{Pb}/^{232}\text{Th}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages of allanite observed in sample DE43 is most likely due to preferential ^{206}Pb loss. Therefore, the high Th/U ratios and strong retentivity of ^{208}Pb in allanite suggest that the Th–Pb isotopic system of allanite can provide robust ages even following an event that caused severe loss of uraniumogenic Pb. Excess ^{206}Pb resulting from ^{230}Th decay can have a significant effect (>1%) on the $^{206}\text{Pb}/^{238}\text{U}$ ages of allanite, particularly if the allanite has high Th/U (>50) and is relatively young (<100 Ma).

6.2. Responses of Allanite and Zircon to the Triassic Metamorphic Overprint

The U–Th–Pb ages of allanite have recorded three distinct events in the tonalitic gneiss samples from Daeijak Island. The first event occurred at ~228 Ma, defined by the mean $^{208}\text{Pb}/^{232}\text{Th}$ ages of the older allanite in samples DE28 and DE43 (228.5 ± 2.2 Ma and 227.1 ± 7.2 Ma, respectively). This age is the same as the mean $^{206}\text{Pb}/^{238}\text{U}$ age of the older allanite from DE28 (222.7 ± 6.6 Ma) within the analytical uncertainties. The second event took place at ~214 Ma, constrained by the mean $^{208}\text{Pb}/^{232}\text{Th}$ ages of the younger allanite from both samples (215.0 ± 3.6 Ma and 213.2 ± 4.1 Ma, respectively). This coincides with the mean

$^{206}\text{Pb}/^{238}\text{U}$ age of the younger allanite from sample DE28 (209.2 ± 15.8 Ma). The third event occurred in the middle Jurassic, and is recorded by the weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of the allanite from sample DE43 (185.6 ± 9.0 Ma, $\text{MSWD} = 2.7$). This event is considered to be Pb loss during final cooling.

These allanite ages demonstrate the widespread late Triassic metamorphic overprint in the study area. Although the geological implications of the two distinct Triassic ages are unclear, it is worth noting that the responses of allanite and zircon to the Triassic metamorphic overprint were very different. The thick metamorphic overgrowths on the zircons from sample DE28 have Neoproterozoic U–Pb ages (~ 2.51 Ga; Cho et al., 2008) and, unlike the allanite, show no evidence of a Triassic event. This geochronological contrast has significant implications for zircon geochronology. It is common that zircon overgrowths are too narrow ($< 5 \mu\text{m}$) to measure the U–Th–Pb isotopic composition of the area precisely, even though the overgrowth is clearly visible by its contrasting cathodoluminescence. The disparate ages between allanite and zircon overgrowths show that events not recorded by zircon can be dated using allanite.

7. CONCLUSIONS

The careful examination of the concordance between the U–Pb and Th–Pb isotopic systems in allanite has allowed us to unravel the widespread late Triassic metamorphic events in Daeijak Island, in addition to a major Pb-loss event in the middle Jurassic. Moreover, the $^{208}\text{Pb}/^{232}\text{Th}$ analyses of allanite gave an identical age pattern in two different samples, in contrast to the disagreement between the $^{206}\text{Pb}/^{238}\text{U}$ ages, suggesting that the Th–Pb isotopic system of allanite is robust enough to retain radiogenic ^{208}Pb through an event capable of causing significant loss of uraniumogenic Pb. The application of allanite geochronology can uncover details of the metamorphic history of a migmatitic terrane that are not recorded by other chronometers.

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REFERENCES

- Barth, S., Oberli, F., and Meier, M., 1994, Th–Pb versus U–Pb systematics in allanite from co-genetic rhyolite and granodiorite: implications for geochronology. *Earth and Planetary Science Letters*, 124, 149–159.
- Catlos, E.J., Sorensen, S.S., and Harrison, T.M., 2000, Th–Pb ion-microprobe dating of allanite. *American Mineralogist*, 85, 633–648.
- Cherniak, D.J. and Watson, E.B., 2003, Diffusion in zircon. *Review in Mineralogy and Geochemistry*, 53, 113–143.
- Cherniak, D.J., Watson, E.B., Grove, M., and Harrison, T.M., 2004, Pb diffusion in monazite: a combined RBS/SIMS study. *Geochimica et Cosmochimica Acta*, 68, 829–840.
- Cherniak, D.J. and Pyle, J.M., 2008, Th diffusion in monazite. *Chemical Geology*, 256, 52–61.
- Cho, M., Kim, Y., and Ahn, J., 2007, Metamorphic evolution of the Imjingang belt, Korea: Implications for Permo-Triassic collisional orogeny. *International Geology Review*, 49, 30–51.
- Cho, M., Kim, H., Lee, Y., Horie, K., and Hidaka, H., 2008, The oldest (ca. 2.51 Ga) rock in South Korea: U–Pb zircon age of a tonalitic migmatite, Daeijak Island, western Gyeonggi massif. *Geosciences Journal*, 12, 1–6.
- Cox, R.A., Wilton, D.H.C., and Košler, J., 2003, Laser-ablation U–Th–Pb in situ dating of allanite and zircon: an example from the October Harbour granite, central coastal Labrador, Canada. *Canadian Mineralogist*, 273–291.
- Cumming, G.L. and Richards, J.R., 1975, Ore lead isotope ratios in a continuously changing earth. *Earth and Planetary Science Letters*, 28, 155–171.
- Dempster, T.J., Hay, D.C., Gordon, H., and Kelly, N.M., 2008, Micro-zircon: origin and evolution during metamorphism. *Journal of Metamorphic Geology*, 26, 499–507.
- Ernst, W.G., Tsujimori, T., Zhang, R., and Liou, J.G., 2007, Permo-Triassic collision, subduction-zone metamorphism, and tectonic exhumation along the East Asian continental margin. *Annual Review of Earth and Planetary Sciences*, 35, 73–110.
- Gieré, R. and Sorensen, S.S., 2004, Allanite and other REE-rich epidote-group minerals. *Reviews in Mineralogy and Geochemistry*, 56, 431–493.
- Gregory, C.J., Rubatto, D., Allen, C.M., Williams, I.S., Hermann, J., and Ireland, T., 2007, Allanite micro-geochronology: A LA-ICP-MS and SHRIMP U–Th–Pb study. *Chemical Geology*, 245, 162–182.
- Gregory, C.J., Buick, I.S., Hermann, J., and Rubatto, D., 2009, Mineral-scale trace element and U–Th–Pb age constraints on metamorphism and melting during the Petermann Orogeny (central Australia). *Journal of Petrology*, 50, 251–287.
- Harley, S.L. and Kelly, N.M., 2007, Zircon: tiny but timely. *Elements*, 3, 13–18.
- 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. *Journal of Metamorphic Geology*, 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.
- Jeong, Y.-J., Yi, K., Cheong, C.-S., and Kamo, S.L., 2008, ID-TIMS single zircon age determination of mangerite in the eastern Gyeonggi massif, Korea. *Journal of the Geological Society of Korea*, 44, 425–433 (in Korean with English abstract).
- Kee, W.-S., Lim, S.-B., Kim, H., Kim, B.C., Hwang, S.K., Song, K.Y., and Kihm, Y.-H., 2008, Geological report of the Yeoncheon sheet, scale 1:50,000. Korea Institute of Geosciences and Mineral Resources, 83 p.
- Kim, J., Cheong, C.-S., Lee, S.R., Cho, M., and Yi, K., 2008, In-situ U–Pb titanite age of the Chuncheon amphibolite: Evidence for Triassic regional metamorphism in central Gyeonggi massif, South Korea, and its tectonic implication. *Geosciences Journal*, 12, 309–316.
- Kim, S.W., Oh, C.W., Williams, I.S., Rubatto, D., Ryu, I.-C., Rajesh,

- V.J., Kim, C.-B., Guo, J., and Zhai, M., 2006, Phanerozoic high-pressure eclogite and intermediate-pressure granulite facies metamorphism in the Gyeonggi massif, South Korea: Implications for the eastward extension of the Dabie-Sulu continental collision zone. *Lithos*, 92, 357–377.
- Kim, Y., Yi, K., and Cho, M., 2009, Parageneses and Th–U distributions among allanite, monazite, and xenotime in Barrovian-type metapelites, Imjingang belt, central Korea. *American Mineralogist*, 94, 430–438.
- Kramers, J., Frei, R., Newville, M., Kober, B., and Villa, I., 2009, On the valency state of radiogenic lead in zircon and its consequences. *Chemical Geology*, 261, 4–11.
- Lee, S.R., Cho, M., Yi, K., and Stern, R., 2000, Early Proterozoic granulites in central Korea: tectonic correlation with Chinese cratons. *Journal of Geology*, 108, 729–738.
- Lee, S.R., Cho, M., Hwang, J.H., Lee, B.-J., Kim, Y.-B., and Kim, J.C., 2003, Crustal evolution of the Gyeonggi massif, South Korea: Nd isotopic evidence and implications for continental growths of East Asia. *Precambrian Research*, 121, 25–34.
- Ludwig, K.R., 2003, User's manual for Isoplot 3.00: a Geochronological Toolkit for Microsoft Excel.
- Oberli, F., Meier, M., Berger, A., Rosenberg, C.L., and Reto Gieré, 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. *Geochimica et Cosmochimica Acta*, 68, 2543–2560.
- Parrish, R.R., Gough, S.J., Searle, M.P., and Waters, D.J., 2006, Plate velocity exhumation of ultrahigh-pressure eclogite in the Pakistan Himalaya. *Geology*, 34, 989–992.
- Romer, R.L. and Siegesmund, S., 2003, Why allanite may swindle about its true age. *Contributions to Mineralogy and Petrology*, 146, 297–307.
- Rubatto, D., Williams, I.S., and Buick, I.S., 2001, Zircon and monazite response to prograde metamorphism in the Reynolds Range, central Australia. *Contributions to Mineralogy and Petrology*, 140, 458–468.
- Schärer, U., 1984, The effect of initial ^{230}Th disequilibrium on young U–Pb ages: the Makalu case, Himalaya. *Earth and Planetary Science Letters*, 67, 191–204.
- Steiger, R.H. and Jäger, E., 1977, Subcommittee on geochronology: convention on the use of decay constants in geo- and cosmo-chronology. *Earth and Planetary Science Letters*, 36, 359–362.
- Suzuki, K., Dunkley, D., Adachi, M., and Chwae, U., 2006, Discovery of a c. 370 Ma granite gneiss clast from the Hwanggangri pebble-bearing phyllite in the Okcheon metamorphic belt, Korea. *Gondwana Research*, 9, 85–94.
- von Blanckenburg, F., 1992, Combined high-precision chronometry and geochemical tracing using accessory minerals applied to the Central-Alpine Bergell intrusion (Central Europe). *Chemical Geology*, 100, 19–40.
- Williams, I.S., 1998, U–Th–Pb geochronology by ion microprobe. *Reviews in Economic Geology*, 7, 1–35.
- Williams, I.S., 2001, Response of detrital zircon and monazite, and their U–Pb isotopic systems, to regional metamorphism and host-rock partial melting, Cooma Complex, southeastern Australia. *Australian Journal of Earth Sciences*, 48, 557–580.
- Williams, I.S., Tetley, N.W., Compston, W., and McDougall, I., 1982, A comparison of K–Ar and Rb–Sr ages of rapidly cooled igneous rocks: two points in the Palaeozoic time scale re-evaluated. *Journal of the Geological Society of London*, 139, 557–568.
- Williams, I.S., Compston, W., and Chappell, B.W., 1983, Zircon and monazite U–Pb systems and the histories of I-Type magmas, Berridale Batholith, Australia. *Journal of Petrology*, 24, 76–97.
- Williams, I.S., Buick, I.S., and Cartwright, I., 1996, An extended episode of early Mesoproterozoic metamorphic fluid flow in the Reynolds Range, central Australia. *Journal of Metamorphic Geology*, 14, 29–47.
- 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. *Contributions to Mineralogy and Petrology*, 145, 228–250.
- Wu, F.-Y., Han, R.-H., Yang, J.-H., Wilde, S.A., Zhai, M.-G., and Park, S.-C., 2007, Initial constraints on the timing of granitic magmatism in North Korea using U–Pb zircon geochronology. *Chemical Geology*, 238, 232–248.
- Zhao, G., Sun, M., Wilde, S.A., and Li, S.Z., 2005, Late Archean to Paleoproterozoic evolution of the North China Craton: key issues revisited. *Precambrian Research*, 136, 177–202.
- Zhao, G., Cao, L., Wilde, S.A., Sun, M., Choe, W.J., and Li, S., 2006, Implications based on the first SHRIMP U–Pb zircon dating on Precambrian granitoid rocks in North Korea. *Earth and Planetary Science Letters*, 251, 365–379.

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