Research paper

Multi-step TIMS and CA-TIMS monazite U–Pb geochronology

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ABSTRACT

Multi-step chemical abrasion thermal ionization mass spectrometry (CA-TIMS) methods were developed for monazite using six samples that vary in composition and age—Amelia, Jefferson County, Burke, Elk Mountain, Madagascar and Madagascar. To evaluate whether the multi-step CA-TIMS approach reveals complexities in either age or composition that might be masked by single-step analysis, this study presents a side-by-side comparison of monazite samples dated via multi-step TIMS (not annealed) and CA-TIMS (annealed), and measurement of rare earth element ratios for each dissolution step. The data demonstrate three important contributions. First, annealing reduces solubility—after one partial dissolution step, not-annealed fractions were 3.3–4.1 times more digested than the annealed fractions. The difference in solubility suggests that monazite does not fully self-anneal at low temperatures. Second, multi-step TIMS analyses yielded high-precision U–Pb plateau ages for the Burke and Amelia monazites; CA-TIMS analyses yielded high-precision U–Pb plateau ages for Madagascar and Amelia monazites. Jefferson County, Elk Mountain and Madagascar yielded more complex results and no U–Pb plateau ages. Third, chemical analysis of partial-dissolution steps reveals heterogeneous age and compositional data for annealed samples. Because not-annealed samples yielded more consistent age and compositional data, high-temperature annealing is not recommended for monazite. Instead, optimal TIMS results are provided by slow, partial dissolution of monazite in weak acid.

1. Introduction

Because determining the rates of large-scale tectonic processes—including exhumation, uplift and burial—remains a fundamental issue in geology, the need for more accurate and precise mineral dates is critical. Geochronologists have long appreciated the potential of monazite [(Ce,Th,REE)PO₄] as a geochronometer for several reasons: 1) it is stable at a wide range of pressures and temperatures over a broad range of bulk compositions (Parrish, 1990; Chang et al., 1998; Catlos et al., 2002; Pyle et al., 2002); 2) it contains U and Th (Overstreet, 1967), thus providing three decay schemes to assess concordance (²³⁵U → ²⁰⁸Pb, ²³⁸U → ²⁰⁶Pb, ²³²Th → ²⁰⁸Pb); 3) it generally contains low initial concentrations of common Pb (Parrish, 1990), thereby reducing the correction for common Pb; 4) and, perhaps most importantly, the low diffusivity of elements within monazite (Cherniak et al., 2004) enables the preservation of compositional zoning that may reflect changes in pressure, temperature, fluid composition, and/or the growth or consumption of other minerals (e.g. Chang et al., 1998; Pyle et al., 2001; Williams et al., 2002; Kohn and Malloy, 2004; Janots et al., 2006). Correlation of monazite composition with mineral reactions and pressure–temperature (P–T) histories can provide important pressure–temperature–time (P–T–t) information not attainable by other means (e.g. Pyle and Spear, 1999; Dumond et al., 2008; Janots et al., 2009).

A variety of techniques have been used to determine monazite (U–Th)/Pb dates, including laser ablation inductively coupled mass spectrometry (LA-ICPMS), secondary ion mass spectrometry (SIMS), electron probe microanalysis (EPMA) and thermal ionization mass spectrometry (TIMS). Microbeam techniques, including LA-ICPMS, SIMS and EPMA, provide a means to measure in situ dates from monazite; in favorable circumstances, these dates can be used to determine the timing or rates of metamorphic, magmatic and diagenetic processes (Suzuki and Adachi, 1991; Harrison et al., 1995; Stern and Berman, 2001; Foster et al., 2004; Williams et al., 2007). In the simplest terms, LA-ICPMS and SIMS methods measure Pb/Th and Pb/Th and the isotopic ratios of Pb in monazite to calculate a date, whereas EPMA methods measure the elemental concentrations of U, Th and Pb to calculate a date.

Several recent improvements in analytical techniques afford smaller microbeam sizes (~5 μm), improved counting accuracy and precision, and shorter analytical times; for example ~1 minute total analysis time is now routine via LA-ICPMS (e.g. Gehrels et al., 2008). Unfortunately, the ability to obtain reproducible and accurate dates with many of these techniques has proven problematic for several reasons (Hortonwood, 2008; Kohn and Vervoort, 2008). First, microbeam techniques require the use of a reference material. The accuracy
and precision of microbeam dates are therefore limited by instrumen-
tment reproducibility and the degree of isotopic homogeneity of the
reference material—any heterogeneity in the reference material
must be incorporated into the errors for an unknown. Second, LA-
ICPMS and SIMS techniques extract matrix material (e.g. Zr, Si, P, Ca, REE) that may form polyatomic species that are isotopic with the
isotopes of interest, such as Pb (Ireland, 1995; Stern and Berman,
2001). While methods have been developed to correct for interferences,
the corrections can be large. For EPMA techniques, considerable time
must be devoted in quantifying the background for each sampling do-
main prior to analysis (e.g. Williams et al., 2007; Jercinovic et al.,
2008; Spear et al., 2009). Furthermore, EPMA methods must assume
concordance a priori because electron probes measure elemental con-
centrations, not isotopes. Third, LA-ICPMS and SIMS methods produce
both elemental and isotopic fractionation as a result of differential
vaporization and mobilization of extracted material (Hirata and
Nesbitt, 1995; Horn et al., 2000; Kosler et al., 2001; Fletcher et al.,
2010). Collectively, these “matrix effects” can affect the accuracy of
measured dates by suppressing the ionization of targeted isotopes or
producing isotopic interferences on measured masses.

Although they require significantly more analytical time to mea-
sure (hours vs. minutes), TIMS dates have long been interpreted as the “true” age of reference materials and are therefore commonly
used as the benchmark age for calibrating other methods (e.g. Harri-
son et al., 1995). For TIMS analysis, samples are spiked with an
isotopic tracer (the “isotope dilution” (ID) method) during dissolu-
tion. Spiked samples do not need to be calibrated to a separate ref-
cerence material, thereby eliminating a major source of error. TIMS
methods also do not confront the analytical challenge of “matrix effects” because this material is removed by column chemistry
prior to analysis.

Despite its many advantages, TIMS analysis presents a few chal-
lenges. TIMS analyses do not commonly yield high spatial resolution
and typical preparation methods remove the grains from their petro-
graphic context. However, methods have been developed to measure
multiple ID-TIMS ages from a single grain. Examples of these methods
include fragmenting grains to analyze selected portions such as the
tips of grains (e.g. Schärer and Allègre, 1982). More recently, X-ray
maps are used to guide micro-sampling techniques via microm-
illing (e.g. Corrie and Kohn, 2007).

Many iterations of method development for TIMS analysis have
been published, typically aimed at selectively reducing or removing
discordance. For example, the air abrasion method (Krogh, 1982)
mechanically removes the outer layers of grains, often largely reduc-
ing the degree of discordance. However, air abrasion cannot remove
discordant interior portions of grains, resulting in small amounts of re-
sidual discordance. Chemical abrasion TIMS (“CA-TIMS”, e.g. Mattin-
son, 2003, 2005) is the latest technique for preferentially removing discord-
ant portions of grains, both inside and out. The CA-TIMS method was
pioneered with the accessory mineral zircon (ZrSiO₄) and uses high-
temperature pre-dissolution annealing followed by one or more partial
dissolution steps. The high-temperature annealing process converts
metamict zircon to baddeleyite (ZrO₂), which is more easily dissolved
than zircon. This process typically leaves a residue of closed-system
zircon that, in the absence of inheritance, yields concordant results
(e.g. Mundil et al., 2004).

Because of the success of CA-TIMS with zircon, we conducted a
series of experiments to assess the application of CA-TIMS to U-Pb
dating of monazite. In contrast to zircon, monazite is rarely metamict
and is thought to self-annul at low temperatures (Meldrum et al.,
1998). However, previous work has demonstrated that thermal anneal-
ing produces structural recovery (Seydoux-Guillaume et al., 2002a),
indicating that monazite does accumulate some radiation damage.
Annealing at temperatures of 900–1100 °C yielded the most structural
recovery as determined by Raman spectroscopy (Nasdala et al., 2002;
Seydoux-Guillaume et al., 2002a). Although these temperatures are
high, Pb diffusion studies have shown that a 100 μm radius monazite that
cooled at 10 °C/Myr has a closure temperature of 1050 °C, which
is 50 °C higher than zircon for equivalent conditions (Cherniak et al.,
2004). These data suggest that a 48-hour annealing step at 1000 °C
may repair the crystal lattice in monazite, thereby affording slower dis-
solution rates, without affecting the isotopic age. If thermal annealing
converts radiation-damaged domains in monazite to a different phase
– as seen with zircon – these domains should be chemically distinct
and therefore identifiable via geochemical analysis.

The purposes of this study were to 1) evaluate the effects of
annealing on the dissolution rate and isotopic age, and 2) determine
whether the detailed, multi-step CA-TIMS approach reveals complex-
ities in either age or composition that might be masked by single-step
analysis. These questions were addressed through a side-by-side
comparison of isotopic dates via multi-step TIMS (not annealed)
and CA-TIMS (annealed), and measurement of rare earth element
ratios for each dissolution step.

1.1. Sample selection criteria

Monazite samples were selected for this study because 1) their
differences in composition (Fig. 1) reflect the range in natural mona-
zite. For example, among the samples analyzed, ThO₂ ranges from
~3.5 to 15 wt.%; Ce₂O₃ from ~17 to 30 wt.%; Y₂O₃ from 0.5 to
2.5 wt.%; and CaO from 0.14 to 1.4 wt.% (Table 1; further EPMA data
are compiled in the Data Repository). 2) Previous LA-ICPMS and
SIMS analysis (Peterman et al., 2006) yielded relatively homogeneous
isotopic data, despite elemental heterogeneity within some grains
(e.g. Fig. 2). 3) The samples exist in sufficient quantity that they
could be used as reference materials. Although the best reference
materials are both isotopically and compositionally homogeneous,
isotopic homogeneity is the most critical characteristic of a reference
material. Because 554, Jefferson County, Madagascar, Amelia and Elk
Mountain were previously distributed as potential age reference
materials, these samples were analyzed to evaluate their suitability.

1.2. Sample descriptions

554 is an accessory mineral from the peraluminous granite Catnip
sill, a member of the Wilderness intrusive suite in the Santa Catalina
Mountains, Arizona. This monazite is commonly used as a reference
material for ion microprobe analysis (e.g. Harrison et al., 1999) and
is the only sample for which whole grains—not fragments—were
used in this study. Grains measure ~200 μm in diameter. In

Fig. 1. Electron microprobe composition data of monazites analyzed in this study, normalized to monazite standard ‘44069’ (Aleinikoff et al., 2006).
comparison with other monazites, 554 is low in U₂O₃ and ThO₂ (Table 1; full EMPA dataset in the Data Repository). Previous U–Th–Pb work on this sample yielded ages of 44–47 Ma (Shakel et al., 1977); the Th–Pb age of 554 is 45±1.3 Ma (measured by M. Tatsumoto, as cited in Harrison et al., 1999). The age heterogeneity presents an opportunity to assess whether the CA-TIMS technique can elucidate complex monazite samples.

Amelia is a compositionally homogeneous Th-rich megacryst (Figs. 1 and 2; Table 1). Pegmatites from this mining region yielded a mica Rb–Sr age of 279±14 Ma (Deuser and Herzog, 1962). Conventional TIMS analysis yielded a 206Pb/238U age of 274.58±0.58 Ma (Table 1 and Data Repository). This sample was provided by the Smithsonian Institution and has previously been referred to as Smithsonian (Peterman et al., 2006).

Burke is a commercially purchased orange–yellow megacryst with patchy zoning and some (micro)cracks (Fig. 2); it is largely free of visible inclusions. It is the most Ca-rich monazite analyzed in this study (Fig. 1; Table 1), has more than one domain visible in backscattered electron (BSE) images (Fig. 2), and has greater variation in elemental composition than other samples (e.g. Y₂O₃, ThO₂; Table 1; Data Repository).

Elk Mountain is a portion of a pale to dark brown megacryst that has been widely distributed as an electron microprobe standard by M. Bersch (Univ. of Alabama). EPMA analyses of composition are homogeneous among and within grains. Analyses of a different aliquot of this sample yielded 207Pb/206Pb ages from 1391 to 1404 Ma and 206Pb/238U ages from 1413 to 1593 Ma (unpublished data, J. Baldwin, MIT).

Jefferson County is a portion of a brown megacryst that was also distributed as an electron microprobe standard by M. Bersch. Relative to the other samples, Jefferson County is depleted in light REE (Fig. 1; Table 1). It has patchy zoning and abundant (micro)cracks (Fig. 2). Previous LA-ICPMS data yielded an age of 365.5±2.6 Ma (Peterman et al., 2006); conventional TIMS analysis yielded an equivalent 206Pb/238U age of 363.98±0.74 Ma (Data Repository).

Madagascar is a brown–orange megacryst. Relative to other monazites, Madagascar is enriched in Pr and Nd, and depleted in Ca and Dy (Fig. 1; Table 1). LA-ICPMS and SHRIMP data suggested a crystallization age of ~492 Ma (Peterman et al., 2006). Conventional TIMS analysis yielded a 208Pb/235U age of 511.3±4.9 Ma (Data Repository).

2. Methods

2.1. EPMA

Quantitative compositional analyses of the six monazite samples were conducted on Cameca SX-50 and Cameca SX-100 electron microprobes at UCSB, both operated at 15 kV accelerating voltage and 200 nA beam current. Monazite compositions are compared in Fig. 1; selected EPMA data are summarized Table 1. The full EPMA dataset is in the Data Repository.
2.2. Dissolution conditions

Several different sample-dissolution techniques were investigated in this study. Previous methods for monazite dissolution typically used concentrated HCl (≈12 M) at high temperatures (≈180 °C) and were targeted at complete dissolution. We experimented with acid strength (12 M, 6 M and 3.1 M HCl), temperature (120 °C, 100 °C and 80 °C) and step durations (12 and 6 h) to determine optimal conditions to permit multi-step analysis. All dissolution experiments were conducted with PARR digestion vessels. Not-annealed grain fragments of the Jefferson County and Amelia samples were ≈80% dissolved with 6 M HCl at 120 °C for 12 h. Following identical dissolution conditions, grain fragments annealed for 48 h at 1000 °C were only 10–30% dissolved. The reduction in dissolution rate is consistent with results from zircon experiments (e.g. Mattinson, 2005). Because 10–30% dissolution in the first step represents a large proportion of the material, we used 3.1 M HCl and low initial temperature steps (80 °C) to yield sufficient dissolution steps to evaluate the CA-TIMS technique. The temperature and time for each dissolution step are listed in Table 2.

2.3. Sample dissolution and column chemistry

Multiple-grain aliquots of similarly sized grains or grain fragments of monazite samples 354, Amelia, Burke, Elk Mountain, Jefferson County and Madagascar were selected for analysis. Approximately 10 grains (or grain fragments) of each sample were pretreated with a high-temperature annealing step (1000 °C for 48 h in air in high-purity alumina crucibles) and analyzed via multi-step CA-TIMS. An additional 10 grain fragments of the Burke, Amelia and Jefferson County samples were analyzed via multi-step TIMS without high-temperature pretreatment. The not-annealed grain fragments were optically identical to their annealed counterparts. In total, nine multi-grain (or grain fragment) samples were analyzed. Annealed samples are labeled “A”; not-annealed samples are labeled “N.”

To remove surface contaminants, each sample was transferred into a 3 mL Teflon screw-top vial and rinsed with 1.5 μM HCl followed by two ultra-clean H2O rinses. For each dissolution step, 50 μL of a 3.1 M HCl 205Pb/235U spike (converted from the commonly used “zircon” spike (e.g. Mattinson, 2005)) and 450 μL of 3.1 M HCl were added to each sample. The vials were then stacked three deep inside Teflon cups with an additional 1.5 mL 3.1 M HCl to normalize the vapor pressure inside and outside the sample vials. Teflon cups were placed inside PARR digestion vessels and loaded into ovens for dissolution. The paired annealed and not-annealed samples – Jefferson County, Amelia and Burke – underwent parallel dissolution conditions (i.e. the same temperature and time). Because 554 is much younger (Table 1) and smaller (average grain size ≈200 μm diameter vs. 0.5–1 mm grain fragments for other samples), higher temperatures were used to yield enough U and Pb to measure reasonably precise ages on individual steps (Table 2). After every partial dissolution step, each sample was rinsed with ultra-clean water (at the lab bench) and then cleaned twice in 500 μL ultra-clean H2O in the oven at the same temperature and time as the previous step. All rinse and cleaning solutions were pipetted off and discarded.

The Pb and U from each step were purified using the HCl ion exchange chemistry of Krogh (1973) with 0.15 mL column resin beds. Column elutions were reserved for compositional analysis via ICP-MS (see Section 3.5). Pb and U were extracted from the columns together using ultra-clean H2O and were collected in clean 5 mL Teflon beakers containing 6 μL 1 M H3PO4 (after Mattinson, 2005). After samples were fully dried in a HEPA-filtered drying box, Pb and U were loaded together onto outgassed Re filaments in 3.5 μL of silica gel.

2.4. U-Pb measurements

Samples were loaded in the UCSB Finnigan-MAT 261 TIMS and evacuated overnight. Each filament was preheated for 2 min at

2.0 A. U and Pb isotopic ratios were measured in static multi-collection mode. For most samples, 206Pb, 207Pb and 208Pb were collected on Faraday cups while 204Pb was simultaneously collected on a Spectromat ion-counting system; because the Amelia monazite has a high 204Pb/206Pb ratio. 208Pb was collected on a Faraday cup.

The NIST 983 Pb standard was used to calibrate the ion-counter relative to the Faraday cups. Data were fractionation corrected using an assumed value of 0.12%/amu. The sample age was used to estimate the common-Pb correction following Stacey and Kramers (1975); 206Pb/204Pbcommon and 207Pb/204Pbcommon ratios are included in Table 2. Conservative error estimates of ±0.5 and ±0.2 were used for 206Pb/204Pb and 207Pb/204Pb, respectively. Further details regarding error propagation and data analysis are provided in the Appendix A.

2.5. REE, P and Th measurements

Based on EPMA data (Data Repository), compositional domains within monazite grains can be identified by changes in relative concentrations of U, Th, Dy and Nd. To assess if age domains correlate with compositional domains, the composition and amount of monazite digested in each partial dissolution step were measured by analyzing the column elutions via ICPMS. Because each step dissolved different amounts of monazite, blank-corrected ratios (not concentrations) were used to identify changes in composition among the steps.

P and REE were measured on the Element XR at UC Santa Cruz, which has a sensitivity of 106 cps/ppb. Samples were spiked with 10 ppb Ho as an internal standard. The samples were aspirated with additional P-10 carrier gas (15 mL/min) to enhance P sensitivity and reduce oxide formation. 139La, 140Ce, 141Pr, 143Nd, 145Nd, 146Nd, 147Sm, 148Sm, 153Gd, 157Gd, 161Dy and 163Dy were measured in low-resolution mode using 165Ho as an internal standard; 31P was measured in medium-resolution mode. 232Th and 140Ce were measured on the Element X-Series Quadrupole ICPMS at UC Santa Cruz; 140Ce was used to intercalibrate the REE, P and Th data (Data Repository Table 2). The external precision of the ratios measured on the X-Series ICPMS was <0.2% (1σ) with a detection limit of 2 ppt; the instrument sensitivity is ~50,000 cps/ppb. Blank-corrected compositional data can be found in the Data Repository. An external isotope ratio precision of <0.4% (1σ) was determined by calculating the standard deviation of seven analyses of a monazite solution interspersed throughout the analytical run.

For this dataset, U/P, Th/P, Nd/P and Dy/P were used to determine if partial dissolution steps were sampling multiple compositional domains. Changes in U and Th might indicate dissolution of different age domains; Nd and Dy are the most reliable indicators of variation in REE for these six samples.

2.6. Single-step dissolution and TIMS analysis of Elk Mountain

Discrepancies between measured U/Pb and Pb/Pb ages for Elk Mountain merited further analysis. Eight new grain fragments were selected for analysis (grain images in Data Repository 2) and annealed at 1000 °C for 48 h prior to single-step dissolution. Each fragment was rinsed with water to remove surface contamination, spiked and dissolved in a PARR digestion vessel in ~500 μL of 3.1 M HCl at 200 °C for 12 h, ensuring complete single-step dissolution. The grain fragments were run through column chemistry and analyzed following methods described in Sections 3.4 and 3.5.

3. Results

3.1. SEM imaging

BSE imaging of annealed monazite shows the development of platy textures along the grain margins (Fig. 2). Although not-
Table 2
Experimental conditions and U–Pb geochronology data for CA-TIMS and multi-step TIMS analyses.

<table>
<thead>
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<th>Step conditions</th>
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<th>Calculated ages (Ma)</th>
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<td>P (%)</td>
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annealed grains also have platy textures along the margins, they are less developed than on the annealed grains. BSE images of the annealed Jefferson County grain fragment also contain white wisps that are not evident in the not-annealed sample; these wisps may indicate recrystallization, but the scale of these features is too small to directly analyze via SEM or EPMA.

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The acid used in all steps was 3.1 M HCl.

a Fractionation and spike corrected ratio.

b Calculated following Stacey and Kramers (1975).

c Analyses in italics were either contaminated or contained too little U to calculate meaningful ages.
Secondary electron (SE) images provide a qualitative indication of the effect of annealing on monazite and monazite dissolution patterns. Prior to dissolution, grains are commonly devoid of holes or pits, but locally have rough surfaces or fracture planes (Jefferson County; Fig. 3a). Partial digestion of the annealed Jefferson County monazite produced etch pits and significant removal of material from the interior and exterior of the grain fragment (Fig. 3b). Not-annealed (Fig. 3c) and annealed (Fig. 3d) fragments of the more crystalline Amelia monazite exhibit different responses to partial dissolution. In the not-annealed aliquot, etching followed microcracks and produced small (1–2 μm deep) etch pits throughout the grain fragment. In contrast, the larger etch pits (5–10 μm) in the annealed fragments are apparently restricted to the outermost portion of the fragment. The volume fraction of dissolved material is greater in the not-annealed aliquot than in the annealed aliquot. In both samples, acid primarily followed pre-existing lines of weakness (e.g. microcracks, crystal defects).

3.2. Geochronology and compositional data

The calculated dates for each dissolution step are reported in Table 1 and plotted in Figs. 4–9. CA-TIMS plots commonly follow the convention of Ar step-heating diagrams where the width of each box is proportional to the amount of sample dissolved in each step (e.g. Fig. 4, Mattinson, 2005); for monazite, the percent of total P is used as a proxy for the amount dissolved per step. The height of the box represents 2σ uncertainty.

For zircon CA-TIMS plateau diagrams, the plateau age is calculated according to the following five criteria summarized from Ludwig (2003): 1) a plateau is composed of three or more contiguous steps, 2) the probability-of-fit of the weighted-mean plateau age is greater than 5%, 3) the slope of the error-weighted line through the plateau is not different from zero at 5% confidence, 4) the dates of the two outermost plateau steps are not significantly different (at 1.8σ) than the weighted-mean plateau age (for plateaus with 6 or more steps), and 5) the outermost steps do not have nonzero slopes (at 1.8σ) with the same sign (for plateaus with 9 or more steps). Plateau ages that meet these criteria are compiled in Table 3.

In Figs. 4–9, steps included in the calculated plateau age are filled. Annealed samples are red (206Pb/238U) and purple (207Pb/235U); not-annealed samples are dark blue (206Pb/238U) and light blue (207Pb/235U). Compositional data from each dissolution step are plotted below the geochronology data (Figs. 4–9). As with the geochronology data, the width of the box is proportional to P measured in that step. Because each step dissolved different amounts of monazite, blank-corrected ratios (not concentrations) were used to depict changes in composition among the steps. Based upon BSE imaging and EPMA data, four elemental ratios were selected to provide representative information about variability among steps—Nd/P, Dy/P, Th/P and U/P. Nd and Dy were the most reliable indicators of variation in REE among the six samples; changes in U and Th might indicate dissolution of different age domains.

Conventional, Wetherill (1956), concordia diagrams for each sample are also plotted. These are preferable to Tera–Wasserburg diagrams for monazite because visual assessment of the effect of unsupported 206Pb is not hindered by the common/206Pb axes in Wetherill diagrams.

3.3. Amelia

Amelia A (annealed; Fig. 4a) yielded a 206Pb/238U plateau age of 274.29 ± 0.60 Ma (MSWD = 1.07; Table 3). Because the measured 206Pb/204Pb for this sample ranges from 36 to 94 (Table 2), the calculated dates are sensitive to common-Pb corrections. Amelia N (not annealed; Fig. 4b) gave an equivalent 206Pb/238U plateau age of 274.67 ± 0.71 Ma (MSWD = 0.80; Table 3). The 207Pb/206Pb plateau
Ages for Amelia A and Amelia N are equivalent at 275.6 ± 6.4 Ma (MSWD = 1.3) and 275.5 ± 7.3 Ma (MSWD = 0.87), respectively (Table 3). Errors on the individual $^{207}$Pb/$^{235}$U measurements for this sample are large (~25 Ma), owing to high common-Pb and low U. To prevent visually obscuring the more precise analyses, the $^{207}$Pb/$^{235}$U data are not plotted with the $^{206}$Pb/$^{238}$U data, but all steps are

Fig. 4. Amelia. Apparent age spectra: (a) annealed, (b) not-annealed; compositional data: (c) annealed, (d) not-annealed; Wetherill concordia: (e) annealed, (f) not-annealed. Steps A-B are excluded from (e); step A is excluded from (f).
Fig. 5. Burke. Apparent age spectra: (a) annealed, (b) not-annealed; compositional data: (c) annealed, (d) not-annealed; Wetherill concordia: (e) annealed, (f) not-annealed. Step A is excluded from (e) and (f).
Fig. 6. Madagascar. Apparent age spectra (a); compositional data (b); Wetherill concordia (c).

Fig. 7. 554. Apparent age spectra (a); compositional data (b); Wetherill concordia (c). Steps A and I are excluded from (c).
included in Table 2. Step A of Amelia N (~10% of the total Pb) is younger than subsequent steps and has the most common Pb ($^{206}$Pb/$^{204}$Pb = 19.1). Because of the large error on this analysis (attributed to high common Pb), the date is within error of the other steps. Step B of Amelia A gave the youngest date with the largest error and highest common Pb ($^{206}$Pb/$^{204}$Pb = 36.4). The plateau ages for Amelia

Fig. 8. Jefferson County. Apparent age spectra: (a) annealed, (b) not-annealed; compositional data: (c) annealed, (d) not-annealed; Wetherill concordia: (e) annealed, (f) not-annealed. Step A is excluded from (e) and (f).
A and Amelia N are equivalent. Nearly all analyses of Amelia A and Amelia N (Fig. 4e–f) samples are “technically” concordant; i.e., in agreement within analytical errors, but given the large uncertainties in the $^{207}$Pb/$^{235}$U dates, the apparent concordance has little meaning.

Amelia A and Amelia N have the same integrated elemental composition, but yield different compositional spectra. The first three steps of Amelia A decrease in Nd/P, Dy/P, Th/P and U/P, and all subsequent steps slowly increase (Fig. 4c). Although there is some variability in composition from step-to-step for Amelia N (Fig. 4d), the data are less variable than the Amelia A data.

3.4. Burke

Burke A (annealed) yielded crankshaft-style age spectra (Fig. 5a). The first four steps are younger than the mean age of the remaining steps. Burke N (not annealed) gave a $^{206}$Pb/$^{238}$U plateau age of 371.14 ± 0.20 Ma (MSWD = 1.4; Fig. 5b; Table 3). The $^{207}$Pb/$^{235}$U plateau age is slightly younger at 369.06 ± 0.19 Ma (MSWD = 0.97; Table 3). The consistent offset between $^{206}$Pb/$^{238}$U and $^{207}$Pb/$^{235}$U dates and the reverse discordance of nearly all steps for both Burke A and Burke N (Fig. 5e–f) are presumably related to unsupported $^{206}$Pb. Whereas the Burke N ellipses tend to cluster, Burke A ellipses are dispersed along a line parallel to concordia.

Elemental analyses indicate divergent patterns for Burke A and Burke N. Burke A (Fig. 5c) is characterized by steadily increasing Nd/P and U/P ratios whereas Burke N has more consistent Nd/P and U/P ratios. Th/P follows the U/P trend for Burke A, but the first two steps of Burke N have a higher Th/P than subsequent steps. Dy/P yielded a curved pattern for Burke A; in contrast, Dy/P is constant for ~70% of Burke N until the last four steps, which decrease (Fig. 5d).

3.5. Madagascar

Madagascar (annealed only; Fig. 6a) gave a $^{206}$Pb/$^{238}$U plateau age of 518.05 ± 0.26 Ma (MSWD = 1.3; Table 3) and a $^{207}$Pb/$^{235}$U plateau age of 512.11 ± 0.35 Ma (MSWD = 1.6; Table 3). The offset between $^{206}$Pb/$^{238}$U and $^{207}$Pb/$^{235}$U dates is presumably related to unsupported $^{206}$Pb, the magnitude of offset between $^{206}$Pb/$^{238}$U and $^{207}$Pb/$^{235}$U...
To directly evaluate the effect of annealing on dissolution rate, both aliquots of annealed and not-annealed monazite need to be identical. Aliquots of the Burke and Amelia monazites are well matched, but the Jefferson County aliquots apparently differ in elemental composition (Fig. 8c and d; Data Repository). Nevertheless, the proportion of monazite dissolved in the first step for all three annealed samples is significantly greater for the not-annealed aliquots than the annealed aliquots: 9% vs. 2% for Burke; 15% vs. 3% for Amelia; and 16% vs. 5% for Jefferson County (Figs. 4a,b, 5a,b, 9a and b). These data suggest that annealing reduced the solubility of monazite, which is consistent with previous studies that have demonstrated that thermal annealing repairs structural damage caused by radiation (e.g. Seydoux-Guillaume et al., 2002a). Although the specific mechanism by which this occurred was not determined, the differences in etch pit morphologies between annealed and not annealed grains (Fig. 3) suggest that annealing repairs microcracks, dislocations, or lattice damage from alpha-recoil and fission.

4.2. Annealing, composition and age

The three samples that were analyzed via both CA-TIMS and multi-step TIMS permit assessment of the effects of annealing on composition and apparent age. Not-annealed samples tend to have broadly homogeneous chemical spectra (e.g. Figs. 4d, 5d and 8d). In contrast, the annealed counterparts tend to yield much more complex spectra (Figs. 4c, 5c and 8c). Because the not-annealed and annealed aliquots of the Burke and Amelia monazites are elementally well matched (Data Repository), the difference in morphology of the elemental spectra between Fig. 4c vs. 4d and Fig. 5c vs. 5d is most likely attributed to annealing. The Jefferson County aliquots also yielded similar patterns to Burke and Amelia, but differences in chemistry between Jefferson County A and Jefferson County N may also affect dissolution.

Although not all six samples have not-annealed counterparts, the compositional spectra of all six samples either increase monotonically or are hump shaped. These patterns suggest that annealing affects how monazite dissolves; this is further supported by the variation in dissolution rates.

The effect of annealing on apparent age is less clear—monazite, the $^{206}\text{Pb}/^{238}\text{U}$ ages are equivalent, regardless of whether the sample was dated via CA-TIMS, multi-step TIMS or conventional TIMS analysis. The Burke monazite, however, yielded different apparent ages for the CA-TIMS and multi-step TIMS analyses. In Burke A, annealing appears to have induced a crankshaft pattern in apparent age (and
composition) that is not evident in Burke N. Although there are chemical differences between the Jefferson County aliquots, the annealed aliquot yielded a more complex spectra than the not-annealed aliquot. Jefferson County A yielded a hump-shaped pattern in age and composition whereas Jefferson County N was more homogeneous, apart from the older first step (–960 Ma), which is also enriched in U and Th.

The relationship between variability in apparent age and composition is complex. BSE imaging and EPMA point analyses indicate that the Burke and Jefferson County samples have different compositional domains characterized by changes in Dy, Nd, Th and U content. Because monazite is often poly-metamorphic, compositional domains may differ in age (e.g. Williams et al., 2007). If partial dissolution steps were micro-sampling multiple age and composition domains, one might expect to see a correlation between apparent age and composition. Evidence of this is seen in the first step of the Jefferson County N sample, which yields an age of ~960 Ma (Fig. 8b) and is compositionally distinct in U/P and Th/P; Nd/P and Dy/P are chemically indistinguishable from younger steps (Fig. 8d). For all other samples, composition and apparent age of partial dissolution steps are not correlated. For example, the first step of Burke is significantly younger than all subsequent steps (Fig. 5a), but the compositional data show an increasing trend across the spectra, not an anomalous first step followed by more homogeneous steps. The same trend is evident in Madagascar—the first step is anomalously young (Fig. 6a), but there is no corresponding pattern in composition (Fig. 6b).

In general, variation in age cannot be linked to increases or decreases in a specific compositional parameter. Instead, only broad associations between patterns can be made. For example, annealed samples that generally do not yield plateau ages have curved or hump-shaped compositional patterns. Not-annealed samples have flat compositional spectra and, typically, a plateau age.

These data prompt the question of why the spectra of not-annealed monazite are simpler than those of annealed monazite. One possibility could be that (epitaxial) recrystallization, or dissolution/recrystallization occurred during annealing and the newly formed crystals behaved differently. If epitaxial recrystallization occurred, the newly formed crystals might be visible along the grain exteriors in BSE (e.g. Seydoux-Guillaume et al., 2002a, 2002b); the BSE images are equivocal, however, showing platy new growth at the margins of the annealed grains (Fig. 2) as well as evidence of platy minerals on some of the not-annealed grains.

Annealing-induced recrystallization at the sub-micron scale should be reflected by changes in dissolution patterns because repaired crystal structures should respond differently to acid etching. As described in Section 4.1, annealed grains dissolve more slowly than not-annealed grains. However, not all samples contain the same initial radiation damage. The degree of initial radiation damage, therefore, might be a predictor of the extent of recrystallization. More-crystalline samples likely contain less accumulated radiation damage; thus the effects of annealing should be minimized, resulting in less recrystallization and reducing the possibility of chemical redistribution within a grain. More-crystalline samples would therefore yield more consistent apparent age spectra because the degree of recrystallization is lower (i.e. there is a smaller relative change in crystallinity from start to finish for the more-crystalline samples). The higher degree of disorder in the crystal lattice in the less-crystalline/more radiation-damaged samples may enhance recrystallization, resulting in more heterogeneous apparent age and compositional spectra. The divergence in behavior between the annealed and not-annealed monazites in this study may be explained by this hypothesis. Amelia is generally more crystalline than the other samples, is homogeneous in composition, and yielded homogeneous dates, regardless of how it was treated. The difference in compositional spectra for Amelia A and Amelia N would then reflect partial recrystallization induced by annealing (Fig. 4c).

In contrast to Amelia, Jefferson County is less crystalline, has patchy compositional domains and did not yield homogeneous dates. The white wisps in the annealed Jefferson County (Fig. 2) may be evidence of annealing-induced recrystallization. Furthermore, the heterogeneous compositional spectra may reflect annealing-induced larger-scale recrystallization of Jefferson County A (Fig. 8c).

Burke provides a middle ground between these end-member behaviors. It is more crystalline than Jefferson County, but has patchy compositional zoning. Annealed aliquots yielded heterogeneous age and composition spectra whereas not-annealed aliquots yielded plateau ages and more consistent composition spectra. Annealing apparently degrades Burke, but multi-step dissolution of not-annealed grain fragments yielded plateau ages, despite the presence of patchy compositional domains.

4.3. Elk Mountain

CA-TIMS analysis of the Elk Mountain monazite yielded unexpectedly complex age spectra that rise and fall between ~1500 Ma and 2400 Ma. All steps are moderately to strongly reversely discordant (Fig. 9c), far beyond what could be attributed to unsupported 206Pb. The single-step dissolution data are also strongly reversely discordant and define a discordia line identical to the CA-TIMS data. Furthermore, not-annealed grains yielded an equivalent discordia line (unpublished data, J. Baldwin, MIT). The consistency of the Pb–Pb apparent ages among these datasets and the equivalence of the discordia lines suggest that 1) high-temperature annealing is not responsible for the discrepancy between U/Pb and Pb/Pb ages or the extreme reverse discordance, 2) the Pb–Pb system was likely undisturbed, and 3) the U–Pb system has been apparently compromised; a potential cause could be preferential removal of U at ~100 Ma.

4.4. Recommendations for use as monazite reference materials

Amelia is a good candidate for use as a Th-rich, U-poor monazite reference material. The ages are consistent with the Rb–Sr mica age (279 ± 14 Ma; Deuser and Herzog, 1962) and conventional TIMS data (274.6 ± 0.6 Ma; Table 1). Although the high Th content may preclude its use with some microbeam techniques (e.g. SIMS), advances in detector design (e.g. beam attenuation) may permit it to be used with certain instrumentation.

Burke has potential for use as a reference material. The not-annealed sample yielded a plateau age with homogeneous compositional release. Annealing appears to induce scatter in measured composition and age.

Because of the complex age patterns, Jefferson County should not be used as a reference material.

The isotopic complexity of the Elk Mountain monazite renders it unsuitable for use as a reference material. Instead, the similarity in discordia lines among CA-TIMS, annealed single step TIMS and conventional TIMS analyses (unpublished data, J. Baldwin, MIT) suggests that the age variation is most likely attributed to a geologic disturbance at ~100 Ma (the lower intercept) that preferentially removed U and left the Pb–Pb system intact.

Madagascar is a good candidate for use as a reference material, but the age discrepancy of ~6 Myr between CA-TIMS and conventional TIMS data suggests there may be differences in age among grain fragments. Furthermore, the difference in 206Pb/204Pb ratios between the aliquots analyzed via CA-TIMS and conventional TIMS suggests heterogeneity among fragments of the megacryst. Further consideration for use as a reference material requires analysis of additional aliquots.

Because 554 is young (~45 Ma) and U poor (~400 ppm U), obtaining high-precision U–Pb ages can be analytically challenging. The weighted-mean ages (for non-contaminated steps) are 47.7 ± 1.5 Ma (MSWD = 94; 206Pb/238U) and 45.5 ± 2.2 Ma (MSWD = 6.4; 207Pb/
Although these results are consistent with previous data (44–47 Ma; Shakel et al., 1977), the lack of an age plateau and the high MSWD values indicate that the dates do not form a single population and instead suggest (re)crystallization from ~45–50 Ma. Because it is heterogeneous and has ages known to a precision of only 5%, 554 should not be used as a reference material.

5. Conclusions

Multi-step partial dissolution of monazite can be an effective way to unravel the complex histories of poly-metamorphic grains. Annealing apparently reduces the solubility of grains by repairing structural damage of the crystal lattice; larger defects such as cracks or micro-cracks remain. The data suggest that annealing induces recrystallization that affects the style of dissolution and produces more variable age and composition spectra than observed with not-annealed samples. High-temperature annealing is therefore not recommended for monazite.

Step-wise digestion of monazite can reveal isotopic complexities that might be missed by single-step TIMS analysis or microbeam analyses, including discordance between 206Pb/238U and 207Pb/235U ages. The 207Pb/235U plateau ages afforded by multi-step CA-TIMS permit accurate age determinations that are unaffected by unsupervised ±0.2 and ±0.5 for the assumed 207Pb/204Pb common and 0.1% error in the 206Pb/238U analyses incorporates uncertainty in U and Pb fractionation corrections. Final sample ages and propagated errors were calculated as the weighted mean of the plateau steps, as defined in Isotop 3.0/3.2 (Ludwig, 2003).

Appendix B. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2012.04.006.

References


