

Monazite chemical dating via electron probe microanalysis



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Introduction

Accurate geochronology is an essential part of any geological investigation into crustal evolution, sedimentary provenance or metallogenic process. Monazite, a rare earth elements (REE) rich phosphate ((Ce, La, Pr, Nd, Th, Y)PO₄), is a particularly useful accessory phase for geochronology. It incorporates significant amounts of Th and U during formation, so electron probe microanalysis (EPMA) measurable amounts of radiogenic Pb begin to accumulate in as little as 100 My. Monazite is a common accessory phase within many felsic igneous and metasedimentary rocks and can form detrital grains within sediments, providing useful geochronological information for many geological processes. Monazite is also useful for constraining the age of hydrothermal alteration and mineralisation. Hydrothermal monazite is a common accessory phase associated with REE-, Th- and U-rich fluids. A number of recent studies have dated hydrothermal monazite associated with alteration in Archaean orogenic gold deposits (Lobato et al. 2007), porphyry tin (Kempe et al. 2008), iron oxide – copper–gold type deposits (Grainger et al. 2008), supergene-enriched Cu–Au deposits (Grainger et al. 2008) and gold mineralisation associated with auriferous quartz reefs (Rasmussen, Sheppard and Fletcher 2006; Ugarkar et al. 2007). The ability to date hydrothermal monazite is particularly useful for South Australia, where many mineralised areas are associated with elevated levels of U, Th and REE (e.g. Curnamona Province, Mount Painter and Olympic Dam). Directly constraining the age of hydrothermal alteration and mineralisation allows for the development of better constrained ore deposit models and may lead to the recognition of new timelines for mineralisation in South Australia.

The most powerful tools currently available for isotopic monazite dating are secondary ion mass spectrometry (SIMS; e.g. Foster et al. 2000) or laser ablation - inductively coupled mass spectrometry (LA-ICPMS; e.g. Payne et al. 2008). Both techniques allow for high precision isotopic ages to be determined with relatively good spatial resolution (spot sizes between ~8–60 µm). EPMA chemical dating of monazite provides a useful additional or alternative method for obtaining good precision age data (e.g. Williams and Jercinovic 2002; Pyle and Spear 2003). This technique is relatively cheap, readily performed in situ, has excellent spatial resolution (<10 µm), good age precision (± ~7–30 Ma) and, uniquely amongst other methods of analysis, can provide a full range of chemical and zoning information for each analytical site (Pyle et al. 2005; Williams et al. 2006). The main disadvantage with the EPMA technique is that it is not an isotopic method, and as a result discordant data due to Pb loss can be hard to discern.

This article provides a review of EPMA monazite dating theory together with a detailed description of the analytical method and procedures for the EPMA monazite dating technique developed at Adelaide Microscopy. To verify the accuracy of the method, a comparative study using previously isotopically dated monazite grains was carried out. The results indicate a good correlation between the EPMA ages obtained from the developed setup and the isotopically derived ages.

Review of EPMA monazite dating theory

The theoretical basis for monazite geochronology consists of measuring the total Th, U and Pb concentrations in a monazite crystal and calculating the age (τ) based on the decay rates of U

and Th to Pb via the age equation (after Montel et al. 1996):

$$Pb = \left(\frac{Th}{232} \right) \left[e^{(\lambda^{232}\tau)} - 1 \right] 208 + \left(\frac{U}{238.04} \right) 0.9928 \times \left[e^{(\lambda^{238}\tau)} - 1 \right] 206 + \left(\frac{U}{238.04} \right) 0.0072 \times \left[e^{(\lambda^{235}\tau)} - 1 \right] 207 \quad (1)$$

where Pb, U and Th are in ppm and λ^{232} , λ^{238} , λ^{235} are the radioactive decay constants of ²³²Th, ²³⁸U and ²³⁵U respectively. Individual ages are determined iteratively by entering age estimates into Eq. (1) with the known concentrations of U and Th until the calculated Pb value matches the measured Pb concentration.

The validity of the above method is dependant on two assumptions: (i) that non-radiogenic Pb content is negligible; and (ii) there has been no subsequent modification of the U–Th–Pb ratios except by radioactive decay. Studies by Parrish (1990) indicate that monazite incorporates very little non-radiogenic Pb in its structure, and therefore common Pb contents are typically <1 ppm and are therefore negligible for most >200 My old monazites.

The second assumption is that the monazite grain remains a closed system. Of the two decay systems active in monazite the U–Pb system is best documented. Previous studies (e.g. Parrish 1990; Cherniak et al. 2004; Cocherie et al. 2005) have shown that this system typically behaves in a concordant manner. A recent study by Cherniak and Pyle (2008) on Th diffusion in monazite shows that Th diffusion is negligible at most geological temperatures, and that Th diffusion is most likely the rate limiting element in diffusion driven by chemical substitution. Cherniak et al. (2004) concluded that diffusion of Pb in monazite is also negligible. They demonstrated that for a cooling rate

of $10\text{ }^{\circ}\text{C Ma}^{-1}$, a $10\text{ }\mu\text{m}$ monazite grain has an effective closure temperature of $\sim 900\text{ }^{\circ}\text{C}$. This implies that for most geological processes Pb diffusion in monazite is negligible. Monazite has also been shown to be highly resistant to metamictisation (Meldrum, Boatner and Ewing 1997). These arguments indicate that monazite should remain a closed system in most geological settings and provide concordant, geologically meaningful ages.

Monazite is generally suspected to be more susceptible to resetting than zircon, and often gives slightly different ages than zircon from within the same units (Pyle and Spear 2003; Kelsey, Clark and Hand 2008). This is primarily due to its comparatively high chemical reactivity (e.g. Bea and Montero 1999; Spear and Pyle 2002; Cherniak and Pyle 2008), particularly in melt- or fluid-bearing systems. This suggests that Th–U–Pb monazite systematics, and therefore the age, is less likely to be controlled by diffusion than it is by the chemical reactivity of the monazite grains (e.g. Seydoux-Guillaume et al. 2002).

Analytical method

The following analytical setup and procedure has been set up on a Cameca SX51 electron microprobe running SAMx software at Adelaide Microscopy at the University of Adelaide.

The SX51 employs four wavelength-dispersive spectrometers (WDS) and a Gresham 10 mm energy-dispersive spectrometer (EDS). All WDS on the SX51 incorporate a 160 mm radius Rowland circle. Each spectrometer is equipped with a number of interchangeable diffraction crystals with the following configuration being used for monazite analysis: spectrometer 1 PET (pentaerythrite), spectrometer 2 PET, spectrometer 3 LiF (lithium fluoride) and spectrometer 4 TAP (thallium hydrogen phthalate). The SX51 uses four P10 ($\text{Ar } 90\% - \text{CH}_4\text{ } 10\%$) gas-flow proportional X-ray detectors. Polypropylene entry windows are used on all detectors. Gas pressure in detectors 1, 2 and 4 is maintained at $\sim 1\text{ atm}$ while detector 3 is maintained at $\sim 3\text{ atm}$. Prior to calibration it is necessary to optimise the X-ray detectors for analysis.

SX51 operating conditions

The choice of accelerating voltage and beam current is a balance between a number of factors. Higher values increase the intensity of the generated X-rays, giving greater analytical precision, but also increases the size of the X-ray excitation volume in the sample and can lead to greater uncertainties in the ZAF (matrix) corrections (Pyle et al. 2005; ZAF = atomic number (Z), absorption (A) and fluorescence (F)).

To maximise X-ray counts for precision while minimising the excitation volume to $<10\text{ }\mu\text{m}$ diameter (providing optimal spatial resolution) and minimise sample damage over the duration of a typical analysis time of 10 min, an accelerating voltage of 20 kV with a beam current of 100 nA is optimal for monazite analysis on the Adelaide SX51.

Elements and standards

The analytical procedure adopted here is a near complete monazite analysis. It analyses for U, Th and Pb, together with La, Ce and many of the REE which substitute into monazite (Pr, Nd, Sm, Gd, Dy and Er) as well as Al, Si, Ca, Y and P. These elements account for the compositional variation between the monazite–huttonite ($\text{lanthanide}^{3+} + \text{P}^{5+} = \text{actinide}^{4+} + \text{Si}^{4+}$) and monazite–brabantite ($2\text{lanthanide}^{3+} = \text{actinide}^{4+} + \text{Ca}^{2+}$) exchanges (Cuney and Friedrich, 1987; Franz, Andrehs and Rhede 1996). The acquisition of this large amount of chemical data also allows for the ability to link different age and compositional domains to the growth of major mineral phases that can be used to constrain P–T conditions (e.g. Pyle and Spear 2003). Analysis of Si, Ca and Al allows for quality control as monazite typically contains $<1\text{ wt}\%$ Si and Ca and $<0.5\text{ wt}\%$ Al. Higher concentrations of these elements can indicate: (i) a contaminated analysis, such as the incorporation of a micro-inclusion; (ii) significant solid solution exchange between end members away from a true monazite composition; or (iii) hydrothermal or surface weathering and alteration of monazite (Poitrasson, Chenery and Bland 1996; Podor and Cuney 1997). Analysis of all these elements typically produces totals in

the range $99 \pm 4\text{ wt}\%$ and is within the range to give high precision for ZAF corrections.

The use of high-quality standards is essential for accurate determination of elemental concentrations in unknowns. The Pb standard is a synthetic glass NIST K-227, UO_2 for U and a natural huttonite for Th. Calcium and P are calibrated using Durango apatite (Frei et al. 2005). Silicon, Al and Y are calibrated using a multi-element synthetic glass (REE1; Drake and Weill 1972). The REE are calibrated using high concentration single element synthetic glasses (Edinburgh Materials and Micro-Analysis Centre, Grant Institute of Earth Sciences, University of Edinburgh). Age standards are not required for this procedure.

Peaks, backgrounds and interferences

Thorium, U and Pb are all analysed using PET diffraction crystals. For monazite, the high intensity ThMa peak is free from interference and therefore provides a clean energy line to measure for analysis (Fig. 1). The choice of background type (one or two points, linear or curved) and position will depend on the background region near the peak of choice. For the ThMa peak the clean background around the peak means a two-point curved background provides the best fit.

The choice of line for U and Pb is more problematic as both the Ma and $\text{M}\beta$ lines are subjected to a number of interferences. The U region of the spectrum is subject to a number of interferences from ThM lines plus steps in the background caused by the ThM5 , M4 and Ar K absorption edges (Fig. 1). The UMa line suffers from a very large overlap by the $\text{ThM}\beta$ line (Fig. 1) and is very near the large Ar K absorption edge making it difficult to measure. The $\text{UM}\beta$ line is overlapped by the $\text{ThM}\gamma$ peak (Fig. 1), but the peak can be resolved in a typical monazite and the overlap empirically corrected for. In geological samples the $\text{KK}\alpha$ line may also overlap with the $\text{UM}\beta$ peak (Fig. 1). This overlap can be avoided by not analysing monazite grain boundaries that are in contact with K-bearing minerals and monitoring apparent U concentrations throughout

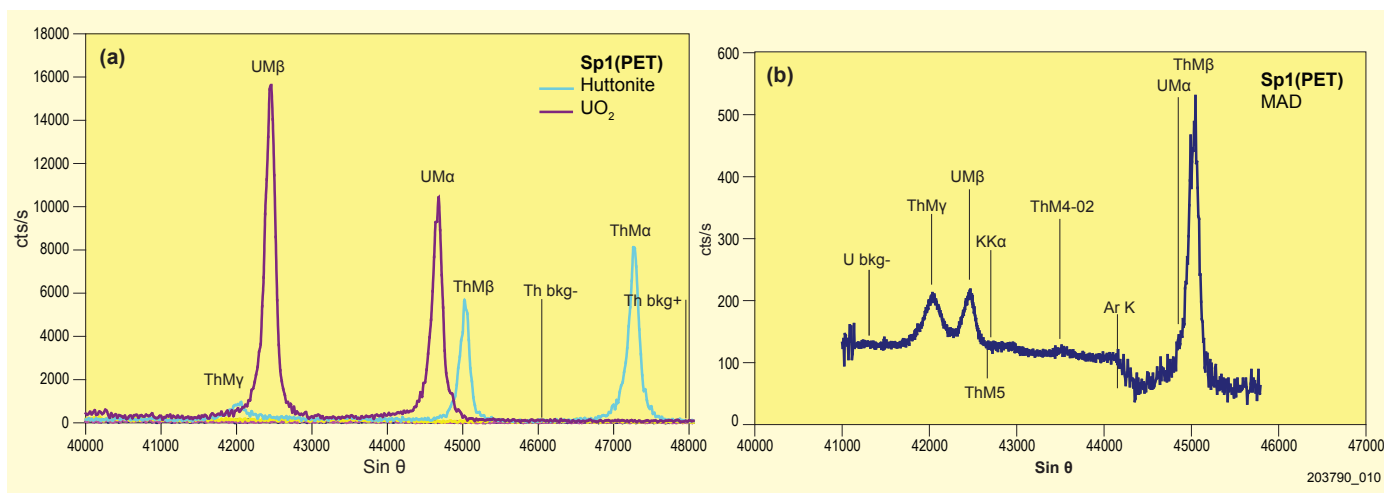


Figure 1 Wavelength-dispersive scans across the U and Th $\sin\theta$ region using a PET crystal. (a) Scans on U and Th standards showing the clean ThMa line and background positions and the ThMy overlap on UM β . (b) Scan on natural monazite showing the relative size of the interference on UM β and the U background locations.

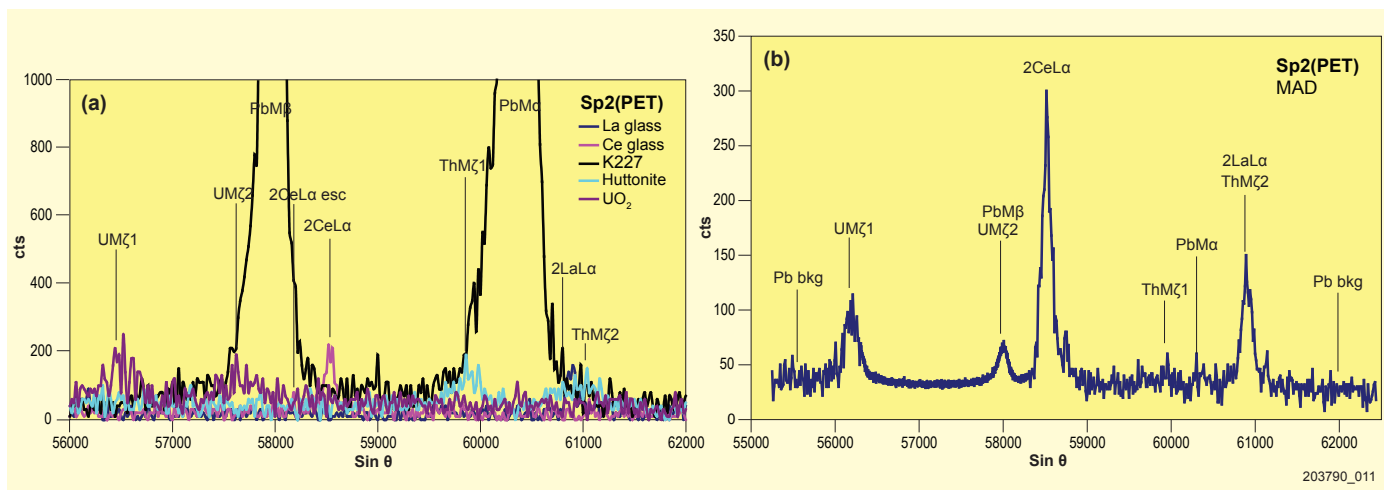


Figure 2 Wavelength-dispersive scans across the Pb $\sin\theta$ region using a PET crystal. (a) Scans on Pb, Ce, La, U and Th standards showing the 2CeLa, 2CeLa escape peak and UM ζ_2 interferences on the PbM β line. (b) Scan on natural monazite showing the relative sizes of the interferences on the PbM β line and the positions of the Pb backgrounds.

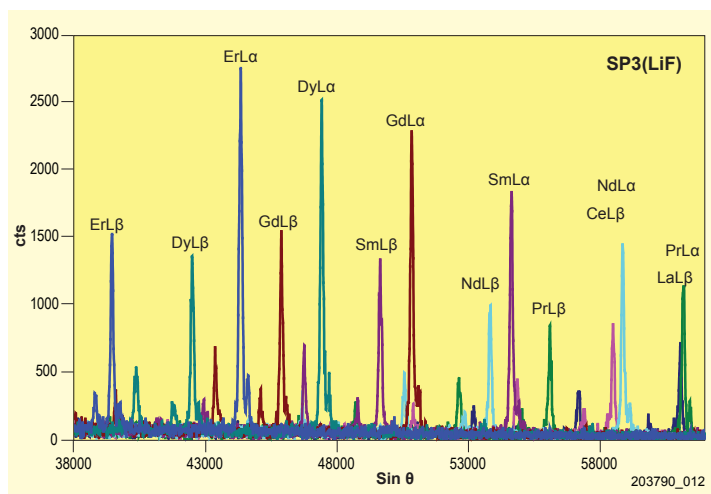


Figure 3 Wavelength-dispersive scans across the REE $\sin\theta$ region using a LiF crystal on the REE standards showing the relatively clean L β lines.

the monazite grains. The choice of background positions is hampered by the numerous ThM peaks and background discontinuities. In order to avoid these, a single point linear background is used and placed 1250 $\sin\theta$ below the UM β peak, after the ThM4 edge (Fig. 1).

The choice of Pb Ma or M β line is similarly constrained by the interferences in the PbM region in monazite. The higher intensity PbMa line suffers from a number of interferences including the ThM $\zeta_{1,2}$, 2LaLa and YL γ lines (Fig. 2). The PbM β line, although of slightly lower intensity, provides a better choice of energy line because of its cleaner spectrum. The PbM β line has one first-order overlap by the UM ζ_2 line and also the second-order (2) CeLa line (Fig. 2). The higher order 2CeLa line can be filtered from the analysis through the differential

mode pulse-height analyser settings. However, there is a small 2CeLa escape peak (an artefact of the low-pressure P10 gas-flow detector) which falls within the energy window of the $\text{PbM}\beta$ peak and must be corrected for (Fig. 2; Pyle et al. 2005). Because the size of the 2CeLa escape peak is very small, and is proportional to the CeLa peak (and therefore the Ce concentration) it is corrected for mathematically offline by the application of a measured correction factor of 0.0003% of the Ce concentration. The $\text{UM}\zeta_2$ interference is corrected for empirically online. Because of cascading interferences, the corrections must be done in order with the $\text{ThM}\gamma$ on $\text{UM}\beta$ done first followed by the $\text{UM}\zeta_2$ on $\text{PbM}\beta$. To get clean background positions for the Pb region a two-point curved background is used (Fig. 2).

The choice of REE lines is dependant on which diffraction crystal is used. High concentrations of both Ce and La in typical monazites results in no interference issues with the CeLa and LaLa lines, and the need for accurate Ce concentrations for Pb overlap corrections means the high-intensity La lines are measured on a PET crystal. Machine restrictions (long count times on elements using PET crystals means the non-essential REE cannot be efficiently analysed using a PET crystal on the SX51) forces the remaining REE to be analysed using a LiF crystal. Because of the low concentrations of most REE in monazite and the reduced intensity of the REE lines when using a LiF crystal (Fig. 3), only the high-pressure X-ray counter will give enough counts to maintain precision. The high-pressure P10 counter also has the advantage of suppressing higher order interferences on the REE. Because of less interference issues the REE $L\beta$ lines are used.

The remaining element lines have been chosen as there are no interference issues with them and they are the highest intensity lines available. The YLa , CaKa and PKa lines are measured using a PET crystal. The trace elements of Si and Al are also measured using the Ka lines using a TAP crystal.

Counting times

Using the SX51 at Adelaide Microscopy at an accelerating voltage of 20 kV and a beam current of 100 nA, an intrinsic detector response of between 0.2 and 0.05 counts of $\text{Pb/s}\cdot\text{nA}\cdot\text{wt}\%$ is measured using a PET crystal and a low pressure P10 gas flow proportional counter. As the precision of the spot age is dependant on the precision of the Pb, U and Th analysis, it is necessary to count for a number of minutes on each of these peak and background positions. For a typical monazite, in order to collect enough counts to produce a statistically meaningful (and precise) peak to background ratio it is necessary to count on the Pb peak for ~240 s and on each background position for 120 s. For a typical monazite with a Pb concentration of ~2500 ppm, a 1σ error of ~110 ppm Pb is achieved (a 1σ counting error of <5%). Similarly U count times are 160 s for peak and 160 s background which produces a 1σ counting error of ~2%. The generally high concentration of Th in monazite (~5–20 wt%) allows the count times to be considerably lowered, with a peak count time of 60 s and 30 s on each of the backgrounds. This produces a 1σ counting error of <0.5%. A typical single spot analysis of the entire 16 element package takes ~10 min, however these counting times are not fixed, and can be adjusted to suite particular monazite compositions.

Sample preparation

The method outlined here is generally undertaken on polished thin sections but can also be applied to mounted grain separates. The effectiveness of EPMA is highly dependant on the polish of the sample; a good quality polish is vital for accurate analyses. Because of the low levels of U and Pb in monazite it is particularly important to minimise contamination from the polishing process. To minimise contamination, no Pb bearing samples should be polished on laps used to prepare samples for EPMA dating, and the plates should be cleaned and replaced periodically. The samples need to be thoroughly washed in acetone and deionised water between each stage and should be kept in sealed containers to avoid contamination when transporting. Avoid polishing medium

which contains Ce as this will directly effect the apparent Pb concentration.

Data collection strategy, analysis and reduction

The approach developed here involves the collection of large numbers of point analyses from individual samples. Individual monazites are first located either optically or using backscattered electron imaging on a scanning electron microscope or the SX51. Individual grains are then characterised texturally (e.g. located within the fabric, shielded within major phases). Selected grains are targeted with as many point analyses as are practical within the spatial constraints required for clean analysis. The collection of a large data set allows for better precision ages (lower errors) as individual spot errors can be between ± 30 to 60 Ma (1σ).

The analytical method adopted here analyses a full suite of elements to allow for greater precision in ZAF corrections and also because it can produce geologically important additional information. Spot ages and chemical zoning in individual grains can be investigated by plotting various elements and spot ages (e.g. Y wt% vs Th/Ce wt% or age vs Y wt%). Grains which show significant age/compositional variation can then be further imaged by X-ray compositional mapping without affecting the precision of the ages.

Prior to age calculation, the raw compositional data is assessed and filtered to remove suspect analyses. Generally any data with totals below 95% or above 103% are excluded from the age pool as analyses outside these ranges can introduce uncertainties into the ZAF corrections (subject to monazite composition). The raw compositional data is then further scrutinised with analyses containing >1 wt% Si, Ca or Al being excluded from the age pool, as high values may indicate a contaminated spot analysis.

Prior to the age calculation, the Pb concentration is corrected for the small 2CeLa escape peak overlap by the relationship:

$$\text{Pb}^* = \text{Pb}(\text{wt}\%) - [\text{Ce}(\text{wt}\%) \times 0.0003] \quad (2)$$

The individual spot ages are then calculated using the age equation (Eq. 1). Individual spot errors are calculated using the approach of Montel et al. (1996). Individual errors for U, Th and Pb are calculated on the basis of the counting (Poisson) statistics of the elemental analysis where U, Th and Pb counting errors are calculated using the equation:

$$M(\sigma) = M(ppm) \times \sqrt{\frac{(pk + bg)}{(ct \times (pk - bg))}} \quad (3)$$

where M is either Th, U or Pb, pk and bg are the peak and background counts respectively and ct is the counting time for that element. The uncertainty is then calculated on the age by propagating the uncertainties on U, Th and Pb into Eq. (1). All statistical analysis and data presentation thereafter is done using the Excel geochronology add-in ISOPLOT (Ludwig 2003).

Test case results

As a test of the validity of the EPMA monazite setup on the Cameca SX51 outlined here, four monazite samples have been analysed using the described protocols. The analysed samples have been selected to reflect a variety of ages, from Palaeoproterozoic to Ordovician.

Sample SB17

Sample SB17 is a grain mount of monazite from a felsic mylonitic shear zone from the southern Gawler Craton. These monazites have been isotopically dated using SHRIMP (sensitive high resolution ion microprobe) II and produced a concordant $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1720 ± 7 Ma and a $^{206}\text{Pb}/^{238}\text{U}$ age of 1715 ± 35 Ma (Dutch, Hand and Kinny 2008). The monazites are quite heterogeneous, with 3.6–18 wt% Th, 0.16–1.13 wt% U and 0.22–1.68 wt% Pb, and as such represent a good test that the various peak overlap protocols are effective and provide accurate analyses of Pb and U concentrations. The resultant EPMA age is 1703 ± 7 Ma ($n = 60$, mean squared weighted deviates (MSWD) = 0.54; Fig. 4). This age is slightly younger than the $^{207}\text{Pb}/^{206}\text{Pb}$ SHRIMP age but is within error of the $^{206}\text{Pb}/^{238}\text{U}$ age.

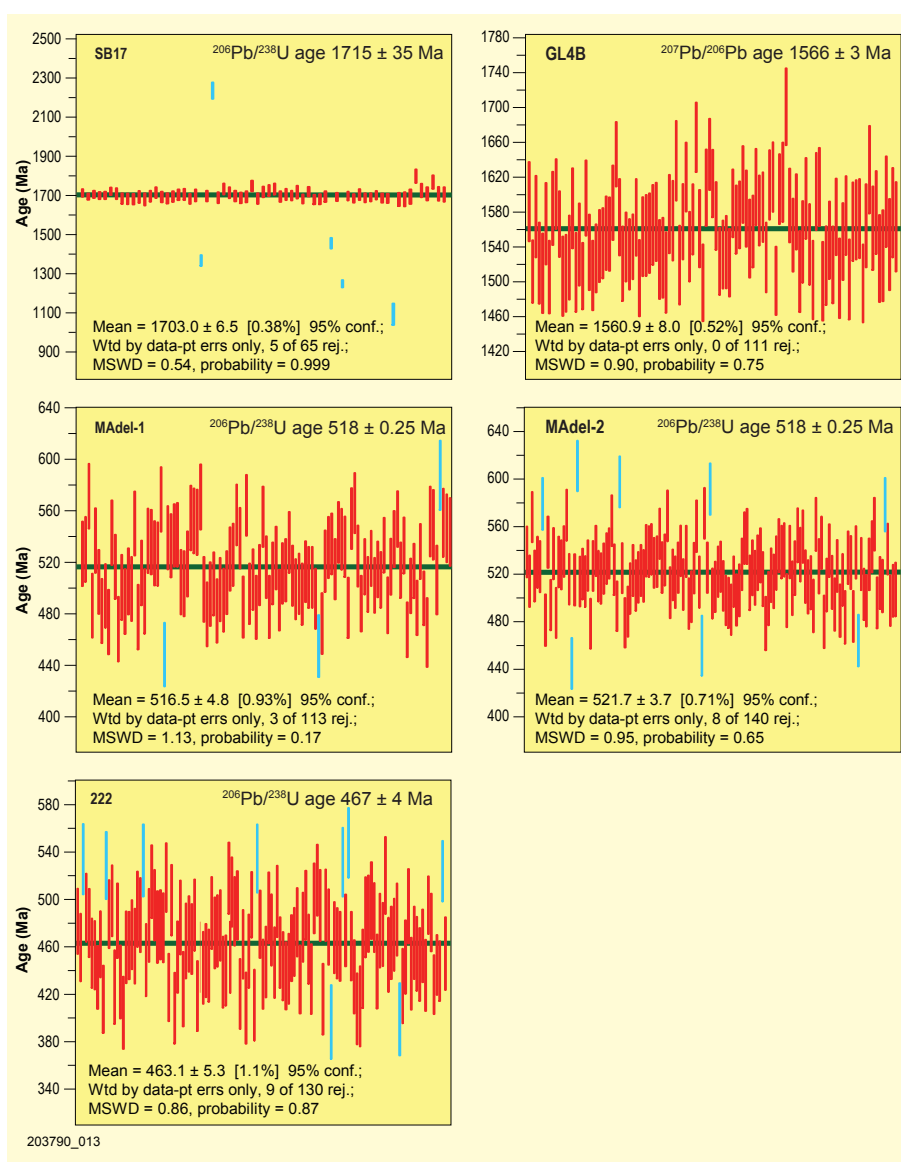


Figure 4 EPMA geochronological results from the selected comparison samples. Plots show individual analyses with 1σ error. Blue analyses were outside 95% confidence and were excluded from weighted average calculations.

Sample GL4B

Sample GL4B consists of monazite grains extracted from a leucosome within granulite facies metapelites from the Reynolds Range in central Australia. These monazites were dated isotopically using SHRIMP II and produced a concordant $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1566 ± 3 Ma (Rubatto, Williams and Buick 2001). Chemically the monazite grains are reasonably homogenous in composition with 3.61–5.92 wt% Th, 0.11–0.63 wt% U and 0.32–0.51 wt% Pb. The calculated EPMA age is 1561 ± 8 Ma ($n = 111$, MSWD = 0.9; Fig. 4) which is within error of the $^{207}\text{Pb}/^{206}\text{Pb}$ isotopic age.

MAdel standard

The MAdel monazite standard consists of chips of a Pan African aged monazite from Madagascar. MAdel has been isotopically dated using thermal ionisation mass spectrometry (TIMS) at the Massachusetts Institute of Technology and has a $^{206}\text{Pb}/^{238}\text{U}$ age of 518 ± 0.25 Ma and a $^{207}\text{Pb}/^{235}\text{U}$ age of 514 ± 0.3 Ma (Payne et al. 2008). MAdel was dated twice using EPMA, once at the start of the analytical session and again at the end of the session (five days apart). The EPMA monazite ages are 517 ± 5 Ma ($n = 110$, MSWD = 1.136; Fig. 4) and 522 ± 4 Ma ($n = 132$, MSWD = 0.95; Fig. 4) respectively. These ages are within

error of the isotopically determined age and demonstrate the stability and consistency of the SX51 and the developed monazite protocol.

Sample 222

Sample 222 consists of monazite grains extracted from the matrix of garnet-bearing leucosomes within a biotite–sillimanite–plagioclase–garnet–quartz metapelite from the Harts Range Group in central Australia. These monazite grains were dated isotopically via SHRIMP (Hand et al. 1999) and LA-ICPMS (Payne 2008). SHRIMP isotopic analysis produced a $^{206}\text{Pb}/^{338}\text{U}$ age of 467 ± 4 Ma (Hand et al. 1999), while LA-ICPMS analysis produced a $^{206}\text{Pb}/^{238}\text{U}$ weighted average age of 450 ± 5 Ma and a concordia age of 453 ± 4 Ma (Payne 2008). The monazite grains are reasonably homogeneous in composition with 5.9–8.13 wt% Th, 0.17–0.42 wt% U and 0.13–0.22 wt% Pb. The EMPA monazite age is 463 ± 6 Ma ($n = 121$, MSWD = 0.86; Fig. 4). The EMPA age is within error of the SHRIMP isotopically determined age and the LA-ICPMS concordia age.

Implications for EPMA monazite geochronology

EPMA monazite dating provides an accurate and reasonably inexpensive tool for age determination. It is readily performed in situ and, using the method developed here, provides extra chemical information which can aid in the geological interpretation of the calculated ages. With the correct protocols, machine setup and calibration, it is possible to achieve monazite chemical ages that are comparable with those obtained via isotopic methods. Although the precision of the technique is not generally sufficient to resolve individual events within an orogenic event, it provides an efficient way to add geochronological data to any determined P–T path and allows for rapid verification of the ages of deformation and metamorphism of individual assemblages which are used to constrain them. This technique also has the potential to place direct geochronological constraints on the timing of alteration and mineralisation by directly dating and geochemically

characterising hydrothermally grown monazite within the alteration assemblage, providing a useful technique in South Australia for constraining and testing ore deposit models.

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MINERAL ROYALTIES

Expiry of transitional arrangements

Significant changes to the royalty provisions of the *Mining Act 1971* were introduced on 1 January 2006 following the introduction of the *Mining (Royalty No 2) Amendment Act 2005*. Since that time many leaseholders have been covered by transitional arrangements pertaining to calculation of royalty on mineral leases, however all transitional arrangements expired on 31 December 2008.

Prior to 31 December 2008, any minerals recovered from a mineral lease had the royalty determined according to values set by the Minister for Mineral Resources Development. From 1 January 2009, the royalty on all minerals other than extractive minerals is calculated at the rate of 3.5% of the value of the minerals pursuant to section 17 of the Mining Act.

Prescribed costs (allowable deductions)

Included in the Mining Regulations 1998 are provisions for prescribed costs genuinely incurred in transporting the minerals from the relevant tenement to a port; to be deducted from the value of the mineral to ascertain the royalty value.

Prescribed costs which may be claimed include:

- packaging, storage, loading, permit fees and insurance costs
- costs genuinely incurred in the shipping of the minerals from a port to a genuine purchaser in a sale at arms length.

New mine status

'New mine status' is an initiative included with the 2005 amendments to promote investment and development of new mines in South Australia. New mine status allows for a discounted royalty rate of 1.5% of the value of the minerals for a period of five years commencing on the date of paying the first royalty payment.

The discounted royalty rate is not applied automatically to a new mine; an application must be in writing outlining all relevant details. All applications are assessed to ensure the criteria outlined in section 17A of the Mining Act have been met.

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