Microprobe Monazite Geochronology: Understanding Geologic Processes by Integrating Composition and Chronology

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Abstract
Monazite is a light rare earth element (LREE)-bearing phosphate mineral that is present in a wide variety of rock types, has an extremely variable composition reflecting host rock conditions, and is a robust geochronometer that can preserve crystallization ages through a long history of geological events. Monazite crystals typically contain distinct compositional domains that represent successive generations of monazite, which in turn, can provide a detailed record of the geologic history of its host rocks. The electron microprobe can be used to characterize the geometry of compositional domains, analyze the composition of each domain, and, when carefully configured, determine the U-Th-Total Pb age for domains as small as 5 μm in width. These data allow the monazite to be linked with, and place timing constraints on, silicate processes in the host rocks. Current applications span a broad range of geologic processes in igneous, metamorphic, hydrothermal, and sedimentary rocks.
INTRODUCTION

One of the great challenges in all fields of geoscience is determining the absolute time and duration of geologic processes. The goal is to find geochronometers that can record the progress of geologic processes (i.e., deposition, deformation, metamorphism, etc.) and can yield constraints on absolute or relative time. Monazite, a rare earth element (REE) phosphate mineral, is in many ways ideal, having an extremely variable composition that reflects the changing intensive and extensive parameters of its host rocks and preserving ages of crystallization or growth through a long history of geologic events. The use of monazite for geochronology, thermobarometry, geochemistry, and petrology has increased dramatically over the past decade. The reasons for the increase include (a) the recognition that monazite is present in a wide variety of igneous, metamorphic, and sedimentary rocks; (b) the recognition that diffusion rates of many elements in monazite is very slow, and thus monazite can retain a record of previous geologic conditions; (c) the expansion and refinement of techniques for analysis and dating of monazite, particularly in situ analysis; (d) an increasing understanding of the conditions under which monazite can crystallize and recrystallize in rocks; and (e) an increasing realization of the geochemical and petrologic links (in the sense of hydrothermal interaction, metamorphic reactions, crystallization from melt) between the silicate assemblages and monazite, and thus an increasing ability to integrate monazite into the geologic history of the major phases.

Many recent studies have shown that monazite crystals in all types of rocks commonly contain a number of distinct compositional domains. The domains are generally interpreted to represent stages in the geologic history during which new monazite grew or recrystallized (Williams & Jercinovic 2002, Pyle & Spear 2003). Because diffusion is slow, the composition and texture of each monazite generation may reflect geologic conditions and geologic processes active at the time of growth. Further, the ratio of U + Th (parent) to Pb (daughter) can, under the right circumstances, indicate the time of crystallization and/or growth (Figure 1). In this respect, monazite can be thought of as a petrologic tape recorder. The challenge is to read the tape and link it to the evolving host rock. Electron probe microanalysis (EPMA) plays several key roles in the process of reading and interpreting the monazite record. First, through high-resolution compositional imaging, the electron probe can delineate the geometry of compositional domains. Monazite texture provides a link between compositional domains and geologic processes. Second, the microprobe can accurately measure the composition of each domain, providing a compositional link or fingerprint of host rock petrology and/or geochemistry at the time of crystal growth. Finally, although monazite separates have been isotopically dated for decades, the electron microprobe can now provide age constraints on the generally small and irregular domains that have been linked to geologic processes.

This review focuses on the integration of monazite composition with geochronology and on the specific roles that the EPMA can play in building this integration. The goals are to (a) summarize and synthesize the compositional variability of monazite and related minerals and our growing understanding of the relationships between monazite composition and its silicate host rocks; (b) to summarize the use of the
X-ray compositional map (yttrium) of monazite from felsic granulite, Legs Lake shear zone, Snowbird tectonic zone, Saskatchewan, Canada. High-Y rims are ca 1860 Ma, overgrowing polygenetic Archean (ca 2520 Ma) core domains. Age histograms on right, derived via EPMA, represent 2σ standard error of the mean of analysis populations corresponding to domains shown on the compositional map.

EPMA in acquiring major and trace element compositions of monazite, particularly high-precision analysis of U, Th, and Pb for dating; and (c) to summarize the current progress in integrating monazite into geologically relevant chemical reactions and thereby use monazite as a recorder of the nature and timing of geologic processes.

**MONAZITE STRUCTURE AND CRYSTAL CHEMISTRY**

The orthophosphate minerals, with an idealized formula A(PO₄) include the two anhydrous REE phosphates monazite and xenotime [REE(PO₄)], which may be differentiated on the basis of structure and REE composition. Structurally, monazite has a framework built upon a nine-oxygen coordinated polyhedra and distorted PO₄ tetrahedra (**Figure 2a**). The polyhedra form continuous b-axis parallel chain-like strands that are interlocked in the c-direction by PO₄ tetrahedra (Mullica et al. 1985a,b; Ni et al. 1995). The interlocked chains form layers parallel to (100) that are stacked by sharing edges between polyhedra in the a-direction (**Figure 2b**). The polyhedra in xenotime are coordinated by eight oxygen ions with two sets of four equivalent bond distances oriented orthogonal to each other resulting in a dodecahedron cation site.

The distribution of REEs between monazite and xenotime is a reflection of the coordination and size of the polyhedral site. In monazite, the nine coordinated site is larger than the eightfold site in xenotime and, consequently, is more favorable to the accommodation of the larger light rare earth elements (LREEs, La to Eu).

**Light rare earth element (LREE):** include lanthanum, cerium, praseodymium, neodymium, promethium, samarium, and europium.
Compositional variation in monazite is also significantly greater than in xenotime, perhaps a reflection of a relaxation of compositional constraints resulting from the irregular ninefold coordination (Beall et al. 1981). In monazite, eight LREE–O bond lengths are equivalent. The ninth, the apical bond, is slightly shorter, resulting in the irregular polyhedron and a unit cell with monoclinic symmetry (space group $P2_1/1 n$, $Z = 4$). The REEO$_8$ dodecahedra of xenotime, as well as being slightly smaller and more compatible with smaller heavy rare earth elements (HREEs), display orthogonal and equidimensional bond distances and tetragonal symmetry (space group $I4_1/amd$).

Compositional variation in monazite may occur by isomorphous chemical substitution at either of the two independent cation sites or by coupled substitution at both sites. Simple isomorphous substitution requires the substitution of one REE$^{3+}$ ion (or Y$^{3+}$) by another. The monazite structure can accommodate significant quantities of HREE, but will remain monoclinic only as long as $>50$ mol% of the A-sites are occupied by LREEs. In natural examples, measured concentrations of individual HREEs are generally $<0.02$ cations per 4 oxygen ions, and Y$^{3+}$ contents are not known to exceed 0.1 cations per 4 oxygen ions (Heinrich et al. 1997).

A second isomorphous substitution occurring in the A-site involves the replacement of REE ions by non-REE species. The most common substitution of this type,

$$2\text{REE}^{3+} \leftrightarrow \text{Ca}^{2+} + \text{Th}^{4+},$$

has been referred to as the brabantite [Ca,Th(PO$_4$)$_2$] substitution. [Ca,Th(PO$_4$)$_2$] is an end-member of a ternary system that includes monazite [2REE(PO$_4$)] and huttonite.
IMA-CNMC: International Mineralogical Association Commission on New Minerals, Nomenclature, and Classification

[2ThSiO₄]. A recent decision by the IMA-CNMC has simplified nomenclature in the system and advised that [Ca, Th(PO₄)₂]-dominated members of the system should be referred to as cheralite. Cheralite forms one end-member of an isostructural solid-solution with monazite. Naturally occurring compositions across the whole compositional range have been reported (Förster 1998, Montel et al. 2002). A wide range of other M²⁺ cations, such as the common trace elements Sr, Pb, and Ba, together with Th, can also take part in a cheralite-type substitution (Montel et al. 2002). The cheralite substitution has a second, albeit rarer, parallel involving U⁴⁺. However, there are no end-member U minerals that form solid-solutions with monazite or are isostructural with it, and the Th/U ratio of monazite is typically > 1.0.

Montel et al. (2002), in addition to proving the existence of a monazite-cheralite solid solution, synthesized a Pb end-member equivalent of cheralite [Pb, Th(PO₄)₂]. This mineral has a monazite structure, and a series of synthesized intermediate compositions along the [Pb, Th(PO₄)₂]-[2La(PO₄)₃] join shows that a complete isostructural solid solution exists between the end-members. The concentration of Pb incorporated into natural monazite during growth is extremely low; this is one of the underlying principles of the total Pb dating method. However, it would be incorrect to state that Pb is completely incompatible with natural monazite. Common Pb is routinely detected during mass spectrometry studies (e.g., Hawkins & Bowring 1997). Pb is incorporated into the ninefold polyhedra of the crystallographic lattice in concentrations dictated by the partition coefficient between the monazite and the local chemical system. In addition, the concentration of total Pb in the crystallographic lattice will increase with time as a result of radiogenic decay of ²³²Th, ²³⁸U, and ²³⁵U. The increase in total Pb will be a function of monazite age, and the original concentrations of Th and U. This new radiogenic Pb⁵⁺ replaces an original Th⁴⁺ or U⁴⁺ atom, creating a structurally ideal formula (i.e., all A-sites filled), but one with a charge imbalance.

Electron paramagnetic resonance (EPR) spectroscopy has also shown that other Me²⁺ ions may be incorporated into the A-site of synthetic xenotime (Boldú et al. 1985), Mn occurring in natural monazite has, to our knowledge, not been reported, but concentrations of FeO ranging from below detection limit to 0.95 wt.% have been reported (Kingsbury et al. 1993). However, it is also probable that the Fe can be present in the ferrous state (Rappaz et al. 1982).

A second type of isomorphous substitution in monazite involves the tetrahedrally coordinated B⁴⁺ ion. There are two isomorphous variations of xenotime that are achieved via substitution of P. The first is solid solution with the vanadium end-member wakefieldite-(Y) and the second is the arsenate end-member chernovite-(Y). Although both of these minerals belong to the zircon group, their close structural relationship with xenotime and its continuous solid-solution with monazite suggests that small amounts of V and As may be incorporated in monazite without affecting a change from monoclinic to tetragonal symmetry. Extrapolating from xenotime, it may also be postulated that the incorporation of As and/or V into the monazite structure would result in an increase in the ninefold coordinated polyhedra, which would similarly promote the incorporation of larger cation species, such as Ba and Sc. However, no published examples of a V₂O₅ component in natural monazite are
known, and those including As₂O₃ are rare (Jercinovic & Williams 2005, Baldwin et al. 2006).

A second set of compositional exchanges in monazite require coupled substitution, where substitution occurs in both the A- and the tetrahedral site. The most commonly observed and reported substitution of this type is the huttonite exchange,

\[ \text{P}^{5+} + \text{REE}^{3+} \leftrightarrow \text{Si}^{4+} + \text{Th}^{4+}. \]  

(2)

Huttonite (ThSiO₄) is a rare monoclinic mineral, occurring in high-temperature rocks of igneous or granulite facies origin. A complete solid-solution between it and monazite has been shown to exist from experimentally synthesized compositions (Kucha 1980), but continuity across the solid-solution has not been well demonstrated in natural examples (Fürster & Harlov 1999). There is a U equivalent to the monazite-huttonite substitution, with U taking the place of Th (coffinite solid solution).

Another set of elements that are increasingly reported in monazite analyses are the halogens F and Cl. Very few data have been published to date, particularly for Cl, but F has been reported in concentrations as high as 0.80 wt.% (Andreoli et al. 1994, Baldwin et al. 2006), which equates to ~0.08 apfu. It is predicted that Cl and F substitute for oxygen with a second substitution to balance the charge. The situation is further complicated by the great strength of the P–O bonds. It is logical that the introduction of F⁻ is a coupled system requiring the substitution of a PO₄³⁻ group for one with a lower O–bond strength or partial charge. One possibility is Si, via the exchange

\[ \text{PO}_4^{3-} \leftrightarrow \text{SiO}_3^{2-} + \text{F}^- \]  

(3)

Such a substitution may account for the small excess Si atoms per formula unit in many monazite analyses after the cheralite and huttonite substitutions have been taken into consideration.

Even rarer are monazite compositions where S is documented (e.g., Cressey et al. 1999, Jercinovic & Williams 2005). The incorporation of SO₃ into monazite also requires a coupled substitution, but in this case, the partial charge in the tetrahedral site is increased by one and requires either an isomorphous substitution, such as

\[ \text{S}^{6+} + \text{Si}^{4+} \leftrightarrow 2\text{P}^{5+}, \]  

(4)

or, a coupled substitution involving the A-site, such as

\[ \text{S}^{6+} + \text{Ca}^{2+} \leftrightarrow \text{REE}^{3+} + \text{P}^{5+}. \]  

(5)

This substitution may partially account for monazite compositions where there is little correlation between the Ca and Th content (e.g., Schaltegger et al. 2005). Substitution of Al³⁺ into tetrahedrally coordinated sites is a common feature of silicate minerals; however, the significantly greater ionic radii of Al³⁺ compared with P⁵⁺, coupled with the charge imbalance, makes it unfavorable. Nevertheless, Al₂O₃ contents of 2.4 wt.% in monazite from Steenskampskraal have been reported (Andreoli et al. 1994).
Chemical Substitution and the Development of Complex Compositional Zoning

Monazite crystallizing from an igneous melt, like many other igneous minerals, may be concentrically zoned, reflecting an evolution in the composition of the melt and the equilibrium composition of the crystallizing monazite (Figure 3a). The high affinity of Th for the monazite structure is reflected in many examples of concentric growth zoning, with differences between individual growth zones typically reflecting...
Figure 4

Compositional maps and corresponding backscattered electron image of monazite from Snowbird Tectonic Zone, Saskatchewan (Legs Lake shear zone). The enhanced-contrast BSE image shows little of the pertinent zoning. This grain has intergrown domains of ca 2.5 Ga and 1.9 Ga (generally following lower uranium).

variation in the cheralite or huttonite substitutions. Alternatively, some elements may preferentially crystallize onto one crystal face rather than another, resulting in sector zoning (Figure 3b) (Cressey et al. 1999). When metamorphic monazite is considered, the scope for compositional domain and sector development coupled with extensive compositional variation increases. There are many examples of spectacular compositional variation in individual grains (Figure 3), including examples where metamorphic monazite overgrows or cross-cuts primary growth zoning in igneous monazite, or multiple metamorphic domains have complex overgrowth relationships where relative timing constraints may be identified through to complex interfingered or interspersed metamorphic domains where the establishment of relative timing is difficult to establish (Figures 3c, 4). Along with the increasing complexity of the textural information, there is an increase in the compositional complexity of the operating substitutions. Although the cheralite and huttonite substitutions, and their U equivalents, are commonly dominant, many of the other substitutions, especially those involving Y, have been documented.

Closure. The interpretation of the compositional and geochronologic datasets collected from multidomain monazite are of most straightforward value when they are interpreted as growth features and element diffusion is negligible. The concept of element diffusion in a crystallographic lattice is commonly referred to in the context of a closure temperature, formally defined as “the temperature of a mineral-isotopic system at the time corresponding to its apparent age” (Dodson 1973). An alternative definition, more relevant to those making analytical measurements, is the temperature at which solid-state diffusion of elements in the crystallographic lattice effectively ceases to be statistically meaningful at the resolution of an analytical technique. The closure temperature of monazite has been given much attention with the increasing use of monazite geochronology. A series of contributions on the diffusion of U, Th,
Pb, and REE in monazite have determined that monazite must spend prolonged periods of time at temperatures of 800°C or more for diffusion rates of any significance to operate and potentially alter the trace element compositions (Cherniak et al. 2000, Gardes et al. 2006). The experimental results documenting the sluggishness of diffusion in monazite are consistent with many observations of sharp domain boundaries, even in high-T monazite, and with the preservation of significantly older ages through younger high-T events. However, as discussed below, the monazite system can apparently be fully or partially reset owing to dissolution/reprecipitation or recrystallization processes at temperatures considerably below the nominal closure temperature.

MICROANALYSIS OF MONAZITE FOR GEOCHEMISTRY AND GEOCHRONOLOGY

Basic Compositional Characterization of Monazite for In Situ Analysis

A basic premise of monazite analysis and geochronology is that an overwhelming majority of monazite grains contain distinct compositional domains or zonation. Although an analytical challenge, this is one of the great strengths of the monazite geochronometer: multiple stages in the geologic history are preserved. Although some monazite grains do contain large compositionally homogeneous domains that are amenable to bulk analysis, this homogeneity is the exception and thus must be documented before analysis. Clearly, any comprehensive approach to compositional analysis of monazite must be done in situ to be able to relate composition to occurrence (host mineral and microstructure relations) and must be done on a scale commensurate with observed zoning patterns. This has led to the widespread use of EPMA and other microbeam techniques (e.g., laser ablation, micro-XRF) for compositional analysis.

The first step in the analysis of monazite is to locate the grains in thin sections or polished sections. Although commonly approached by backscattered electron (BSE) imaging surveys, more effective EPMA mapping approaches are advocated (Williams et al. 1999, Williams & Jercinovic 2002). BSE imaging is laborious and tends to miss important populations of small monazite grains. An automated full-section EPMA stage map can locate monazite down to a few microns in size in direct textural context. Monazite grains associated with particular mineral growth or deformation events can be recognized (e.g., monazite within particular porphyroblasts or occurring aligned in an identified fabric orientation). This approach allows the analysis strategy to focus directly on those grains that will potentially give the most insight into the timing of the processes in question.

Then, the critical step for all types of monazite analysis is to determine the distribution and character of compositional domains within monazite grains by micromapping (via EPMA wavelength or combined wavelength/energy spectrometry). Although BSE imaging can reveal significant differences in average atomic number (Z), it may not accurately show the distribution of important compositional differences if the variation in average Z is below the sensitivity of the detection system.
Elemental mapping, on the other hand, reveals the spatial variation of geochemically important elements, which will be critical for guiding further quantitative analysis as well as geochronology. Elements such as Y, Th, U, Ca, and Pb have proved to be very useful for domain delineation, but the particular choice of elements will evolve along with the general understanding of how monazite composition varies with petrologic setting, geologic history, and geochemical environment.

Once the essential domain structure of individual monazite grains has been established, quantitative analysis can proceed by EPMA point analysis. The accurate microanalysis of natural REE-phosphates is made difficult by the complexity of the REE X-ray spectrum. Numerous authors have addressed EPMA applied to REE-phosphates for major element determinations (see Amli 1975, Amli & Griffen 1975, Roeder 1985, Scherrer et al. 2000, Pyle et al. 2002, Jercinovic & Williams 2005), and refinements in wavelength analysis continue. The current spectral resolution of energy-dispersive analyzers precludes their use for the accurate quantitative analysis of natural rare earth–bearing phosphates by analytical electron microscopy.

**Microgeochronology**

The analysis of monazite for geochronology has rapidly progressed beyond dating multiple-grain separates by conventional isotope dilution and thermal ionization mass spectrometry (ID-TIMS) as the existence of complex, polygenetic monazite has become widely recognized. Isotopic analysis of monazite now includes single-grain analysis, and even subgrain or intragrain analysis. Monazite picked, microdrilled, or cut directly from polished sections can be analyzed with ultrahigh precision by ID-TIMS (e.g., Hawkins & Bowring 1997, Baldwin et al. 2006), thus retaining some degree of structural context, but other microbeam-based techniques now offer the advantage of exceptionally high spatial resolution and true in situ capability.

An array of instrumentation is currently available that can be brought to bear on the problem of microgeochronology applied to monazite. These can be broadly categorized as mass-ablation/isotopic techniques and ionizing-radiation/nonisotopic techniques (Table 1). These techniques each offer unique capabilities, and each has limitations. Assembling the most comprehensive geochronologic story typically involves the use of several techniques. Increasing spatial resolution and more precise analysis will undoubtedly continue to gain importance, emphasizing the strong symbiosis between microanalytical instrumentation development and the needs of the research community. As an example, recent work employing focused ion-beam (FIB) sampling for transmission electron microscopy (TEM) (e.g., Seydoux-Guillaume et al. 2003) is providing nanoscale chemical information about chemically complex monazite grains.

**Electron Microprobe Geochronology**

Radiogenic Pb accumulates in monazite and other minerals with significant Th and/or U (e.g., thorite, uraninite, xenotime). With sufficient time (generally hundreds of millions of years or more), Pb can reach concentrations of hundreds or thousands of parts...
Table 1 Methods of monazite microanalysis

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<tr>
<th>Technique</th>
<th>Analysis method</th>
<th>Reference/example</th>
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<tr>
<td>Mass-ablation/isotopic techniques</td>
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<tr>
<td>Microsampling by grain separation</td>
<td>ID-TIMS</td>
<td>Hawkins &amp; Bowring 1997</td>
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<tr>
<td>Grain separation by microdrilling</td>
<td>ID-TIMS</td>
<td>Paquette et al. 2004</td>
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<td>Laser techniques</td>
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<tr>
<td>Multicollector sector field</td>
<td>LA-MC-ICP-MS</td>
<td>Boyce et al. 2005, 2006</td>
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<td>Secondary ion mass-spectrometry</td>
<td>SIMS IMP SHRIMP</td>
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<td>Ionizing radiation/nonisotopic techniques</td>
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<td>Proton microprobe</td>
<td>μPIXE</td>
<td>Bruhn et al. 1999, Mazzoli et al. 2002</td>
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per million, well within the detection limits of EPMA. Knowledge of the concentrations of Th, U, and Pb can then be used to calculate an age by the following expression, assuming that the amount of common Pb is negligible relative to radiogenic Pb:

\[
Pb = \left[ \frac{Th}{232} \left( e^{232t} - 1 \right) \right]_{208} + \left[ \frac{U}{238} \cdot 0.9928 \left( e^{238t} - 1 \right) \right]_{206} + \left[ \frac{U}{235} \cdot 0.0072 \left( e^{235t} - 1 \right) \right]_{207},
\]

where Pb, Th, U are concentrations in parts per million; \( t \) = age (years); and \( \lambda_{232}, \lambda_{238}, \) and \( \lambda_{235} \) are decay constants for Th\(^{232}\) (4.95E-11/year), U\(^{238}\) (1.55E-10/year), and U\(^{235}\) (9.85E-10/year), respectively. Total Pb age determinations (sometimes referred to as chemical dating) have been attempted for several decades (see Bowles 1990), and the application to monazite in particular has recently become more prevalent.

EPMA is fundamentally a technique for the determination of microscale elemental concentration, and is traditionally employed for the analysis of major and minor elements in solid phases. However, because monazite geochronology requires accurate measurement of very low concentrations of Pb, U, and Th (essentially trace-element analysis), the relatively straightforward techniques commonly employed for major element analysis must be abandoned in favor of more rigorous protocols. The analysis of Th, U, and Pb in monazite by EPMA involves two equally critical aspects: (a) obtaining adequate precision (sufficient counts) to achieve acceptable detection limits and errors relative to the questions being asked and (b) obtaining accurate concentrations. The first point is primarily a function of counting parameters (intensity, total acquisition time per point, and total number of points in the analysis). The second point is far more difficult to evaluate and is a function of many possible analytical effects (Jercinovic & Williams 2005, Pyle et al. 2005). Both aspects contribute to the full description of analytical error.
Spectral properties: background determination and interferences. The measured X-ray lines for monazite age analysis are ThMα, UMβ, and PbMα (see Jercinovic & Williams 2005 and Pyle et al. 2005 for overviews). Aside from obtaining a correct major element analysis to insure proper matrix corrections, accurate analysis of these three elements also requires corrections for spectral interference. For example, YLγ interferes with PbMα, and there are numerous pertinent interferences from Th to the measurement of Pb and U (Jercinovic & Williams 2005). The concentration is calculated from the net intensity of the X-ray line in question relative to a standard of known composition. The net intensity is arrived at by precise measurement of the peak X-ray line intensities, and the accurate subtraction of background intensity. As the concentration decreases, the peak/background ratio decreases, approaching 1.0 in the trace element realm. Errors in background estimation have increasingly large effects at lower concentrations. Inaccurate interference corrections, or inaccurate measurements of concentrations of interfering elemental lines, will also grow in significance as the net intensity of the line in question decreases.

Major element analysis in EPMA traditionally involves background measurement by linear interpolation of two preselected wavelength positions on either side of the peak being measured. There is an implicit assumption that the peak/background value is high enough that any curvature in the background will be insignificant; this is true in the analysis of major elements but certainly false for that of trace elements. Background is expected to exhibit curvature, dependant on predictions of bremsstrahlung as a function of energy, modifications of bremsstrahlung emission owing to charge dynamics (Cazaux 1996) and the effects of wavelength-spectrometer efficiency (motion of crystal through the cone of X-rays in the spectrometer). The exact shape will be both specimen and spectrometer dependant.

Figure 5 shows the Pb-M and U-M spectral regions from natural monazite. The preponderance of interferences and noise in the wavelength spectra make assessment of background shape problematic. To simplify this evaluation, we can run detailed wavelength dispersive spectrometer (WDS) scans of synthetic REE phosphates free of Th, Pb, U, and relevant high-order interfering REEs (see Pyle et al. 2002, 2005). These scans demonstrate the exponential curvature of the background through the regions relevant to analysis of Pb and U elements. Linear interpolation of background intensity will clearly truncate the peaks, resulting in an overestimation of background and underestimation of net intensity (Figures 6, 7). As the peak intensity decreases, the magnitude of error from linear interpolation increases following a power function, resulting in dramatic inaccuracies in concentration and age.

Many workers have selected a background position in the spectral region between the PbMα and PbMβ peaks in an attempt to choose a narrow, and thus more linear, segment of the background spectrum. However, an important feature of the Pb-M spectrum in natural monazite (Figure 6b) is that there is no point in the wavelength region between PbMα and PbMβ that consistently includes true background. ThMζ1 and CeLα (second order) interfere [particularly when using Ar-CH₄ counters, as the strength of the Ar K ionization escape peak contribution increases (see Pyle et al. 2005), but also true for Xe-CH₄ counters, which show contributions from second-order CeLα owing to XeL ionization], such that the low point between
Figure 5
Examples of wavelength scans from natural monazite GSC 8153. Upper scan is from the Pb-M region on PET and the lower scan is of the U-M region. All labeled REE-L lines are second order. Note minor sulfur content revealed in the Pb scan. The Pb scan was done using VLPET, and the U scan using LPET on the Cameca SX-Ultrachron electron probe at the University of Massachusetts.
Pb region on GdPO₄ (VLPET)

\[ y = 8.520777 \times 10^{1}e^{-7.237583 \times 10^{-5}x} \]

Intensity (cps/nA)

54000 56000 58000 60000 62000 64000

Wavelength (sin \( \theta \) 10⁵)

Figure 6

Comparison of GdPO₄ high-precision scan and natural monazite. (a) Scan of synthetic GdPO₄ (three passes, 100 s per point at 200 nA). Individual points are indicated with 2σ error bars. This material is completely free of Th, Pb, U, Y, and the REEs that could generate second-order interferences in the region. The solid line represents exponential regression of scan data. (b) Pb scan from GSC 8153 overlain on GdPO₄ scan. Exponential regression is compared to two possible linear backgrounds illustrating overestimation of background in linear interpolation.

PbMα and PbMβ shifts depending on the Th/Ce ratio (Figure 8a). The most reliable means of obtaining accurate background intensities is by carefully scanning the wavelength region and extracting background by exponential regression of noise-filtered background regions. The background intensity will be strongly compositionally dependant (Figure 8b), necessitating background acquisition from each compositional domain in a zoned monazite.

The quantitative analysis of U, Th, and Pb in monazite is additionally challenging because of the numerous interferences of the Th-M series on the UMβ region, affecting both peak and background measurement (Jercinovic & Williams 2005). A complicating factor is the existence of the ThM4 and M5 absorption edges in this region (see Figure 5). Great care must be taken to extract background by detailed scanning, accounting for (a) the combined interference effects from ThMγ, ThM3-N4, ThM5-P3, ThM4-O2, and ThM4-P2 on both peak and background measurements; (b) absorption edge effects in high Th monazite; and (c) interferences from unexpected elements substituting in monazite [e.g., sulfur near PbMα (see Jercinovic & Williams 2005)]. In cases where mica or potassium-feldspar host, or are adjacent to monazite, fluorescence of the potassium K-level is possible from REE-L radiation near the interface. Potassium Kα will interfere with UMβ, and if unaccounted...
Figure 7
(a) Plot of error growth originating from background error caused by linear interpolation. The resulting % error in the net intensity is a function of the peak height above background, such that very large errors result at low peak/background. (b) Relationship between net intensity and measured concentration. Inset shows relationship below 2000 ppm. Very large (15% and up) inaccuracies will result when Pb concentrations fall below 1000 ppm if linear interpolation is used rather than exponentially regressed background intensity.

Beam effects and instrument stability. Although EPMA is considered to be a non-destructive technique, there are numerous cases where samples are adversely affected by even modest beam dose (e.g., Walker & Howitt 1989, Stormer et al. 1993, Jbara et al. 1995, Morgan & London 2005, Fialin & Chopin 2006). The high beam current density necessary for precise trace element determinations, however, has a much greater propensity for inducing beam-damage effects (Jercinovic & Williams 2005). The use of high electrical and thermal conductivity coating materials is advocated. Gold coating can dramatically reduce the beam damage, but even thinly applied, significantly affects both electron penetration and X-ray emission and produces additional interference effects for background determination (Jercinovic & Williams 2005). Aluminum coating produces a much cleaner spectrum for monazite analysis and higher net intensities.

Even in the best case, where elemental migration is moderated or eliminated, the issues of contamination buildup at the point of beam impingement and of dynamic evolution of the excitation and X-ray production volumes (Cazaux 1996, 2004) are additional sources of measurement error. High conductivity at the surface at least allows the possibility of steady-state interaction during the course of trace element analysis,
and the use of standards of similar physical characteristics undoubtedly improves accuracy. Improvements in counting efficiency could also play a significant role in lessening beam exposure effects. The extraordinary improvements in monochromator efficiency and advances in software design (such as multiple spectrometer integration) continue to increase the number of counts per second during analysis relative to the electron dose, improving precision and allowing shorter measurement time.

**Analytical strategy.** One of the first attempts at the application of EPMA to monazite geochronology involved the development of the Chemical Isochron Method (CHIME) established by Suzuki & Adachi (1991). This technique relies on the accumulation of many analyses from grains or domains of constant age that also have sufficient compositional variation to allow the construction of a pseudoisochron. As originally posited, two-dimensional isochron plots are created by casting U in terms of equivalent Th (Th*), or casting Th in terms of equivalent U (U*), and ages are calculated by regression. This technique has been recently augmented by multidimensional approaches, calculating both U and Th pseudoisochron ages for a more complete evaluation (Rhede et al. 1996, Cocherie & Albarede 2001). Linearly related arrays identified in Pb/Th* and Pb/U* diagrams can be used to identify different age populations. Small grains or domains are not accessible by this technique, and therefore the pseudoisochron method has found most application in the analysis of larger monazites obtained from mineral separates (Suzuki & Adachi 1991, 1998; Suzuki et al. 1994; Cocherie et al. 1998; Cocherie & Alberede 2001). Some recent studies
have attempted to apply this technique in situ (e.g., Tickyj et al. 2004). The pseudoisochron approach relies on large arrays of analyses and significant compositional, but not age, variation. An alternative top-down approach involves calculation of individual point ages, then extraction of age populations from histograms of analyses (Montel et al. 1996, 2000). Both of the above approaches have been described as top-down approaches (Williams et al. 2006) because they produce large composite data sets, which are then statistically evaluated to extract age populations (e.g., Cocherie & Albarede 2001, Montel et al. 2000).

An alternative approach, termed bottom-up, has evolved from the in situ, mapping-based analysis initially advocated by Williams et al. (1999) and Williams & Jercinovic (2002). Monazite is never removed from its thin-section textural context, allowing composition and age information to be viewed within the overall compositional and textural analysis of the sample (i.e., integrated with petrology and microstructure). The bottom-up approach begins with detailed compositional mapping of selected monazite grains (grains selected from full-section maps). Compositional domains are identified and evaluated by simultaneous processing of all grain maps for each element, allowing rapid comparison of domains of similar composition in different monazite grains (Williams et al. 2006). In appropriate cases, age maps can be constructed if Y, Th, Pb, and U are mapped (Williams et al. 1999, Goncalves et al. 2005). Major element quantitative analysis is then performed on each distinct domain, or ideally, quantitative trace element and major element analysis are performed together in a single integrated analysis.

Background intensities for Th, Pb, and U are acquired by WDS scanning and regression for each domain to be dated. Each domain to be dated is analyzed separately, and point analyses are accumulated in a domain until either a prescribed level of precision is obtained or until available surface area is exhausted (typically, a small ring of perhaps—six to eight analyses are made around the background measurement point). This strategy follows the mass spectrometry approach in which blocks of data are accumulated progressively to reach the level of prescribed precision. Likewise, an age in EPMA is arrived at by accumulation of compositional analyses within a domain and computed from the statistically constrained data within that domain. Five to ten point analyses will typically achieve an age error of 1% at the 2σ level (see below). Once a number of domains have been analyzed, they can be evaluated comparatively, and weighted means can be calculated when appropriate. A consistency standard is analyzed in a similar manner both before and after the run (see Williams et al. 2006).

**Analysis of error.** High counting precision can be accomplished by increasing count acquisition parameters, using higher beam current, longer count times, and employing higher count-rate spectrometers. However, simple propagation of counting statistics does not adequately describe all sources of error (Pyle et al. 2005, Williams et al. 2006). In fact, the longer count times and higher current that give a more precise analysis can actually result in further inaccuracy owing to beam damage, internal charge dynamics and instrumental drift. Counting statistics dominate short-term random error, but short- and long-term systematic errors also contribute substantially to the question of accuracy (Williams et al. 2006).
Short-term random error can be estimated using the standard deviation of the mean (SDOM) (Taylor 1997, Bevington & Robinson 2003) or by propagation of trace element uncertainties through the age equation. To use the SDOM estimation, the analyses to be averaged must all represent samples from the same, normally distributed population (i.e., data from single, compositionally homogeneous domains). If the short-term random error originates entirely from counting statistics, then propagated count errors will yield a comparable result. If there is a large deviation between the two estimates, it may indicate that the domain in question is not truly homogeneous or that beam damage is causing erratic results.

Short-term (day-to-day or session-to-session) systematic error originates from variation in background estimation, calibration, and coating thickness and effectiveness. The largest source of inaccuracy stems from variation in background estimation. With background curvature properly taken into account, the addition of the short-term systematic component can increase the error by 50%–100% over count statistical (random) error alone (Williams et al. 2006). Background estimation by two-point interpolation can result in much larger errors, on the order of tens of millions of years or more (Jercinovic & Williams 2005). Checking procedures, session to session, by comparing results on the consistency standard provides a means to minimize short-term systematic error.

A third source of error, long-term systematic error, involves aspects of analysis and calculation, such as matrix correction algorithms and constants, implementations of interference corrections, refinements of decay constants, the quality and characterization of standards, and instrumental parameters affecting intensity measurements (detector dead times, counter gas, beam current measurement, etc.). Rigorous analytical protocols can minimize much of this error, but numerical refinements will always have the potential to affect results, similar to effects such as spike recalibrations or refinements of decay constants inducing long-term systematic error in isotopic results.

APPLICATIONS OF MONAZITE COMPOSITION AND CHRONOLOGY TO GEOLOGIC STUDIES

Early applications of monazite geochronology generally involved separation of monazite crystals from the host rock for dissolution and dating. For a given rock, these types of studies tended to yield one or several dates, which generally were interpreted to reflect the peak of metamorphism or the age of initial crystallization. The limitations of this approach, as shown below, include the loss of textural context and mixing of ages in polygenetic monazite. The goal of this section is to summarize and integrate new uses of monazite for interpreting the (metamorphic, igneous, sedimentary, tectonic) history of rocks. In all rock types, monazite zonation can be very complex. Compositional X-ray mapping is an essential first step for most current studies. As noted, backscattered electron imaging can be used to distinguish some domains, but it is relatively insensitive to other compositional variations in monazite (see above, also Gibson et al. 2004).
Igneous Petrology

Monazite is one of the most common accessory phases in many low-CaO peraluminous granitoids, ranging from those of dioritic composition through evolved micaceous granites, pegmatites, and hydrothermal deposits. Its occurrence is considerably less common in peralkaline rocks, but is more common in rocks derived from carbonatite-related magmatism; such rocks host several important economic REE deposits. Monazite has not been reported from primary mafic lavas or plutons, and there are very few reported occurrences in rhyolites (Mungall & Martin 1996), although to some degree this may be a function of grain size. The most probable cause for the low occurrence of monazite in peralkaline rocks is that the high CaO content of such melts promotes the stability of apatite and allanite, which incorporate the LREE budget of the melt (Meyer et al. 1994, Watt & Harley 1993).

Monazite in granitoids typically has significant quantities of ThO₂, which is stoichiometrically and charge balanced by a combination of the cherelite and huttonite substitutions (Franz et al. 1996, van Emden et al. 1997). There are some examples in which one substitution is clearly dominant, such as the monazite-cherelite dominated examples from the Erzgebirge-Fichtelgebirge region granites (Fürster 1998), or the huttonite dominated examples of the Xihuashan granitic complex, southern China (Wang et al. 2003). In some cases, while both SiO₂ and CaO are present in significant quantities, only one positively correlates with the ThO₂ content, indicating that two separate substitutions must be operating (c.f. Schaltegger et al. 2005).

The application of monazite petrology to igneous systems has most commonly been used to provide a crystallization age in rocks in which zircon is not present, or as a companion to U-Pb zircon dating (Miller et al. 2006). Some workers have begun to use the subtle age differences between monazite generations or between monazite and zircon ages to monitor the evolution of igneous systems (Harrison et al. 1999, Catlos et al. 2002). The electron microprobe does not have the age precision to distinguish stages in a single magmatic system or to date a young igneous system, but high-resolution compositional mapping, textural analysis, and compositional analysis could provide critical information as to the distribution of trace components and trace phases.

Inherited monazite has been widely documented (e.g., Watt & Harley 1993, Harrison et al. 1995, Cocherie et al. 1998; see also Bea & Montero 1999). An inherited core domain may have any number of subdomains. These can help to link igneous rocks to their source terrains, and they provide a means to monitor the evolution of igneous systems, for example, recognizing magma mixing events (Dini et al. 2004), documenting the evolution from igneous to hydrothermal processes (Schaltegger et al. 2005), and recognizing and interpreting later hydrothermal effects (Townsend et al. 2001).

REE minerals in carbonatites are particularly common (Le Bas 1989). In many outcrops, bastnäsite [(Ce, La)(F, CO₃)] is the dominant REE-carrier, but in many cases it occurs together with monazite. The monazite in such rocks is commonly characterized by low ThO₂ concentrations and significant enrichment of chondrite-normalized LREE over HREE with a very steep negative trend (Kim et al. 2005,
Schematic chondrite-normalized REE distribution patterns of typical monazite compositions from metamorphic, peralkaline granitoids, and hydrothermal environments. Y-axis not to scale.

Wall & Mariano 1996) (see Figure 9). One further common connection observed in many examples is a negligible, to very slightly positive, Eu anomaly. In the late-stage carbonatite phases where monazite is most common, the highest concentrations of Sr and Ba are reported (Kapustin 1982, Chakhmouradian & Mitchell 1998).

Pegmatite and hydrothermal monazite comprise one further compositional class that has significant importance to the study of ore deposits. Distinguishing with certainty between hydrothermal monazite and magmatic monazite is difficult (Schandl & Gorton 2004) and is greatly aided by studying the texture and mode of occurrence of the monazite. One characteristic feature is that hydrothermal monazite commonly occurs in clusters of multiple grains, as opposed to the more homogenous distribution in igneous rocks. Furthermore, monazite in pegmatites and hydrothermal systems commonly have very low ThO₂ concentrations (< 1 wt.%) and Eu anomalies are commonly small or absent (Demartin et al. 1991, Mannucci et al. 1986, Schandl & Gorton 2004, Smith et al. 2000, Zhu & O’Nions 1999). The general trend of the REE chondrite normalization is still LREE enriched relative to HREE with a negative slope (Figure 9). Monazite occurring as inclusions in secondary replacement sheet silicates, feldspars, or quartz is also another diagnostic feature (Schandl & Gorton 2004).

The primary application of pegmatitic monazite has been related to granite and charnockite mineralization events, such as dating the REE-Th-Cu deposit formation in the Steenskampkraal Monazite deposit in South Africa (Andreoli et al. 1994), or improving understanding of the relative and absolute timing of epigenetic or mesothermal mineralization, such as the gold deposits of the Archean Greenstone Belt of Canada (Carpenter et al. 2005), Th mineralization at Lemhi Pass, Idaho
Metamorphic Petrology

Monazite is nearly ubiquitous in pelitic and psammitic metamorphic rocks at amphibolite facies and above, and it has been reported from greenschist facies rocks. It is common in meta-clastic rocks, especially quartzites, where grains may have originated as detrital grains, but metamorphic overgrowths are also common. Monazite has also been reported, although less commonly, in metamorphosed mafic, ultramafic, and calc-silicate rocks. The characteristics and paragenesis of monazite in metamorphic rocks have been presented by Spear & Pyle (2002). Here we focus mainly on applications of monazite to understanding the pressure-temperature-time (P-T-t) history, and in the following section the deformation history, of metamorphic rocks.

Monazite in many metamorphic rocks is characterized by a number of compositional domains, some of which may represent distinct age domains. Domain ages may be interpreted as monazite forming events, assuming that they are not the product of alteration or partial recrystallization (see below), but they cannot be assumed to represent the ages of geologic or tectonic events. Growth events reflect reactions that led to the production of monazite. They may result from several monazite-forming reactions with a single P-T loop; they may reflect fluid infiltration or possible deformation-induced dissolution precipitation without a change in P-T conditions. Alternatively, they may result from reactions within more than one P-T loop (i.e., metamorphic event). The goal is to link the various monazite-forming events with specific points within P-T-t-D histories.

Perhaps the most straightforward use of monazite in metamorphic analysis is the recognition of monazite inclusions in porphyroblasts with ages or compositions that are distinct from those in other porphyroblasts or in the matrix (e.g., Montel et al. 2000, Catlos et al. 2002). In the simplest interpretation, the age of the inclusions place an upper limit on the age of the porphyroblast and may constrain the age or identity of some earlier metamorphic event. For applications based on inclusion relationships alone, it is particularly important to evaluate compositional variation and to consider multiple inclusions. Monazite crystals connected to the matrix by even fine cracks can be partly or completely recrystallized (Terry et al. 2000), complicating P-T path chronometry. Such pathways may not be directly observable, depending on the geometry of the section.

The most powerful and unambiguous approach to monazite geochronology and geochemistry, and a clear trend of current research, involves integrating monazite into chemical reactions with the major silicate phases in metamorphic rocks. The addition of REEs and trace elements into the phase equilibrium can add additional constraints on the petrologic history (Spear & Pyle 2002) and, importantly, monazite can be used to specifically date the metamorphic reactions and the silicate phases produced in those reactions (e.g., Wing et al. 2003). Several of the most common and successful links (reactions) between monazite and silicate minerals are summarized here. Most of the reactions explored to date involve a single monazite component
that is related to a particular silicate phase (for example Y in garnet), but a clear future trend is to model the spectrum of trace elements and REEs during chemical reactions.

**Monazite-in reaction.** Monazite is relatively rare in low-grade pelitic metamorphic rocks but is relatively abundant at amphibolite and higher grades. This has led to interest in the monazite-in reaction for pelites. Investigations of metamorphic field gradients generally point to diagenetic monazite as a major source of REEs in shales, but monazite is generally unstable relative to allanite at low grade (Kingsbury et al. 1993, Wing et al. 2003). The breakdown of allanite and growth of monazite at approximately 550°C is one of the most commonly cited monazite-in reactions (Overstreet 1967, Smith & Barreiro 1990, Parrish 1990, Kingsbury et al. 1993, Wing et al. 2003). However, Wing et al. (2003) observed low-grade monazite growth around detrital cores, indicating a possible stage of diagenetic to very-low-grade metamorphic monazite. Others have suggested that garnet breakdown near the staurolite-in isograd is primarily responsible for monazite growth (Pyle & Spear 2003, Kohn & Malloy 2004). In clastic rocks, particularly quartzites, monazite is apparently stable throughout prograde metamorphism, and detrital cores are associated with a series of metamorphic overgrowths (Kopera 2003). These considerations and those presented below indicate that although monazite may originate via allanite breakdown in some pelitic rocks, this is by no means a general conclusion. Many metamorphic rocks have a number of monazite generations and thus a number of monazite-in reactions. It is important to develop compositional and textural tools to link these generations to a reaction history (e.g., Pyle & Spear 2003, Gibson et al. 2004, Mahan et al. 2006) (Figure 10).

**The yttrium-garnet-monazite connection.** The partitioning of Y and HREE between garnet, monazite, and xenotime may be the most commonly used and successful link between monazite and chemical reactions. After xenotime, garnet is the major repository of HREE and Y in metamorphic rocks, and the relative timing of garnet formation or breakdown strongly underpins the HREE and Y distribution in metamorphic monazite (Pyle & Spear 1999, Zhu & O’Nions 1999, Pyle et al. 2001, Yang & Rivers 2002). Typically, if monazite growth precedes garnet nucleation it will be richer in (HREE + Y) than if it postdates the garnet-in reaction (Zhu & O’Nions 1999). This connection is fortuitous because Y is readily measured in monazite by EPMA, and many metamorphic histories, and temperature and pressure calculations, are importantly based on reactions involving garnet. Examples integrating Y-monazite in metamorphic reactions include Foster et al. (2003), Pyle & Spear (2003), Gibson et al. (2004), Foster et al. (2004), and Mahan et al. (2006), with the latter two examples notable for utilizing compositional pseudosections to characterize the petrologic history and then link monazite to modal changes in garnet (see Figure 10).

These studies fall into two broad groups. The first involves the prograde path of pelitic rocks, whereas the second involves the retrograde path of garnet-bearing granulites. In pelitic rocks with xenotime present, both garnet and monazite can grow during the progressive breakdown of xenotime (Pyle & Spear 1999). Once xenotime has been depleted, monazite and garnet are generally on opposite sides
Figure 10

Summary model for evolution of felsic granulites in retrograde shear zones (Snowbird Tectonic Zone, Saskatchewan) with illustration of corresponding monazite (see also Figure 1) and xenotime growth. Age populations have been linked to corresponding monazite compositions in this sample, and four out of five of the populations are represented in this monazite. The growth of population 4 is schematically illustrated with a dashed line. Possible intermediate periods of resorption are not shown. LLsz: Legs Lake shear zone, GRsz: Grease River shear zone. Modified from Mahan et al. 2006.

of reactions because they represent the two dominant sinks for Y in pelitic rocks. Monazite growth reactions correspond to garnet breakdown and vice versa. One particular reaction that has received attention in pelitic rocks is the staurolite-in reaction at which garnet is commonly consumed. The loss of garnet may be partly or even dominantly responsible for the “bloom” of monazite that has been observed at the staurolite-in isograd (Smith & Bareiro 1990, Pyle & Spear 2003). A second monazite growth event may occur in migmatitic pelites if garnet is consumed during melt crystallization (see below).
The second broad group of garnet-monazite connections involves decompression of a wide variety of garnet-bearing rocks, where cordierite, orthopyroxene, or plagioclase are produced at the expense of garnet. These decompression reactions can involve loss of a significant amount of garnet and workers have interpreted an associated generation of Y-rich monazite (Gibson et al. 2004, Mahan et al. 2006, Kelly et al. 2006; M.L. Williams, unpublished data).

Yttrium partitioning between garnet and monazite has also been calibrated as a thermometer (see Pyle et al. 2001). This provides an additional constraint on temperature in metamorphic rocks. Importantly, it also provides a means to evaluate equilibrium between monazite and garnet, providing a further petrologic linkage for the purpose of placing timing constraints on metamorphic reactions.

**Monazite-migmatite connections.** Monazite is common in migmatitic rocks, and under the right circumstances, may offer a means of dating partial melting reactions. Monazite may offer a means of linking certain igneous rocks with their migmatitic source rocks. Workers have noted the relatively low solubility of monazite (and zircon) in peraluminous melts (Rapp & Watson 1986, Montel 1993, Wolf & London 1995). One implication of this, along with the generally slow diffusion rates, is that prograde monazite may be preserved through partial melting events, providing a record of premelting metamorphic events. Conversely, if the goal is to date the melting event, it is essential to chemically and/or texturally link particular generations of monazite to melting reactions.

Three potential opportunities for monazite growth during a partial melting event might be considered. Monazite may precipitate as a result of (a) melting, (b) melt crystallization, or (c) reactions with phases associated with melting or crystallization. Incongruent melting of REE-bearing phases, most importantly apatite, may lead to growth of new monazite (Wolf & London 1995, Zeng et al. 2005). In addition, new monazite may be produced due to differences in monazite-melt versus monazite-host rock partitioning of elements. Bea & Montero (1999) suggested that new monazite with significantly higher Th/U ratios than earlier metamorphic monazite reflects the increased partitioning of U into melt. During melt crystallization, it is possible, and perhaps likely, that monazite may precipitate directly from melts, especially peraluminous melts in which monazite is saturated (Watt & Harley 1993). This can be evaluated using monazite-melt equilibrium models, such as that of Montel (1993), to suggest that a particular generation of monazite was in equilibrium with a particular igneous rock composition. Finally, monazite growth during migmatization may not be directly tied to the melt, but instead to phases involved with melting or melt crystallization reactions [e.g., breakdown of peritectic garnet during melt crystallization (Pyle & Spear 2003)].

**Additional phases and reactions.** The emphasis thus far on monazite-garnet and monazite-migmatite relationships mainly reflects the emphasis on these phases in the literature, and in the case of garnet, the ease of mapping and analyzing yttrium. An additional stimulus for monazite growth may come from plagioclase breakdown, particularly at high pressure. Besides the release of P and LREE (Kohn & Malloy 2004),
plagioclase breakdown has also been correlated with significant SrO concentrations (up to 1.85 wt.%) (Krenn & Finger 2004) and a distinct Eu anomaly in monazite (Figure 9) (G. Dumond, personal communication). Bingen (1996) concluded that a reaction consuming hornblende, allanite, and apatite (+ titanite) and producing monazite and plagioclase coincided with the amphibolite to granulite transition in southwestern Norway. Although the REEs probably mainly come from allanite, the proposed reaction also involves a contribution of medium and heavy REEs from hornblende and titanite, and thus monazite is linked to the silicate reaction and a specific point on the P-T path.

The absence of primary monazite in mafic magmatic rocks implies that most monazite in mafic rocks is metamorphic in origin. The growth of monazite is controlled by P and REE partitioning and subsequent breakdown of primary magmatic phases. With the high Ca concentration of many mafic rocks, the primary P repository is typically apatite, which is also an important host for REEs and some large ion lithophile elements, including Th and U, in the mantle (O’Reilly & Griffen 2000). Thus, it follows that apatite stability during metamorphism of mafic rocks plays an important role in the growth of monazite. There is also a strong partitioning of the REEs and Y into clinopyroxene, and to a lesser extent orthopyroxene, in peridotites (Witt-Eickschen & O’Neill 2005), and P toward olivine. Concentrations of Y in olivine and spinel are rarely above detection limit. REE-rich titanite has also been reported in lamprophyre (Seifert 2005). The stability of each of these phases, and their participation in metamorphic reactions, may influence the growth and composition of metamorphic monazite. The REE budget in igneous and metamorphic rocks is a rich field for further study.

**Deformation**

Providing absolute timing constraints on deformation events is one of the major challenges of tectonic analysis. Although cross-cutting relationships of plutons, dikes, and other igneous rocks remain some of the strongest constraints, these tend to place rather coarse limits, and ambiguities can be introduced because of differing rheological properties between igneous and metamorphic rocks. In multiply deformed rocks, deformation histories commonly depend on interpretations of fabric relationships involving porphyroblasts, foliations, lineations, etc. Monazite can be a component of the fabric of deformed rocks and thus can offer a more direct means of constraining the timing of deformation events.

Constraints on the timing of deformation can come through metamorphic reactions to which monazite has been linked. For example, Mahan et al. (2006) associated movement on the Legs Lake shear zone, northern Saskatchewan, with a reaction in which garnet was partly replaced by cordierite. The reaction produced a generation of Y-rich monazite dated at approximately 1850 Ma, and interpreted to represent the time of shearing. Technically, the reaction may have occurred at some time after shearing when the rocks reequilibrated under new pressure conditions (see McFarlane et al. 2006), but the deformation is still more tightly constrained than by any other means. In addition to metamorphic reactions, deformation events may be the cause or
product of fluid flow events, which in turn lead to growth or dissolution of accessory phases such as monazite (Rolland et al. 2003). These provide opportunities for dating individual shearing events and for understanding fluid plumbing in crustal-scale fault zones.

Monazite itself can be a fabric-forming mineral, with platy or elongate grains aligned in the fabric (Williams & Jercinovic 2002), and it can also behave as a porphyroclast with inclusions and inclusion trails of other phases that can place constraints on the timing and character of deformation (Dahl et al. 2005a,b). In general, the interpretation of elongate monazite grains aligned in a foliation can be ambiguous. The straightforward interpretation is that the grains either predate or are synchronous with deformation in order to be aligned during the event, but it is also possible that monazite grains growing among foliated minerals (e.g., micas) may inherit the alignment. Compositional mapping and high-resolution textural analysis can help to resolve the ambiguity in that compositional domains can have kinematically significant orientations. For example, syntectonic monazite may grow in lineation directions or in extensional quadrants of porphyroclasts (Shaw et al. 2001, Williams & Jercinovic 2002, McCoy et al. 2005), perhaps directly dating deformation events. Finally, monazite crystals have been seen to be offset by fractures that can be related to larger-scale fracture systems (Shaw et al. 2001), and locally, fractures may be filled with later monazite bracketing the time of deformation. In many of these examples, the particular domain that offers the constraint is a volumetrically minor component of a larger monazite grain. This emphasizes the need for in situ analysis, high-resolution compositional mapping, and, at least in many cases, the high-precision analytical capability of EPMA.

Sedimentary/Diagenetic (Authigenic) Monazite

Monazite is a common accessory mineral in some sedimentary rocks, particularly clastic sedimentary rocks, where it is typically concentrated with other heavy minerals (Evans 1993). In addition, workers have increasingly concluded that monazite can be precipitated as overgrowths on other minerals or as new pore-filling grains during diagenesis of sediments. Because detrital monazite grains tend to contain internal compositional domains and because diagenetic monazite grains tend to be small, these settings provide new opportunities for microprobe monazite geochronology to constrain both the age and the source area of sedimentary rocks.

Detrital monazite. Geochronologic analysis of detrital minerals, particularly zircon, is now used in a large number of studies to constrain the depositional age, provenance, tectonic history, and setting of clastic sedimentary rocks. Detrital monazite is also common in many rocks, especially clastic rocks, and has already been used in a number of provenance studies, but mostly as whole-mineral analyses. With improved and more efficient analytical techniques, the electron microprobe may play an increasingly important role as a companion to analysis of other detrital minerals. Detrital monazite grains carry distinctive zoning and domainal patterns that correspond to a sequence of petrologic, tectonic, and fluid flux events that may help to fingerprint
the source terrane. The youngest age domains in detrital grains may be related to exhumation events in the source region that immediately preceded erosion and deposition. Metamorphism of clastic sedimentary rocks is commonly preserved as narrow overgrowths that truncate the detrital monazite cores, and hence the youngest detrital ages can be combined with the oldest metamorphic overgrowth ages to bracket the depositional age. Detrital monazite data may be strongly complementary to data from detrital zircon age spectra. Zircon ages are commonly biased toward igneous events in the source regions, whereas monazite commonly records metamorphic, tectonic, and fluid flux events in the source. Monazite has the additional benefit of revealing a sequence of postdepositional monazite growth events in meta-clastic rocks.

Figure 11 summarizes results from a pilot study in metamorphosed 1.7 Ga orthoquartzites of the Tusas Mountains, New Mexico. In the Tusas Mountains, detrital...
monazite grains, or detrital cores with metamorphic rims, are very common (Kopera 2003). Preliminary microprobe monazite ages fall in two main groups (ca. 1.75–1.73 Ga and 1.72–1.70 Ga). The older ages are common in the Yavapai province. For example, the dominant granitoid in the Moppin Formation of the northern Tusas Mountains is ~1.75 Ga and volcanic rocks from the nearby Pecos and Cochetopa greenstone belts are slightly younger. The youngest ages (1.70 Ga) may be sourced from the Vadito volcanic rocks immediately underlymg the quartzite. These data support the conclusion from zircon studies that a component of the detritus comes from the immediately underlying basement (e.g., Jones 2005). Metamorphic overgrowths in the central and southern Tusas Range (ca. 1.45–1.42 Ga) have been used to verify an important, but cryptic, fault that juxtaposes higher-grade rocks against lower-grade rocks (Davis 2002, Kopera 2003). Interestingly, these rims are nearly uranium-free (<100 ppm). The fact that U is highly soluble in oxidized fluids, coupled with the fact that the quartzite is extremely oxidized, suggests that uranium may have remained in solution during reprecipitation of monazite. This provides an opportunity to track formerly quartzite-hosted monazite as a detrital mineral or clast component in younger deposits.

**Diagenetic/authigenic monazite.** A number of workers have documented or hypothesized diagenetic (authigenic) monazite in turbidites (Tomkins & Ross 2005), nodular monazite in mud rock (Evans et al. 2002), and black shale (Lev et al. 1999, Williams et al. 2003). Several studies have indicated a biogenic component in the monazite-forming process (Williams et al. 2003, Tomkins & Ross 2005). The presence of diagenetic monazite in sedimentary rocks offers a powerful tool for dating sedimentary basins, especially Precambrian basins with little paleontological age control, and also for monitoring the geochemical and thermal evolution of sedimentary basins (Lev et al. 1999, Evans et al. 2002). This seems to be a particularly appropriate application for the electron microprobe in that the diagenetic monazite are generally very fine grained (1–10 μm), inclusion rich, and compositionally heterogeneous (Evans et al. 2002, Williams et al. 2003).

**MONAZITE RECRYSTALLIZATION AND COMPOSITIONAL/AGE RESETTING**

Both the homogenization of compositional domains and postcrystallization Pb loss as a result of diffusion have been shown experimentally to be insignificant at temperatures below 800 °C (Cherniak et al. 2000, Gardes et al. 2006), which explains why distinct compositional and chronologic domains survive younger amphibolite to lower-granulite facies metamorphism. There are, nevertheless, numerous examples of monazite that, while retaining complex compositional zoning, provide chronological information that is difficult, if not impossible, to interpret (Seydoux-Guillaume et al. 2003, Baldwin et al. 2006). This is a result of disturbance of the various ratios between Th, U, and Pb, the stability of which is critical to obtaining precise ages for each domain. In many cases, it is also shown that the younger overprinting metamorphic events reached T_max significantly below 800 °C, the supposed closure temperature of
monazite. In such examples, the role of metamorphic and/or metasomatic fluids are promoted as being responsible for the alteration.

Monazite alteration processes were investigated experimentally using homogenous nonmetamict monazite, pure water, and a number of Cl solutions at experimental conditions of 800 to 1200 °C and 7 kbar for between 5 and 60 days (Seydoux-Guillaume et al. 2002). In experiments with CaCl₂ at 1000 °C, significant dissolution and reprecipitation of monazite occurred, mimicking textures observed in diverse natural samples. However, this overgrowth did not inherit Pb from the dissolved monazite. In contrast, a Pb-doped CaCl₂ solution resulted in the growth of a new monazite rim that incorporated Pb from the solution and gave an apparently older age, compared with the original core, when analyzed by mass spectrometry. This result is very important for several reasons: First, it proves that under the correct geochemical conditions, the Pb-cheralite substitution, or some variation of it, may operate, resulting in the incorporation of Pb during monazite growth. Second, it shows that the process of dissolution-reprecipitation, which is dependent on the presence of a fluid (Putnis 2002), may be responsible for the development of compositional zoning in monazite, and that fluid alteration can significantly disturb the chronological data preserved in monazite.

A critical aspect of the dissolution/reprecipitation process is the behavior of Pb. If preexisting Pb is retained within the crystallographic unit cell of the recrystallized monazite (Seydoux-Guillaume et al. 2002, 2003), it will be detected during analysis and contribute to an artificially old date for the dissolution-reprecipitation event. If Pb is completely removed, the isotopic system is reset, and a domain age would reflect the age of alteration, but would be misleading if the relevant domain was misinterpreted as a primary age of mineral formation. A third scenario is that Pb is concentrated into interstitial sites, vacancies, and structural defects, as proposed by Seydoux-Guillaume et al. (2003). It is important to note that these issues are common to all monazite geochronology, and in fact, the electron microprobe may provide some means to characterize and possibly avoid alteration effects. One of the frontiers for monazite geochronology and geochemistry is to recognize compositional or textural features in monazite that may be diagnostic of dissolution-reprecipitation, to understand the influence on Pb mobility and chronological data, and to understand the limits of geochronologic analyses under such circumstances.

CONCLUSIONS

Monazite is a LREE-bearing phosphate mineral that is present in a wide variety of rock types, has an extremely variable composition reflecting host rock conditions, and is a robust geochronometer that can preserve crystallization ages through a long history of geological events. Because diffusion is slow, successive generations of monazite are likely to be preserved as discrete compositional domains with sharp boundaries. If the compositional domains can be linked to specific reactions or events, monazite can provide a detailed record of the geologic history of its host rocks. The electron microprobe is a key tool for integrating monazite into this geologic history: High-resolution compositional maps allow definition of domains and evaluation of
growth/recrystallization textures; compositional analyses allow monazite to be integrated into reactions; EPMA dating allows age constraints to be placed on even the smallest (several-micron-wide) domains. Results are strongest when combined with other techniques, but the microprobe remains the only instrument that integrates the complete compositional, textural, and geochronologic conditions under which crystallization occurred.

Monazite is currently being used to place timing constraints on geologic processes in all branches of solid Earth geosciences. Most studies make use of a limited number of compositional components (e.g., Yttrium) to link generations of monazite to silicate phases or reactions. However, the clear future trend is to integrate the complete composition of trace phases like monazite into the silicate history. This will require significant research on the properties and behavior of trace elements and REEs in silicate minerals and in monazite, and it will require continued improvement of analytical tools. The potential gains are great both for the fields of petrology and geochronology, and especially for linking the subdisciplines of geosciences in the context of an evolving solid Earth system.

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