

Petrochronology Based on REE-Minerals: Monazite, Allanite, Xenotime, Apatite

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INTRODUCTION AND SCOPE

REE-minerals

Monazite, xenotime, and allanite are REE¹-minerals *sensu stricto* because lanthanides (La...Lu) and yttrium are critical constituents in them. Apatite does not require REE, but because it contains substantial REE in many rocks, it is included in this review. All four minerals also host unusually high radionuclide concentrations, notably Th and U, forming the basis of their utility as geochronometers.

This quartet of accessory minerals is playing an increasingly important role in petrochronology because they provide ways to link robust spot ages to petrogenetic (*P–T*) conditions so can lend petrogenetic context to chronology based on other minerals. Part I of this review assembles the basic requisites prior to integrative petrochronologic analysis. Individual characteristics of the four REE-minerals are addressed first, i.e., their crystal chemistry and stability relations. Thermobarometers and trace element geochemistry used for tracing petrogenesis are discussed next, and finally their chronology is summarized. Part II presents case studies to highlight the specific strengths of REE-minerals used to resolve the dynamics of a broad range of processes, from diagenetic to magmatic conditions. Finally, a brief section at the end outlines a few of the current challenges and promising perspectives for future work.

To introduce the four REE-minerals in style, let us recall the origins of their names. The three phosphates have well respected Greek grandparents, and allanite has solid Scottish roots, yet of all four of them show idiosyncracies in etymology or type material.

Apatite had long puzzled naturalists, as it shows great chemical and physical variability and can resemble other minerals. Once properly identified, Abraham Gottlieb Werner named it apatite. His reasoning referred to the Greek root ἀπατάω and giving the precise Latin translation: *decipio*. Taken literally, both mean “I deceive” or “I mislead”, which sounds like an apt confession from this mineral for having fooled humans so long. It is perhaps appropriate that the original material identified probably was fluorapatite.

Monazite derives from μονάζειν = to be solitary. This name probably refers to monazite’s sparse occurrence in early discovered locations as well as its tendency to form isolated crystals rather than aggregates. I have been unable to trace this fully, but the now abandoned synonyms *eremite* (from ἐρημία = solitude) and *kryptolite* (= hidden rock) would affirm this interpretation.

¹ The rare earth elements (REE) *sensu stricto* comprise the lanthanides (La... Lu), plus Sc and Y

Xenotime again has Hellenic roots, but with a twist, as its original name was *kenotime*. An early copy-paste error led to xenotime. Both names contain the stem τιμή = honor. But κενός means “vain”, and the vain honor refers to the false initial claim by Jöns Jacob Berzelius that xenotime was a new element, which he then correctly recognized to be a mineral (e.g., Berzelius 1824) but under a different name. The name xenotime, introduced later (Beudant 1832), must be considered a misnomer, for ξένος means foreign or odd, making little sense, except that it is odd to honor a mere spelling mistake. The first reported kenotime was from a pegmatite in Hidra, SW Norway.

Allanite is named for Thomas Allen (Thomson 1810), an Edinburgh mineralogist who first singled out the mineral from a load of materials he had acquired, but which had previously been pilfered by English warships (Secher and Johnsen 2008). The original collector was Karl Ludwig Giesecke, and the type locality is Aluk, SE Greenland (Ibler 2010; p.86–87).

CRYSTAL CHEMISTRY AND CONSEQUENCES

Mineral structures and compositions relevant to petrochronology are outlined here. Emphasis is placed on clarifying substitution mechanisms, since this is required to appreciate how these minerals incorporate and fractionate REE, U, Th, and other elements used in chronology and petrology. Which exchange vectors operate is essential also to formulate chemical equilibria that constrain conditions of growth or interaction with other minerals, melt or hydrous fluid. Among the REE three groups are often distinguished, i.e., light, middle, and heavy REE, where LREE: La...Nd, MREE: Sm, Eu, Gd, and HREE: Tb...Lu. Y has an ionic radius within the range of HREE and is usually included with these.

More complete and comprehensive mineralogical accounts include the following: Huminicki and Hawthorne (2002) should be consulted for phosphate structure in general; Ni et al. (1995) for monazite and xenotime, Clavier et al. (2011) for monazite, and Hetherington et al. (2008) for xenotime. For apatite refer to White et al. (2005), Hughes and Rakovan (2002), Pan and Fleet (2002) or, for an elegant overview, Hughes and Rakovan (2015). The crystal chemistry of allanite is briefly summarized in Armbruster et al. (2006) and with more background in Gieré and Sorensen (2004).

Monazite and xenotime

Crystal structure, chemical substitutions. Monazite and xenotime are large-ion orthophosphates (REE)[PO₄] with related crystal structures; subtle differences between these help to explain their substantially different REE-fractionation (Ni et al. 1995): The large trivalent ion in monazite is coordinated to nine O-ions that form an irregular polyhedron (REE)O₉; in xenotime, Y (plus other HREE³⁺) is coordinated to eight O-ions that form a regular dodecahedron (Y)O₈ (Fig.1). By sharing edges, these polyhedra form chains in the *b*-direction in both crystal structures. Along *c* these chains are linked by [PO₄] tetrahedra to form a (100) sheet, and these layers are then stacked along *a* by sharing edges with the REE-polyhedra. While monazite is monoclinic and favors LREE, its dimorph xenotime-(REE) is tetragonal (part of the zircon group) and prefers HREE.

Large-ion phosphates show extensive solubility with related Th-phosphates and -silicates, such as cheralite CaTh(PO₄)₂ and huttonite ThSiO₄. Y (or some HREE or Gd) is a required constituent for xenotime; for monazite it is Ce (or La), which can be substituted by other LREE and Sm. Apart from exchanges involving only REE³⁺ and Y³⁺, two main substitutions involve coupled charge balance:



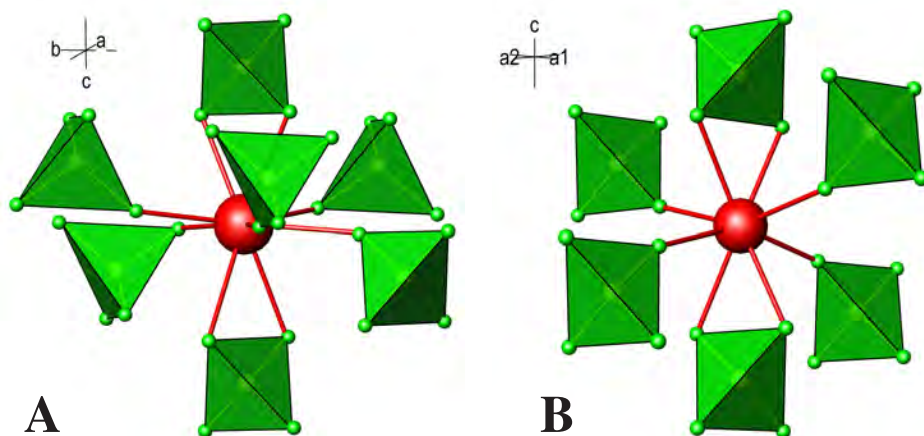


Figure 1. Local structure of REE-sites (A) in monazite and (B) in xenotime. Phosphate (PO_4) tetrahedra shown in green. The large trivalent ion (red sphere) in monazite occupies an irregular $(\text{REE})\text{O}_9$ polyhedron that preferentially accommodates the larger, light to middle REE and Th^{4+} ; in xenotime the regular $(\text{Y,REE})\text{O}_8$ dodecahedron provides a suitable site for Y and the smaller, heavy REE.

In both cases, U^{4+} may stand for Th^{4+} ; most monazites have $\text{Th}/\text{U} > 1$, but xenotime usually shows $\text{Th}/\text{U} < 1$. Data compiled by Spear and Pyle (2002) indicate that the cheralite exchange (Eqn. 1) dominates for monazite, but the huttonite exchange (Eqn. 2) is important as well (Table 1). Experimental data (Stepanov et al. 2012) indicate that huttonite dominates over cheralite at high pressure. In xenotime the chemical correlation plots are less clear; Zr^{4+} may substitute for Th^{4+} , so Zr should be included in xenotime analyses. Other minor substitutions are heterovalent as well, e.g., those involving halogens (mostly F), sulfur (in monazite), As (Janots et al. 2011), and Sr for REE (Krenn and Finger 2004).

As reviewed by Harrison et al. (2002) and Williams et al. (2007), experiments in binary systems of LaPO_4 with cheralite, $\text{Ca}_2\text{U}_{1/2}\text{PO}_4$, and huttonite show complete or extensive solid solutions (at 780°C), but natural compositions cover only parts of the range (e.g., Förster and Harlov 1999). Where the two phosphates are co-genetic, different exchange vectors may dominate, e.g., cheralite in monazite, but huttonite in xenotime (Fig. 7 in Regis et al. 2012).

Compared to xenotime, natural monazite shows considerably more variability in the heterovalent substitutions; this may be due to the flexibility of the larger and less regular polyhedron. The difference in coordination may also account for much of the observed REE-partitioning: Larger LREE ions (and Th^{4+}) find a “happy home” in the larger 9-O polyhedra in monazite, while Y^{3+} and the smaller HREE clearly prefer the smaller 8-O polyhedra in xenotime. In addition, some LREE show a tetrad effect, which seems due to orbital preference (of their unpaired 4f-electrons) for the irregular REE-site in monazite (Duc-Tin and Keppler 2015). The magnitude of these REE-preferences is visible in the distribution coefficients (Fig. 2), and these data also indicate that U^{4+} fractionates but weakly between xenotime and monazite. In general, the actinide ratio (Th/U) is higher for monazite than for xenotime.

Table 1. Main compositional endmembers of REE-phosphates.

Endmember	Name in monazite	Name in xenotime	Notes
$(\text{REE})\text{PO}_4$	monazite-(LREE)	xenotime-(LREE)	LREE: $\text{Ce} > \text{La} \approx \text{Nd} > \text{Sm}$
$\text{Ca}_2\text{Th}_{1/2}\text{PO}_4$	cheralite		formerly brabantite
ThSiO_4	huttonite	thorite	
USiO_4	coffinite		

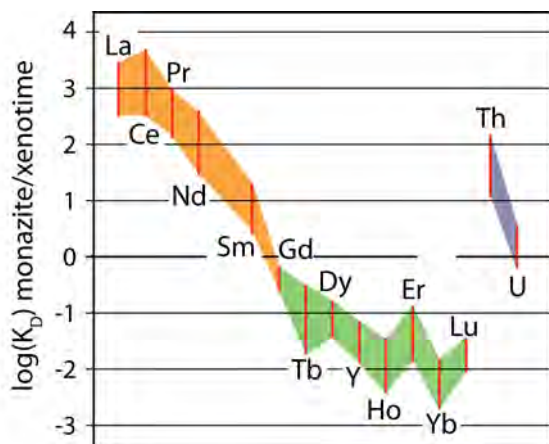


Figure 2. Distribution coefficient (concentration ratio $K_D = C_{\text{mon}}/C_{\text{xen}}$) between monazite and xenotime for REE, U, and Th. Trends for LREE to MREE highlighted in orange, for MREE to HREE in green, for actinides in blue; based on data from Franz et al. (1996).

In the REE-budget of many rocks, monazite plays a major role for the LREE, as does xenotime for the HREE. Monazite is the most common of the radioactive minerals (Overstreet 1967) and the main host of Th and U in many rocks.

Fortunately for geochronology, both monazite and xenotime do not favor incorporation of lead in their structure, although Pb^{2+} readily fits into monazite. Typically, common lead contents are low (often at ppm-level; Parrish 1990), although for precise isotopic data a common lead correction can be significant. In chemical U–Th–Pb dating (Williams and Jercinovic 2017; this volume), such correction is not possible, and its effect often would be within the analytical uncertainty due to electron probe counting statistics. It should be noted, however, that elevated common lead contents in monazite are known, e.g., in high pressure environments (Holder et al. 2015), in rocks altered by interaction with F-rich hydrous fluid (Didier et al. 2013), and occasionally in pegmatites (Kohn and Vervoort 2008); chemical dating of monazite is not advisable for such samples.

Sector zoning. Crystal-chemical controls of monazite can influence its uptake of REE. Cressey et al. (1999) documented differential incorporation of ions due to structural differences between specific growth surfaces. In that study, monazite from a carbonatite was sectorially enriched in La in {011} but depleted in {101} and {100} zones, whereas Nd showed an inverse preference; the effect is insignificant for Ce. Fractionation factors are modest in this case (~ 1.5), but caution is needed when concentration differences are observed, and such chemical heterogeneity in monazite is used to assess reaction relations or local REE-mobility. Stepanov et al. (2012) experimentally confirmed sector zoning in monazite from granitic melt (at 1000 °C, 1 GPa, 16 wt% H_2O); fractionation for the LREE was weak, but much more pronounced for Sm, Gd, Y, and notably also for Th. The data indicate that different growth sectors show substitutions of LREE for huttonite and for MREE (or HREE).

However, sector enrichment is an equilibrium feature of mineral surfaces, and close spatial proximity in a natural sample does not guarantee coeval growth. For instance, in a suite of lower greenschist to middle amphibolite facies metapelites, Janots et al. (2008) found substantially different La/Nd ratios in two populations of monazite (and similar fractionation factors as reported by Cressey et al. 1999), but local textures (Fig.10 in Janots et al. 2008) indicate sequential growth rims, not simultaneous sector fractionation. Sector zoning appears to be particularly common at very high metamorphic grade, notable in the granulite facies (DeWolf et al. 1993; Bingen and van Breemen 1998; Zhu and O’Nions 1999), while magmatic monazite can show oscillatory zoning (Montel 1993).

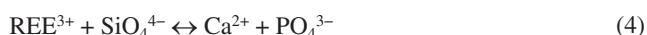
Apatite

Apatite, Earth's most abundant phosphate, has an extraordinarily flexible crystal structure. It incorporates a wide range of minor and trace elements, including some most interesting ones for geochemistry and chronology, e.g., S, Sr, U, Th, and REE. Furthermore, anion substitution in apatite is common; in most rocks apatite shows $F > OH \gg Cl$, but F/OH ratios vary. Apatite usually shows hexagonal symmetry, but anion ordering causes structural changes in $Ca_5[PO_4]_3(F,OH,Cl)$ (Hughes and Rakovan 2002).

In terms of total REE-content, natural apatite is not comparable to monazite and xenotime, but it can be significant in the LREE-budget of rocks, especially in carbonatites and mafic rocks (e.g., Y+La+Ce to 22,000 ppm: Cruft 1966; LREE > 15,000 ppm: Finger et al. 1998), in migmatites (LREE ~ 4,750 ppm: Bea 1996). REE concentrations appear to increase from amphibolite to granulite grade (LREE + MREE > 10,000 ppm: Bingen et al. 1996).

Crystal-chemically, REE do find a "happy home" in the M2 site of apatite, which is coordinated to six O-ions plus one monovalent anion (Pan and Fleet 2002). U^{4+} also favors the M2 site in most apatites (Luo et al. 2009), but Th contents are very low. The site occupancy ratio ($M^{2}REE/M^{1}REE$) changes with ionic radius: MREE such as Nd show no site preference, but HREE prefer the M1 site, which is coordinated to nine oxygen ions; M1 is smaller than M2, so ionic size is the probable cause of the site preference (Wood and Blundy 1997).

Substitution mechanisms involving REE in natural apatite involve charge compensation (Pan and Fleet 2002); the main exchanges proposed are:



Such heterovalent exchange mechanisms typically lead to much slower diffusion than homovalent exchanges; this was indeed found in experiments for REE in fluorapatite (Cherniak 2000). Because coupled exchanges depend on the concentration of other mono- to pentavalent cations on different sites in the crystal lattice, REE-diffusivity in apatite must be sensitive to composition.

Sector zoning. Apatite shows sector preference for certain REE (Rakovan and Reeder 1996); in this case the MREE and HREE are most affected, and fractionation is much more pronounced than in monazite: One study (Rakovan et al. 1997) observed nearly an order of magnitude difference for Nd between {0001} and {10 $\bar{1}$ 0} zones. On petrographic grounds, the sectors analyzed were judged to represent a single growth phase. Paired with substantially different Sm/Nd ratios in the two sectors, the compositional spread from analyses of different sectors of one crystal was sufficient to define an isochron age of 43.8 ± 4.7 Ma (2σ).

Allanite

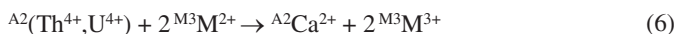
Crystal structure, chemical substitutions. Gieré and Sorensen (2004) gave an excellent entry into the world of allanite; Armbruster et al. (2006) clarified the nomenclature for the epidote-group and the non-trivial task of site-assignment, and they nominally ended the debate of what should be called allanite. Following Ercit (2002), allanite-(Ce), allanite-(La) etc. are now recognised as distinct mineral species. Here, the term allanite refers to what is officially the allanite subgroup.

Minor amounts of REE are often present in epidote group minerals, but in allanite LREE and Fe^{2+} are structurally essential constituents. The structural formula $A_2M_3[SiO_4][Si_2O_7](O)(OH)$ describes the entire epidote group and allows the main substitutions to be understood. Two groups of sites are identified, labeled A and M: A involves A(1) and A(2), which are 9- and 11-fold coordinated, respectively; M comprises three octahedra, of which M(1) and M(2) are essentially occupied by Al. With the main constituent of A(1) being Ca (plus minor Mn^{2+}), most

substitutions occur on A(2) and M(3) (Fig. 3): In natural allanite, A(2) is mostly occupied by REE^{3+} , with M(3) containing Fe^{2+} and minor Mg. By contrast, most natural epidotes (formally members of the clinozoisite subgroup) have A(2) principally occupied by Ca and M(3) by trivalent ions (Fe^{3+} , Al, Mn^{3+}). Allanite frequently shows chemical zoning or overgrowths, demonstrating solid solution with epidotes. The main exchange is heterovalent and can be written in site-specific notation as



Data compiled by Gieré and Sorensen (2004) show chemical analyses covering the complete range possible due to this exchange. In many cases the contents in REE^{3+} and M^{2+} are higher than will fit into the A2 and M3 sites, respectively, indicating that other sites can be involved as well. In addition to 2–3 wt% REE_2O_3 , allanite shows tetravalent substitutions, notably to accommodate Th (typically 1,000–10,000 ppm) and U (mostly <2,000 ppm):



Unless $\text{Fe}^{2+}/\text{Fe}^{3+}$ is analyzed by Mössbauer spectrometry (Fehr and Heuss-Assbichler 1997), the ferrous fraction must be estimated when normalizing chemical analyses for epidote group minerals from electron probe data (and LA-ICP-MS² data for trace elements). Analyses are normalized to 12.5 oxygen atoms on an anhydrous basis, as explained by Gieré and Sorensen (2004; their Figs. 5 and 6), based on Petrík et al. (1995).

As already noted by Goldschmidt and Thomassen (1924), allanite prefers LREE (La–Nd), similar to monazite, but in marked contrast to zircon and garnet, two commonly coexisting phases that tend to be HREE-enriched. Partitioning patterns—often shown in spider diagrams, normalized to chondrite or some suitable reference mineral—can thus be used for paragenetic indications (Hermann 2002). For allanite, the absolute amounts of the REE, the slope and curvature in the diagram, the presence or absence of anomalies (Eu, Ce?) all reflect competition between allanite and other REE-bearing minerals as the allanite grew.

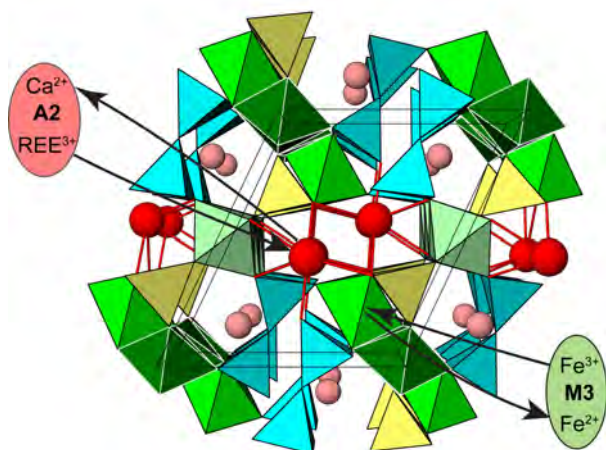


Figure 3. Structural elements of allanite shown as combined coordination polyhedra with specific ions to emphasize characteristic allanite substitutions relative to basic epidote structure. Large red spheres with sticks mark the 11-fold **A2** site for the $\text{REE}^{3+} \leftrightarrow \text{Ca}^{2+}$ exchange; charge balance is via the $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ on the **M3** (distorted) octahedral site, shown in bright green. Isolated SiO_4 tetrahedra in yellow, Si_2O_7 groups in turquoise. Pink spheres show 9-fold coordinated Ca in large cavities.

²Laser ablation inductively coupled plasma mass spectrometry

Sector zoning

Sharply discrepant compositions are often found in epidote group crystals, and their significance is not always clear. Apart from magmatic and metamorphic overgrowths, a possible miscibility gap has been debated, but this option was dismissed by Banno and Yoshizawa (1993) in favor of sector growth.

Radiation damage

Emission of α -particles in the decay chains of ^{238}U , ^{235}U , and ^{232}Th cause ionization and inflict radiation damage on any mineral with appreciable U or Th contents. Spontaneous ^{238}U fission is several million times rarer than α -decay, but causes much more severe structural damage to a host crystal. To indicate the extent of damage, optical effects in thin section (color, reduced anisotropy) and Raman spectra (McFarlane 2016) are useful. Minerals respond differently to the effects of both types of damage: In zircon and allanite with high actinide contents, structural damage accumulates over time, disrupting their crystalline integrity and eventually leading to a metamict (largely amorphous) state. By contrast, REE-phosphates do not become metamict, even though they can accommodate up to 30 wt% $\text{ThO}_2 + \text{UO}_2$ (van Emden et al. 1997); the damage inflicted to their structure appears to heal. Thermal annealing occurs at low temperatures, i.e., at ca. 100 °C in apatite and ca. 300 °C in monazite (Gleadow et al. 2002). While the mechanisms of such restoration are not well understood, they certainly have positive effects: Monazite, xenotime, and apatite remain structurally intact, and are less likely to lose their radiogenic Pb (Seydoux-Guillaume et al. 2004) and interact with fluid than heavily damaged allanite or zircon. Annealing can occur in allanite as well (Karioris et al. 1981), but it is more protracted. Structurally damaged or metamict grains are quite common in actinide-rich varieties, especially in Paleozoic and older rocks. But caution is indicated—even where old grains rich in U + Th now appear structurally intact, radiation-damaged grains may have healed after a period of open system behaviour. Such a scenario may explain why ages from non-metamict allanite occasionally appear implausibly young, such as for the Pacoima Canyon pegmatite (California), for which reportedly non-metamict allanite was dated to 1006 ± 37 Ma (zircon: Weber 1990; allanite: Gieré and Sorensen 2004, p. 466–472), whereas zircon is 1191 ± 4 Ma (SIMS Th–Pb, Catlos et al. 2000).

Disturbed Th–U–Pb dates in radiation-damaged allanite may result from Pb-loss or actinide remobilization (TIMS U–Pb, Barth et al. 1994). In this and other studies, discordances in ages (from TIMS and LA-ICP-MS) are larger between $^{208}\text{Pb}/^{232}\text{Th}$ and Pb/U than between $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$. This implies unequal chemical mobility of Th and U in allanite. Barth et al. (1994) discovered minute grains of thorite and uraninite along fluid pathways (cracks) in two metamict samples. This indicates an indirect effect of radiation damage, and such secondary phases would account for the decoupling between U- and Th-systems. Beyond a critical cumulative irradiation dose, hydrothermal fluid attack appears to be much more effective. According to Smye et al. (2014), a critical dose sufficient to effect isotopic disturbance is an order of magnitude lower in allanite than in zircon. This susceptibility to damage and alteration, and the generally much higher concentration of Th + U, help explain why allanite ages > 300 Ma often show more effects of radiation damage than zircon.

Diffusion and closure temperature

Several aspects of petrochronology must consider diffusive mobility, notably

- when constraining petrogenetic conditions, applying thermobarometers etc., based on local equilibria in sample domains (Lanari and Engi 2017);
- when considering the effects of chemical re-equilibration upon subsequent changes in P – T (pro- and/or retrograde), whether by pure exchange- or combined net-transfer- and exchange-reactions (Kohn and Penniston-Dorland 2017);

- when analyzing geochronological data (e.g., normal / inverse discordance) to assess full/partial isotopic equilibration during mineral growth, and subsequent loss of parent or daughter isotopes (Wasserburg 1963).

The essential theoretical aspects of diffusion, experimental constraints, select analytical data from natural examples, and insight gained from petrochronological studies are presented and evaluated in this volume (Kohn and Penniston-Dorland 2017). Here, a brief account is given only to assess the current state of knowledge about isotopic closure temperatures (T_c) relevant to U–Pb, Th–Pb, and Pb–Pb chronometry. While the link between T_c and diffusivity (D) is well defined (Dodson 1973, 1986; Ganguly and Tirone 1999; Kohn and Penniston-Dorland 2017), minerals differ in their capacity to self-heal damage due to fission and α -decay, e.g., allanite can become metamict with time. Insight gained from work on natural samples occasionally is in conflict with results from experimental diffusion studies, and structural damage certainly increases ionic mobility. While this topic has been addressed in numerous studies, we are far from understanding how closure temperatures change in minerals undergoing (partial) metamictization and thus affect what ages are recorded.

For monazite, Parrish (1990) estimated $T_c = 725 \pm 25^\circ\text{C}$, a value still commonly quoted, but T_c values of 800–850 °C have subsequently been proposed, based on preserved age relations in high-temperature samples (Spear and Parrish 1996; Bingen and van Breemen 1998; Kamber et al. 1998). Experimental diffusion data initially indicated $T_c \sim 500^\circ\text{C}$ for 10 μm monazite (Smith and Giletti 1997), but subsequent work (Cherniak et al. 2004) found $T_c > 900^\circ\text{C}$. Pb diffusion in xenotime was found to be even slower than in monazite, and T_c must be similarly high (Hawkins and Bowring 1997; Cherniak 2006, 2010).

No experimental diffusion data are available for Pb in allanite; closure temperatures have been estimated based on dated high-temperature samples. A minimum T_c of 750 °C is required to account for the retentivity of allanite (Oberli et al. 2004) crystallized in Bergell tonalite during magmatic differentiation (see Case Studies below, Fig. 21). Heaman and Parrish (1991) proposed $650 \pm 25^\circ\text{C}$, but also noted that allanite U–Pb closes at higher temperature than titanite. T_c for titanite has recently been revised upward to near 800 °C (Kohn 2017), and I am not aware of any natural datasets that would indicate a lower T_c for allanite. Note, however, that allanite may seem young because of retrograde growth (Finger et al. 1998; Wing et al. 2003), well below its T_c .

At current understanding, the conclusion is that lead loss by diffusion from monazite, xenotime, and allanite is probably negligible up to temperatures of $> 750\text{--}800^\circ\text{C}$ over 10 Ma for grains $> 20\mu\text{m}$. Such conditions certainly encompass “normal” granulite samples, i.e., U–Th–Pb chronometry applied to high-temperature growth zones should yield formation ages. Recent studies have interpreted monazite data even from UHT terrains ($> 900^\circ\text{C}$) as formation ages (e.g., Suzuki et al. 2006; Korhonen et al. 2013), but rigorous corroboration using diffusion profiles from such samples would be desirable. The shape of concentration profiles across different growth zones should allow diffusion models to be tested (e.g., reasonable $D \cdot \Delta t^3$) and may potentially constrain the T – t history (e.g., Watson and Harrison 1984). However, it is important to remember that fluid- or deformation-induced retrogression can be far more important than purely diffusional processes (Teufel and Heinrich 1997; Seydoux-Guillaume et al. 2002b; Harlov et al. 2011; Shazia et al. 2015).

³ since the diffusion length is $2(D \cdot t)^{1/2}$

GEO-THERMOBAROMETRY

Monazite and xenotime thermometry

A welcome effect of the pronounced Y-HREE fractionation is the miscibility gap between xenotime and monazite, which is quite asymmetric in $\text{YPO}_4\text{--}(\text{REE})\text{PO}_4$. The Y-content of monazite serves as a geothermometer, with only modest pressure-sensitivity (Gratz and Heinrich 1997, 1998; Heinrich et al. 1997; Andrehs and Heinrich 1998). Calibration data are summarized and discussed in Spear and Pyle (2002, Fig.24); they emphasize effects of additional components (Th, U, Ca, Si), but so far only the effect of Th on the miscibility gap has been calibrated (Seydoux-Guillaume et al. 2002a).

Figure 4 compares calibrations based on experiments. From these data, Mogilevsky (2007) developed a generalized regular solution model that can handle other components as well. For thermometry, this formalism (as presented in Mogilevsky's Equations 4–7) demands a numerical solution, and so far it seems that no applications have appeared in geology. Spear and Pyle (2010) used the same experimental data to construct a thermodynamic model based on estimated endmember properties, and approximate temperatures can be obtained from these. This approach is promising, but so far restricted to a very small compositional space; a wider basis of phase equilibrium data is sorely needed to allow a more generalized thermodynamic calibration and then applications thereof.

Apart from such technical issues, applying monazite–xenotime thermometry to rocks has its limits. Notably, xenotime should have been present when monazite grew, else the method yields minimum temperature values only. Since garnet (YAG component) is a major competitor for Y, xenotime is consumed during prograde garnet growth and commonly disappears from the assemblage; it may reappear where garnet is consumed, at higher grade or on decompression or retrogression (e.g., Hallett and Spear 2015). For these reasons, it can be tricky to ascertain that a specific monazite zone grew while saturated in xenotime, and in fact they rarely occur together in equilibrium (e.g., Pyle and Spear 1999). In zoned monazite, the Y-content is a good guide: annuli with high Y are good candidates for thermometry, whereas an abrupt decrease in Y may indicate growth in a xenotime-absent assemblage. Geochemical zoning and textural relations can convincingly discriminate such populations (e.g., Foster et al. 2004; Daniel and Pyle 2006, p. 108–113). In rocks where monazite and xenotime are both present in local assemblages, they often show zoning, and it can be unclear how to assess which compositional pairs were in equilibrium at any stage of the evolution; checking if partition coefficients (notably Gd/Y, Dy/Y; Pyle et al. 2001; perhaps also Th/U) show equilibrium values is preferable to blind trust.

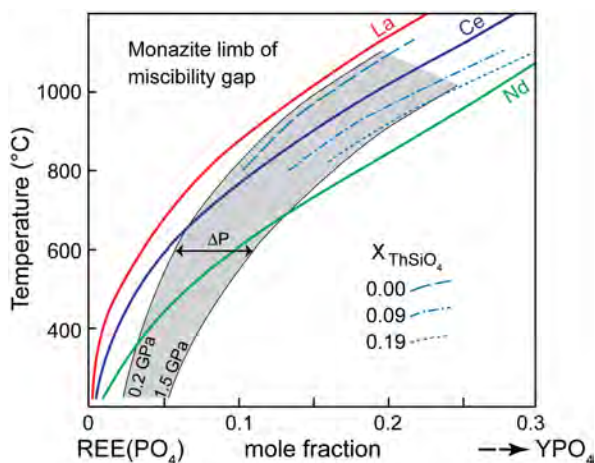


Figure 4. Monazite limb of the miscibility gap to xenotime, comparing calibrations based on experiments. Two isobars (0.2 and 1.5 GPa) from Gratz and Heinrich (1997) show sensitivity to pressure; three isopleths from Seydoux-Guillaume et al. (2002a) display effect of the Th-content of monazite; note that ~20% Th-endmember shows an effect comparable to ~1 GPa pressure increase. Curves labeled Ce, La, Ce, Nd show the dependence on the respective REE from models calibrated by Mogilevsky (2007) using experimental data.

Two further thermometers make use of the Y-contents of garnet in equilibrium with either xenotime or monazite (Pyle and Spear 2000; Pyle et al. 2001), but do not depend on both phosphates being present. The empirical garnet–xenotime thermometer is useful but over a small temperature range (~450–560 °C). As long as xenotime buffers the Y-activity of an assemblage, only the Y-content of garnet (grt) is needed for thermometry (Pyle and Spear 2000):

$$\ln(Y/\text{ppm})_{\text{grt}} = \frac{16031(\pm 862)}{(T/K)} - 13.25 (\pm 1.12) \quad (7)$$

The garnet–monazite thermometer extends this limited temperature range; it is most sensitive up to ~620 °C. At higher temperature the Y-concentration in garnet is low, approaching the detection limit of EMPA⁴ data, hence LA-ICP-MS analyses are preferred. In addition, quartz, plagioclase and apatite must coexist, and the thermometer depends on H₂O, albeit weakly (Pyle et al. 2001):

$$T/K = \frac{[-1.45 \times (P/\text{bar}) + 10^3 \times 447.8(\pm 32.1)]}{[567(\pm 40) - R \ln(K_{\text{eq}})]} \quad (8)$$

requiring analyses and solution models for garnet (grt, Grs: Ca₃Al₂Si₃O₁₂, YAG: Y₃Al₅O₁₂), plagioclase (pl, An: CaAl₂Si₂O₈), monazite (mnz), and apatite (ap, OH-ap: Ca₅[PO₄]₃(OH)) to obtain

$$K_{\text{eq}} = \frac{(a_{\text{grs,grt}}^{5/4} a_{\text{an,pl}}^{5/4} a_{\text{YPO}_4,\text{mnz}}^3 f_{\text{H}_2\text{O}}^{1/2})}{(a_{\text{YAG,grt}} a_{\text{OH-ap,ap}})} \quad (9)$$

Provided the mineral analyses are accurate⁵, the calibration usually yields temperature estimates to within ±30 °C of independent thermometers even if a pure hydrous fluid is assumed. However, to be petrochronologically useful, the thermometer should be restricted to monazite–garnet pairs that grew simultaneously, and to ascertain this, petrographic scrutiny is essential (Pyle et al. 2001).

Monazite–melt thermobarometry

Solubility data for monazite in granitic melt were used to calibrate a thermometer for magmas (Montel 1993; Plank et al. 2009); it relies on low-pressure experiments (0.2 GPa, Montel 1986; Rapp and Watson 1986). A similar thermometric equation, but with a pressure correction, was proposed by Stepanov et al. (2012), incorporating their new data to 5 GPa. All these thermometers assume that monazite dissolves to dominantly associated LREE(PO₄) species. However, recent data (Duc-Tin and Keppler 2015) indicate that at least for some magma compositions partial dissociation in the melt occurs at low pressure, and at pressures of 3 GPa (Skora and Blundy 2012) dissociated LREE³⁺ and (PO₄)³⁻ ions are dominant in hydrous silicic melts. This behavior parallels other hydrous fluids at high pressure (Manning 2004). As pointed out by Skora and Blundy (2012), thermometry such as advocated by Plank et al. (2009) would be seriously (>100°) in error at pressures typical of subduction systems. Stepanov et al. (2012) developed the following equation describing monazite solubility in peraluminous and metaluminous granitic melts:

$$\ln(C_{\text{LREE}}/\text{ppm}) = 16.16(\pm 0.30) + 0.23(\pm 0.07) \times (\text{H}_2\text{O}/\text{wt.}\%)^{1/2} + \ln(X_{\text{LREE}})^{\text{mnz}} - \frac{11494(\pm 410)}{(T/K)} - \frac{1.94(\pm 0.40) \times (P/\text{GPa})}{(T/K)} \quad (10)$$

⁴ EMPA: Electron probe microanalyzer

⁵ As OH-apatite is obtained by difference, F in apatite requires analytical attention

(CLREE := $\Sigma \text{La} \dots \text{Sm}$ in ppm; XLREE := $\text{LREE} / [\text{LREE} + \text{Y} + \text{Th} + \text{U}]$). This linear fit reproduces a large dataset (750–1400 °C, 0.2–5 GPa, 1–20 wt% H_2O and 0.82–1.36 ASI 6), but includes neither the experimental data for melts with $(\text{CaO} + \text{FeO} + \text{MgO}) > 3 \text{ wt\%}$ nor for peraluminous and phosphate-rich melts (Duc-Tin and Keppler 2015). Figure 5 shows that the strong temperature-dependence vanishes for highly aluminous melts (ASI > 1.0).

TRACE ELEMENT GEOCHEMISTRY AND PETROGENESIS

Magmatic and partial melting range

Phosphates. Monazite grains crystallized from melt typically show chemical zoning, and this can be very useful to single out specific growth zones for spot dating. So far, most emphasis has been placed on Th- and Y-zoning (Pyle and Spear 2003; Kohn et al. 2005; Rubatto et al. 2013). This is addressed below, but recent experimental work has clarified the interplay of these elements with the REE, and thus zoning in the LREE and MREE, even in individual REE, should be deciphered in detail. Such information is likely to add useful control on the dissolution and growth history and elucidate the control phosphate solubility plays in fractionation, e.g., of Sm over Nd (Zeng et al. 2005) or LREE showing tetrad effects for monazite (Duc-Tin and Keppler 2015).

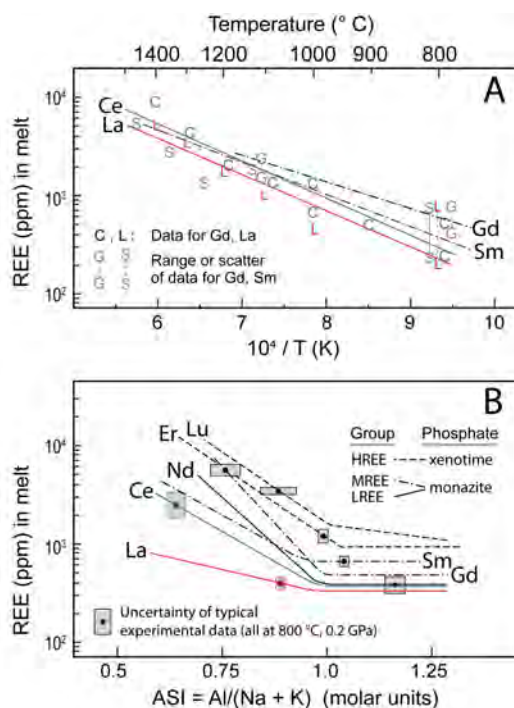
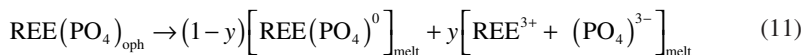


Figure 5. Experimental solubility data for REE-phosphates in granitic melt by Duc-Tin and Keppler (2015) and earlier studies. (A) Monazite solubility is more strongly temperature-dependent for the LREE than for MREE (and HREE); size of symbols shows uncertainty in data. (B) The effect of the aluminum saturation index (ASI) on REE solubility. Select trends (based on data for 800 °C, 0.2 GPa, ~0.1 wt% P_2O_5) show solubility generally increasing from LREE (La–Nd) to MREE (Sm–Gd) to HREE (Tb–Lu); differences are not significant for peraluminous melts (ASI > 1.0), but for peralkaline melts solubility strongly increases. Steep slopes for Nd and Gd indicate tetrad effect.

⁶ ASI := $\text{Al}/(\text{Na} + \text{K} + 2\text{Ca})$

REE. Data on monazite solubility (Montel 1986; Rapp and Watson 1986; Rapp et al. 1987; Montel 1993; Duc-Tin 2007; Stepanov et al. 2012; Duc-Tin and Keppler 2015) show a dependence on temperature, pressure and magma composition, notably the H₂O- and phosphate-content, and the aluminum saturation index (ASI:=molar Al/(Na+K+2Ca)). As explained above, the pressure dependence of the solubility has been attributed to changes in complexation in the melt (Skora and Blundy 2012), but recent data for monazite and xenotime (Duc-Tin and Keppler 2015) indicate that partial dissociation also occurs at low pressures—more notably in peralkaline, less strongly in peraluminous melt (Fig. 5)—a fact that had gone unnoticed in previous studies. In the pressure-composition range of partial dissociation (0 < *y* < 1), orthophosphate (oph: monazite and xenotime) dissolution should be written as:



The *P–T–X* conditions of partial dissociation are not yet fully explored, but solubility is known to increase with H₂O-content and alkalinity (for ASI < 1.0), whilst it decreases with actinide (Th+U) concentration and pressure. Solubility of monazite is most temperature-dependent for LREE, less so for MREE (Stepanov et al. 2012; Duc-Tin and Keppler 2015). With increasing dissociation (higher *y*-values), orthophosphate solubility increasingly depends on the phosphate contents of the melt, which can vary widely—by at least two orders of magnitude for mafic to felsic magmas, and from 0.1 to 1.5 wt% in granitic magmas alone (Pichavant et al. 1992; Breiter et al. 2008). Because REE and P₂O₅ are both incompatible, their concentration depends on the degree of melting: At high melt fractions P₂O₅ concentrations are low, whereas LREE are high; during crystallization they move in the opposite sense. Apatite solubility is low in metaluminous melts ((ASI=1), but increases with the ASI, owing to AlPO₄ complexes (e.g., Wolf and London 1994), and it is also elevated at low ASI, owing to alkali phosphate complexing (Ellison and Hess 1988). In melts derived from apatite-saturated metasediments, phosphate contents may initially be buffered by apatite solubility, but since monazite is considerably less soluble in melt (and hydrous fluid) than apatite, monazite (and xenotime) largely control the REE- (and Y-) content of melts and vice versa. LREE-rich apatite dissolves incongruently (Antignano and Manning 2008; Tropper et al. 2011), so leaves behind a LREE-enriched monazite. Leucosomes in migmatites may well preserve pre-anatectic monazite and xenotime (Rapp and Watson 1986), or apatite in very hydrous melts (Zeng et al. 2005).

Recent work (Duc-Tin and Keppler 2015) shows substantial differences in solubility among pure LREE-phosphates; even neighboring LREE can differ by a factor of two (Fig. 5). This opens the possibility to refine our understanding and interpretation of zoned monazite by analyzing the patterns for individual REE or groups thereof, particularly as solubility is strongly temperature-dependent for LREE but less so for heavier REE.

Current understanding of the solubility of orthophosphates (Fig. 5), especially in granitic systems and their REE evolution, allows some specific conclusions relevant to monazite petrochronology. Attempts to model the behavior of monazite (and zircon) in the partial melting range (Kelsey et al. 2008; Yakymchuk and Brown 2014) have combined computed phase diagrams that show the stable phase relations, computed from thermodynamic models, with the solubility equations. Yakymchuk and Brown used the updated solubility equation (Eqn. 10) and also included open-system scenarios (with intermittent melt loss). The results of both studies predict that partial melting of metapelitic and metapsammitic protoliths will, depending on the exact *P–T* path, lead to dissolution of (most or all) monazite. Noting that melt-isopleths typically have positive *P–T* slope, decompression is expected to lead to dissolution, and monazite growth is expected only upon cooling. In ascending magmas, the oldest monazite age most likely dates cooling after decompression, magma emplacement or injection. This is certainly the most likely moment on a clockwise *P–T–t* path, say in a collisional setting, where initial decompression may be attended by heating: Most monazite

is expected to crystallize sometime *after* cooling from $T_{\max}$, and it seems most unlikely that one could use monazite to date the stage after $P_{\max}$ but before $T_{\max}$ is reached (Kohn et al. 2005). Things are more complicated if magmatic allanite is involved, i.e., in more calcic compositions (e.g., granodiorite and tonalite). At late-magmatic stages, as partial melts become enriched in volatiles, monazite resorption is likely⁷.

In addition, dissolution of phosphates can be kinetically limited, especially in dry melts, where diffusion of LREE and phosphate species away from the dissolving solids is very slow (Harrison and Watson 1984).

Th, Y, and U. These elements partition into monazite, much like the LREE, but to decreasing degrees, i.e., Th most, U least. During crystallization, thorium is dominantly fractionated into monazite, and Rayleigh-like fractionation occurs, except in more calcic magmas, where allanite may interfere. Th/U ratios in monazite of course depend on Th/U in the magma, but also on the modal abundance of coexisting phases competing for actinides, notably allanite—the other main Th-sink—and zircon, xenotime, and titanite, all of which favor U over Th. In migmatites and generally in granitoid magmas, fragments or corroded relics of pre-melting monazite (from one or more prograde generations, discussed below) may survive even long periods of high temperature and extensive melting (Copeland et al. 1988; Harrison et al. 1995; Kohn et al. 2005; Dumond et al. 2015). Their eventual dissolution may explain Th-rich rims in magmatic monazite or allanite. In the absence of such complications, the earliest magmatic monazites typically show the highest Th-contents; subsequent growth zones are Rayleigh-distilled. Such patterns, reported primarily from anatectic, often haplogranitic magmas, have been put to use in deciphering and dating pre- and post-anatectic stages (Pyle and Spear 2003; Kohn et al. 2005; Corrie and Kohn 2011). Xenotime saturation, i.e., growth from melt or resorption in it, is critically dependent on and inversely correlated with garnet and monazite, the main competitors for Y. Competition for actinides during magmatic crystallization is reflected in apatite, which shows Th/U ratios that vary inversely with the modal presence of monazite (and possibly allanite?) during crystallization (Cochrane et al. 2014). Where apatite occurs as magmatic inclusions in zircon or titanite, its composition carries useful petrogenetic information (Bruand et al. 2016).

Allanite

REE-zoning in igneous allanite has long been recognized to reflect fractional crystallization (Levinson 1966), most commonly from a melt of high water contents (Johnston and Wyllie 1988; Beard et al. 2006). Experimental data on allanite solubility (Kessel et al. 2005; Klimm et al. 2008; Hermann and Rubatto 2009) cover a range of melt compositions and pressures. Where allanite forms in magma, it largely controls the LREE contents of the melt simply because it contains LREE at weight-% level. For Th, U, and Y, as noted above, competition from coexisting phases (zircon, monazite, xenotime, titanite or rutile) may intervene. As summarized by Smye et al. (2014) REE-fractionation in allanite depends on magma composition: The most LREE-enriched allanites are found in Ca-rich types (e.g., carbonate); La/Nd and Ce/Nd are high for diorite and granodiorite, intermediate for granite, and lowest for syenite. Allanites in rhyolitic obsidian often show La/Yb 250–2300 and beyond, but only 3 to ~100 for the glass (Mahood and Hildreth 1983). Typically, chondrite-normalized REE-patterns are steep for early-formed allanite, but depletion of LREE then leads to nearly flat patterns, and the overall core-to-rim zoning in allanite may end with REE-enriched (or even REE-poor) peripheral epidote (e.g., Oberli et al. 2004). REE-contents (normalized to chondrite) in >1700 analyses compiled by Gieré and Sorensen (2004) show typical ranges for LREE vs. MREE (e.g. La: 10^4 – $2 \cdot 10^5$, but Sm: $4 \cdot 10^3$ – $6 \cdot 10^4$ only). Allanite preference for LREE is exceeded (in absolute concentration) only by its appetite for Th, i.e., allanite fractionates Th/La relative to the melt (Mahood and Hildreth 1983; Klimm et al. 2008; Hermann and Rubatto 2009).

⁷ However, contrary to previous belief, fluorine in melt was shown to have no effect on solubility of monazite and xenotime, indicating no fluoride complexing of REE (Duc-Tin and Keppler 2015).

The actinide ratio Th/U is often used as a diagnostic means to distinguish magmatic from metamorphic allanite growth zones: Typical magmatic values are $\text{Th/U} > 100$ (Gregory et al. 2007), metamorphic ones are < 50 (Gregory et al. 2009), except under very oxidizing conditions, where U^{4+} may lead to $\text{Th/U} \gg 100$ (Janots and Rubatto 2014). Trends during magmatic differentiation depend on competing minerals; for example, Th/U increases in allanite, whereas it decreases in coexisting titanite. Fractional crystallization of allanite can produce strong zoning in major and minor elements. Figure 6 shows typical compositional data, crystal morphology, and zoning in igneous allanite from a granodiorite. In a tonalite studied by Oberli et al. (2004) allanite shows a striking magmatic evolution, from dark brown core to faintly colored rim, in wt%: REE_2O_3 17.6 $\rightarrow$ 1.9, CaO 13.7 $\rightarrow$ 23.6, Fe_2O_3 5.3 $\rightarrow$ 11.2, ThO_2 1.4 $\rightarrow$ < 0.1 . In mafic rocks at high pressure allanite plays a leading role in sequestering REE and actinides. Data for eclogites show that allanite stores 90–99% of a rock's budget in LREE, Th, and U, $> 60\%$ of its Sm and still about a third of its Eu (Hermann 2002). Allanite finds its main competitor for LREE + Th in the composition range where monazite coexists. This is discussed below jointly with the evolution of the phosphates, since REE-fractionation between these and allanite is petrochronologically significant.

Subsolidus petrogenesis

Apatite, monazite, and xenotime are known to occur from diagenetic conditions (e.g., Kingsbury et al. 1993; Evans and Zalasiewicz 1996; Knudsen and Gunter 2002; Rasmussen et al. 2002; Vallini et al. 2002; Rasmussen 2005) all the way up to upper amphibolite, granulite, and eclogite grades (e.g., Black et al. 1984; Bingen et al. 1996; Zhu and O'Nions 1999; Rubatto et al. 2001; Erickson et al. 2015; Gasser et al. 2015; Tucker et al. 2015).

Diagenetic apatite, monazite and xenotime have proven datable (Evans et al. 2002; Rasmussen 2005; Davis et al. 2008), and ages can be very helpful in understanding diagenetic processes involving phosphates. Remarkably, diagenetic xenotime has proven to preserve its formation age (Vallini et al. 2002), resisting later penetrative deformation and a greenschist facies overprint. This is most welcome because textural relations are complex (Fig. 7), so present a challenge to infer specific irreversible reactions and link them to P – T conditions. In metaclastic sequences, accessory minerals at anchizonal conditions typically include mostly authigenic, diagenetic and/or detrital monazite, apatite, and xenotime, in addition to detrital zircon, but detrital cores show monazite or xenotime overgrowths (Fig. 7 A, F) that form in the lower greenschist (Wing et al. 2003; Rasmussen and Muhligh 2007; Janots et al. 2008, 2011; Allaz et al. 2013) and low-temperature blueschist facies (Janots et al. 2006). Low-grade apatite tends to be high in Th and U, and it is the main REE reservoir in deep sea mud (Elderfield and Pagett 1986; Kato et al. 2011; Kon et al. 2014). Relative to their (mostly clastic) precursors, low-grade metamorphic monazite is typically low in Th and U, depleted in HREE, but enriched in LREE. In many instances, apatite, thorite, and xenotime are visible as satellites or intergrown small grains, indicating local reactions and spatially limited redistribution of REE and actinides over some 50–100 μm . Reaction volumes reach much larger dimensions (mm to cm) in high-strain zones or where ample fluid interacted with the rocks (Janots et al. 2012; Seydoux-Guillaume et al. 2012), even at low temperatures. Most growth zones are small ($< 10 \mu\text{m}$), however, and *in situ* chronometry in very low-grade metamorphic monazite ($< 350^\circ\text{C}$) is probably best done by EMPA (Fig. 7 G, H).

Above the lower greenschist facies, grain coarsening and replacement reactions typically enhance petrochronological options for REE minerals. Grain to grain heterogeneity in trace element contents and isotopes of detrital phosphates, which can hinder correlations, tends to disappear due to such processes above $\sim 500^\circ\text{C}$ (Hammerli 2014; Hammerli et al. 2014, 2016).

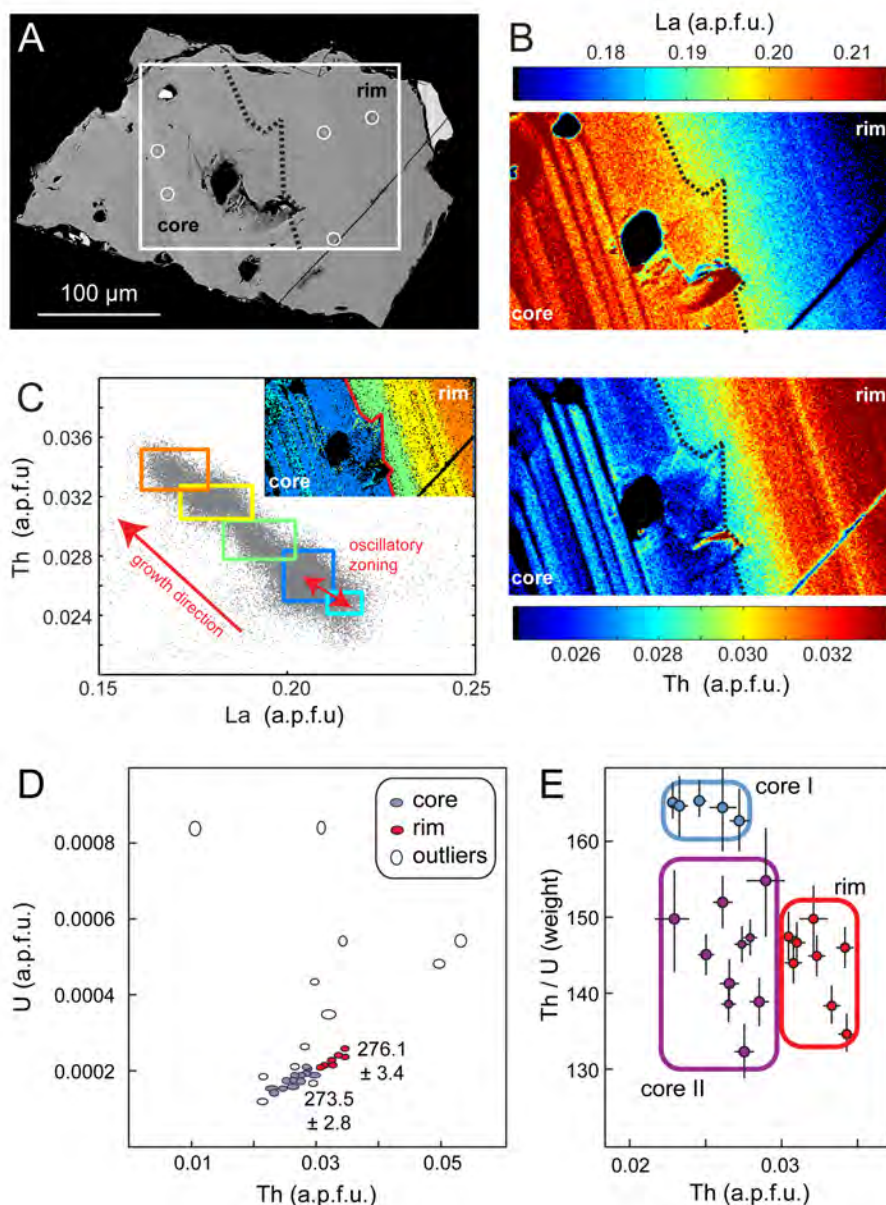


Figure 6. Magmatic allanite from Cima d'Asta pluton (CAP), a commonly used standard reference material (Burn 2016). (A) BSE image of allanite fragment shows weak oscillatory zoning in core; inclusions are apatite, zircon, and quartz; circles mark spots of LA-analysis. (B) X-ray maps (La, Th) of central part (white frame in A) show chemical zoning due to fractionation from melt during growth; rhythmic banding reflects inverse correlation of La and Th (a.p.f.u.: atoms per formula unit). From core to rim, elements with Th-affinity increase (1.1 wt% ThO_2 in core, 1.6% in rim), those with La-affinity decrease in concentrations. (C) Based on the La–Th diagram five magmatic growth zones were identified. (D and E) U–Th diagrams show core to rim evolution and identify two core zones (I, II) based on their Th/U ratio and Th-contents. Their Th/Pb ages are within error, based on LA-ICP-MS data, whilst ages can be resolved between core I and rim (D). All data from Burn (2016). Ages overlap with previous TIMS and LA-ICP-MS analyses (Barth et al. 1994; Gregory et al. 2007), though cores and rim were not separately treated in these (compare Figure 12).

Monazite and allanite

Precursors to metamorphic monazite and xenotime include, in addition to their own ancestors, various low-temperature Al-phosphates, carbonates, and phyllosilicates; textures commonly indicate dissolution-reprecipitation processes (Fig. 7G,H), but few studies have worked out phase relations (e.g., Janots et al. 2006; Spear 2010) or attempted local mass balance for REE and actinides—a topic in need of study. In the greenschist or low-temperature blueschist facies, monazite in clastic metasediments breaks down to form allanite + apatite. Various reactions (Table 2) have been suggested on petrographic grounds, and P – T conditions for the first appearance of allanite clearly depend on rock composition. The limiting reactions of REE-phases have not been studied by experimental reversals, so remain inadequately known. For a small part of the relevant composition space experimental stability relations are available (Janots et al. 2007; Hermann and Spandler 2008) and can be compared (Fig. 8) to those computed from thermodynamic data, which were calibrated using natural assemblage data as well (Spear 2010). Effects of the bulk rock composition are evident when comparing Figure 8A and 8B: allanite is stabilized by an increase in CaO content, and substitutions such as Fe–Mg and La–Nd have a major effect on its stability relative to monazite. These thermodynamic models are a promising start, but at this point none of them adequately reproduce the reaction sequences documented in metamorphic rocks.

A next generation of monazite is known to grow at conditions around the garnet or staurolite isograd in rocks that previously contained allanite (e.g., Smith and Barreiro 1990; Catlos et al. 2001; Spear and Pyle 2002; Wing et al. 2003; Corrie and Kohn 2008; Janots et al. 2008), but it can also grow at lower grades in true (very low-Ca) metapelites and -psammities that did not contain allanite (e.g., Kingsbury et al. 1993). Allanite can persist to higher temperatures in Ca-rich rock types ($\text{Ca}/\text{Na} > 1$) and at high-pressure conditions (Janots et al. 2008; Kim et al. 2009; Radulescu et al. 2009), but phase relations remain poorly understood. Allanite grown in the eclogite facies can be Sr-rich (Rubatto et al. 2008; Cenko-Tok et al. 2011) due to feldspar reacting to sodic pyroxene. Typical prograde reaction textures are shown in Figure 9 from amphibolite facies metapelites and in Figure 10 from eclogite facies micaschists.

Monazite formation in the amphibolite facies has been documented from many rock types and pressure regimes, in some cases reflecting a single growth stage (e.g., Kohn and Malloy 2004), in others showing polyphase growth (Rubatto et al. 2001; Pyle and Spear 2003; Foster et al. 2004; Kohn et al. 2005; Finger and Krenn 2007). Grains that formed early in a growth sequence tend to sequester Th and Y, zones added later thus are more depleted, but since precursors and reaction mechanisms can change, patterns are not always so simple. Unless other accessories intervene, REE- and Y-patterns of monazite often reflect strong partitioning with coexisting major assemblage minerals, notably garnet and feldspar, and monazite REE-patterns essentially reflect the modally abundant REE-competitors. In granulites, for instance, monazite that formed after garnet can become very depleted in HREE (Foster et al. 2000; Holder et al. 2015), a trend noted in apatite as well (Bea and Montero 1999).

Upon partial melting, monazite tends to dissolve and may or may not completely disappear; it typically grows during crystallization of leucosome in migmatites (Williams 2001; Pyle and Spear 2003; Kohn et al. 2005; Yakymchuk and Brown 2014).

Since allanite and monazite can form at several stages, and thus samples commonly contain several (over)growth zones, chronometry is of course tempting wherever these are of sufficient size for *in situ* analysis. Constraining the physical conditions of growth stages is thus a central issue, and in the absence of thermodynamic models for the REE-minerals involved, textural relations (e.g., core–rim) and local assemblages of coexisting minerals currently are our best guides. Detailed observation of inclusions and zoned relics of characteristic phases (e.g., garnet, mica, corroded accessories) may indicate a relative

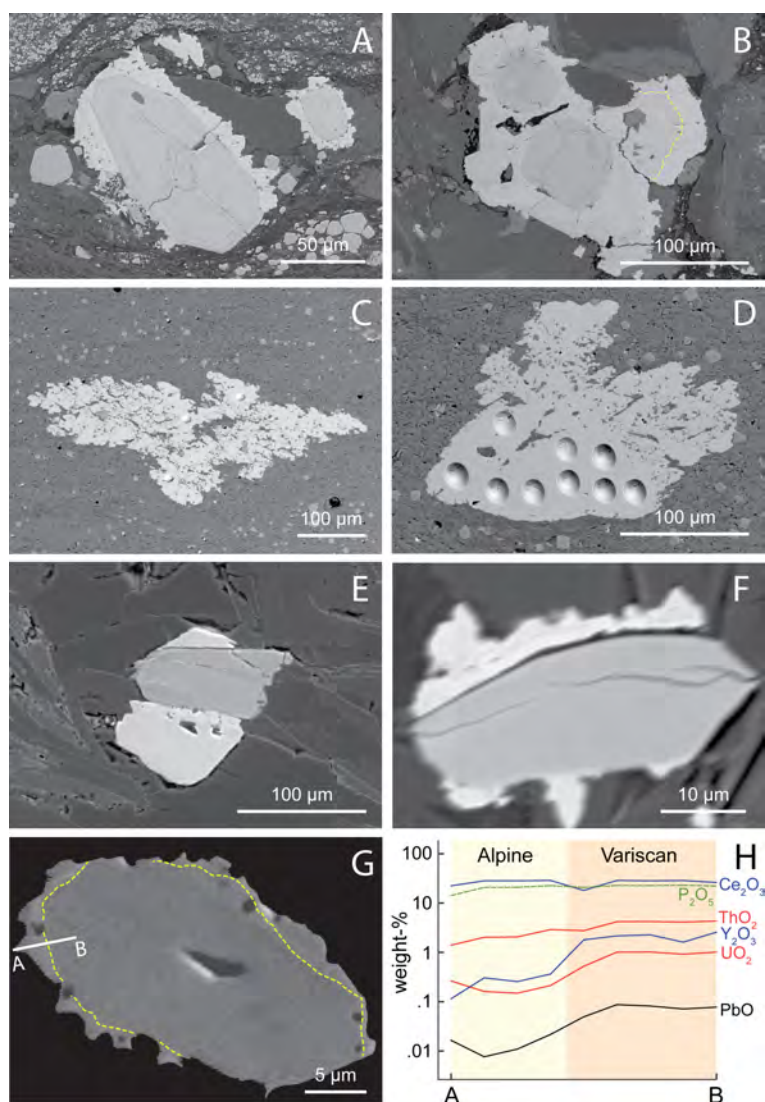


Figure 7. BSE images of low-temperature xenotime and monazite. (A, B) Authigenic/diagenetic xenotime overgrowths on detrital zircon grains and rounded detrital zircon completely engulfed in xenotime; SHRIMP dates of two growth rims yielded 1693 ± 4 and 1645 ± 3 Ma (Vallini et al. 2002, 2005). Samples are from the Mount Barren Group, Western Australia. (C, D) Greenschist-grade monazite (light) in a black shale with abundant pyrite euhedra in matrix; SHRIMP analysis (oval pits) yielded ages of 2416 ± 12 Ma for monazite, and 2430 ± 19 Ma for xenotime. Samples are from the Neoproterozoic Roy Hill Shale Member, Jeerinah Group, Pilbara Craton, Western Australia (Rasmussen et al. 2005). (E) Detrital zircon with euhedral xenotime overgrowths, quartz muscovite schist, Palaeoproterozoic Mount Barren Group (Rasmussen et al. 2011). (F) Xenotime nucleating on zircon fragment in a metapelitic blueschist (350 $^{\circ}\text{C}$, 1 GPa) from Rif, Morocco (Janots et al. 2006). Texturally similar outgrowths were reported by Rasmussen (2005, Fig. 8) from Carboniferous Lower Coal Measures (UK). (G,H) Variscan monazite core (~320 Ma) with thin Alpine rim (<30 Ma) grown in metamarl at chloritoid grade (440 $^{\circ}\text{C}$, 0.6 GPa). EPMA data across profile A–B show rim is low in Th, Y, U, and radiogenic Pb. Sample from Garvera, Central Swiss Alps. Data from (Janots et al. 2008). Photo credits: Birger Rasmussen (A–E) and Emilie Janots (F,G).

Table 2A. Proposed prograde reactions involving monazite, allanite, apatite, and xenotime.

Label	Reactants	Products	Reference
M0	flo ± xen	mnz + ...	Janots et al. (2006)
A1	flo + mnz + carb	aln + syn + ...	Janots et al. (2006)
A2	mnz + mus + carb + qz	aln + bio + ap	Wing et al. (2003)
A3	mnz + chl + pl + cc + qz	aln + ap + ...	Wing et al. (2003)
A4	mnz + chl + cc ± hem	aln + xen + ap + ctd	Janots et al. (2008)
A5	mnz + chl + an ± hem	aln + xen + ap + ctd	Janots et al. (2008)
A6	mnz + ...	aln + xen?	Smith and Barreiro (1990)
A7	mnz + pl + ...	aln + ep + tho + ap	Finger et al. (1998)
A8	mnz + chl + ...	aln + ctd	Radulescu et al. (2009)
A9	mnz + bt + ...	aln + F-ap + qtz + ...	(Yi and Cho 2009)
M1	aln + apa + mu + AS + qz	mnz + bio + pl + H ₂ O	Wing et al. (2003); Ferry (2000)
M2	aln + apa +	mnz + ...	Yang and Pattison (2006)
M3	aln + apa	mnz + pl + mag?	Tomkins and Pattison (2007)
M4	aln + apa + AFM1	mnz + an + AFM2	Janots et al. (2008)
M5	gar + apa + mu	mnz + sill + bio	Pyle and Spear (2003)
M6	gar + chl + mu	mnz + st + bio + pl	Kohn and Malloy (2004)

Table 2B. Pressure–temperature conditions estimated for allanite- and monazite-forming reactions

Label	Temperature	Pressure	Thermobarometry	Isograd	Rock type
M0	350–420 °C	1.0–1.2 GPa	ctd–chl thermometry		metapelite
A1	300–350 °C	0.3–1.0 GPa	ctd–chl thermometry		metapelite
A2/3	~400 °C	0.35 GPa	Ferry (1994)	bio–in	metapelite
A4/5	420–450 °C		TWQ	ctd–in	metapelite/marl
A6	500–550 °C	0.28–0.34 GPa	gar–bio	bio–in	metapelite
A7	550–600 °C	0.4–0.5 GPa	regional?		metagranitoid
A8	540–600 °C	2.0 GPa	phase diagrams		micaschist
A9	500–600 °C		phase relations	(vein)	leucogneiss
M1	~500 °C	0.35 GPa	Ferry (1994)	and/ky–in	metapelite
M2	480–520 °C	0.20–0.44 GPa	Helms and Labotka (1991)	~gar–in	metapelite
M3	530–580 °C	0.30 GPa	Pattison and Vogl (2005)	~cord–in	metapelite
M4	530–580 °C	0.8–0.9 GPa	TWQ		metapelite
M5	580–605 °C	0.3–0.4 GPa	gar–mnz thermometry		metapelite
M6	~600 °C	0.6–0.8 GPa		stau–in	metapelite

Minerals. AFM: Al-Fe-Mg-silicates (bio, mus, gar), aln: allanite, an: anorthite, and: andalusite, ap: apatite, AS: aluminosilicate, bio: biotite, carb: carbonate, cc: calcite, chl: chlorite, cord: cordierite, ctd: chloritoid, ep: epidote, flo: florencite, gar: garnet, hem: hematite, ky: kyanite, mag: magnetite, mnz: monazite, mu: muscovite, pl: plagioclase, qz: quartz, st: staurolite, syn: synchisite, tho: thorite.

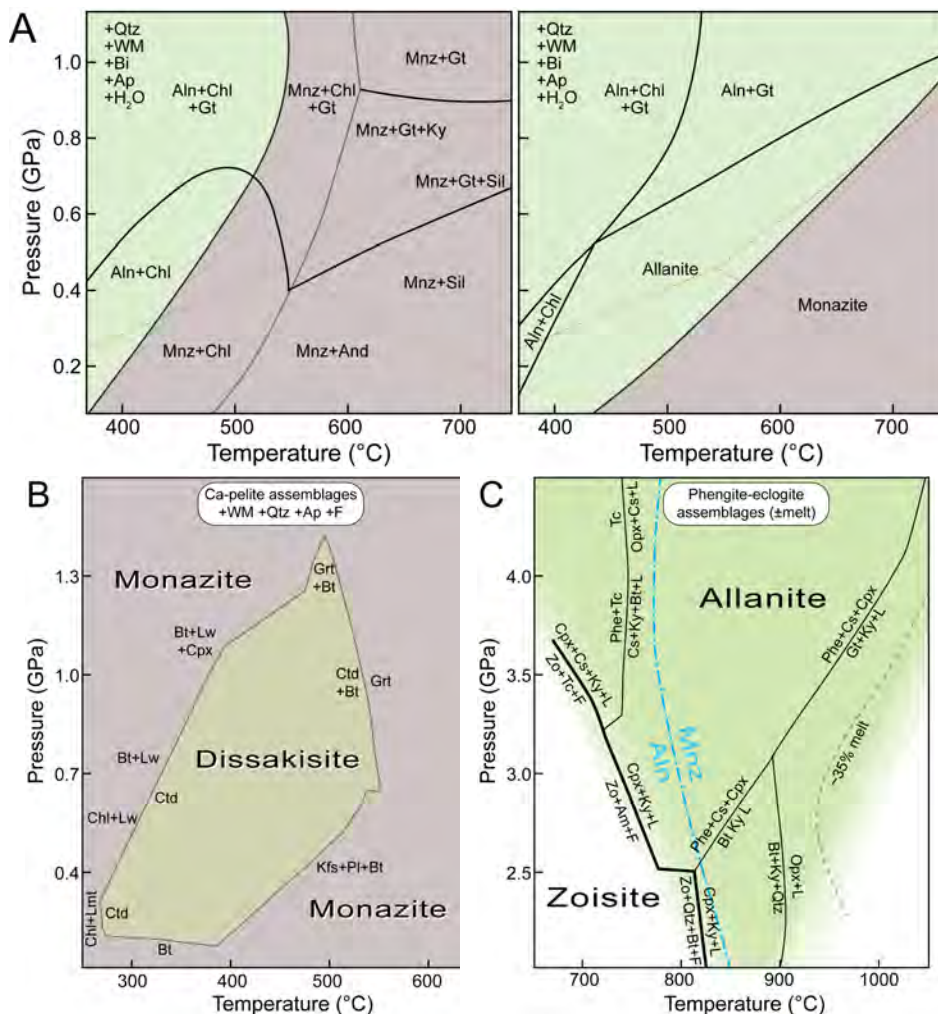


Figure 8. Models for the stability fields of allanite and monazite in P - T space based on thermodynamic data (A,B) and experimental phase equilibria (C). Mineral abbreviations: Aln = allanite, Am = amphibole, And = andalusite, Ap = apatite, Bt = biotite, Cpx = clinopyroxene, Chl = chlorite, Cs = coesite, Cld = chloritoid, Dis = dissakisite, F: hydrous fluid, Gt = garnet, Kfs = K-feldspar, Ky = kyanite, L: melt (64–67 wt% SiO₂), Lmt = laumontite, Lw = lawsonite, Mnz = monazite, Phe = phengite, Qtz = quartz, Opx = orthopyroxene, Sil = sillimanite, Tc = talc, WM = white K-mica, Zo = zoisite. (A): Phase relations calculated for two compositions typical of clastic metasediments (both 16.57 wt% Al₂O₃; left: average pelite, 2.17 wt% CaO; right: slightly marly, 4.34 wt% CaO) using a model for Ce-allanite and Ce-monazite (Spear 2010). The predicted reaction sequence is consistent with those observed in several terrains above 500 °C, but no low-temperature monazite stability field (below 400–450 °C, Janots et al. 2008) is predicted. (B) Calculated medium-pressure stability field of dissakisite (La–Mg allanite–clinozoisite solution) (+apatite) against various assemblages comprising La-monazite in calcic pelite model composition based on calorimetric data (Janots et al. 2007). (C) High-pressure field of Mg-allanite in phengite-eclogite model system (KNCMASH+trace elements), based on experimentally determined phase relations. Allanite first appears in experiments at temperatures just below the zoisite-out reaction. Disappearance of allanite at high temperatures is by gradual dissolution into melt, not linked to the major phase reactions; after Hermann (2002). Blue dot-dashed boundary is for a *pelitic* model system; this limit of allanite versus monazite was inferred by Hermann and Rubatto (2009) from experiments by Hermann and Spandler (2008).

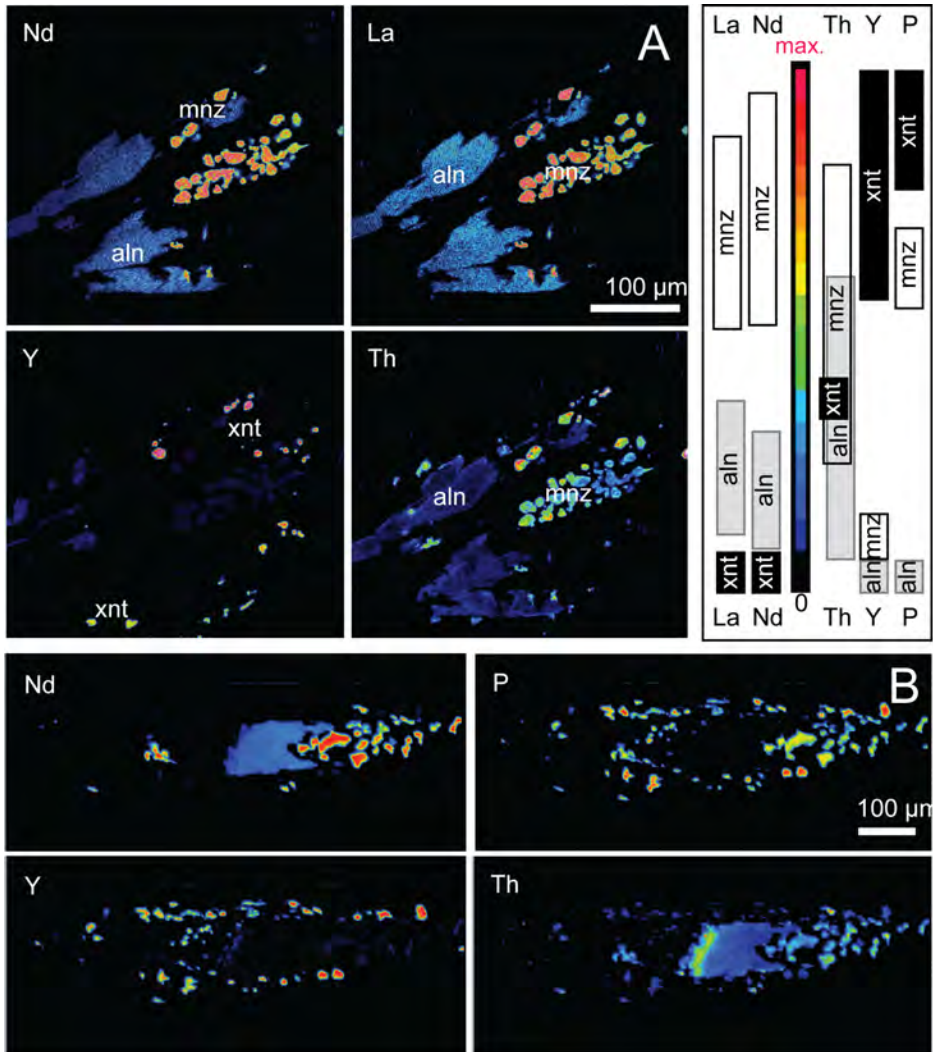


Figure 9. X-ray maps of REE-minerals at middle amphibolite facies, northern Lepontine belt (Central Alps, Switzerland). Textures indicate partial breakdown of allanite (+apatite) to monazite + xenotime. No apatite appears in the assemblage, and its consumption probably terminated the reaction (at ~560 °C, 0.8 GPa; Janots et al. 2008). Color bars (top right) indicate concentrations of elements in maps, with cold colors indicating low contents, red being maximum; typical ranges are shown for main REE-minerals. (A) La-rich allanite cores are preserved, and splay monazite aggregates interwoven with tiny xenotime are probably pseudomorphic after allanite. (B) Similar mineral textures, but preserved allanite cores are rich in Nd and Th (note heterogeneity). Both textures in same sample attest to very limited mobility of REE and actinides even during mineral reactions involving fluid. Heterogeneity in and among reaction domains poses problems in U–Th–Pb chronology (e.g., common Pb). BSE images courtesy of Daniele Regis.

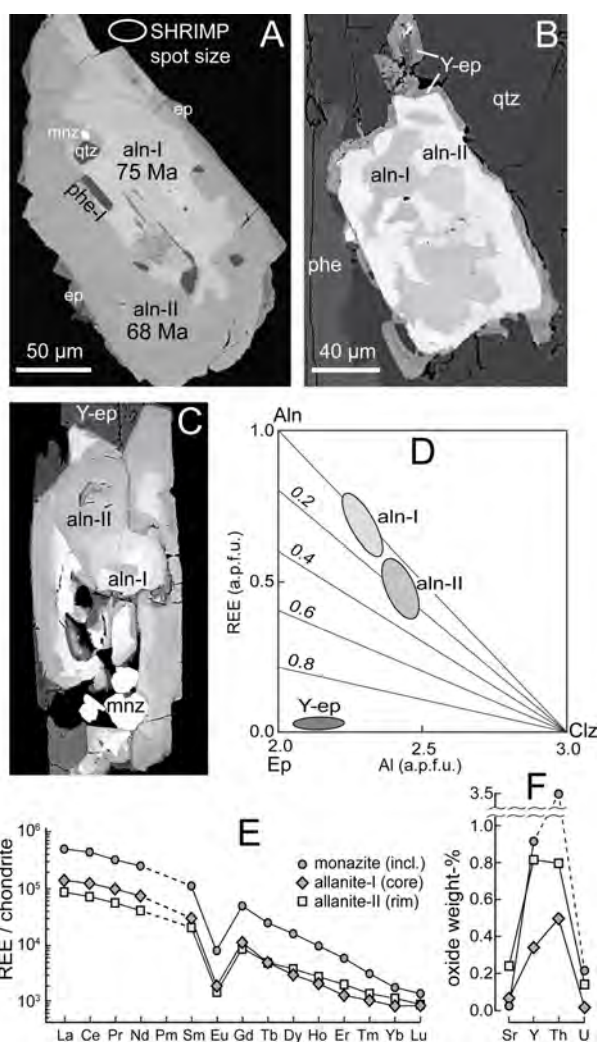


Figure 10. Allanite in eclogite facies phengite quartzite (Sesia Zone, Western Alps). Textures in BSE images show 3 HP-stages (I-III). (A) Corroded core of allanite-I (75 Ma) includes Phe-I (Si: 3.45 a.p.f.u.¹, 540 °C, 1.8 GPa), aln-II overgrowth (68 Ma) contains Phe-II (Si: 3.20 apfu, <520 °C, <1.5 GPa), and thin Y-epidote rim (60–65 Ma) is in equilibrium with matrix assemblage (550 °C, ~1.8 GPa); Ages are from SHRIMP Th/Pb isotopic analyses. Data indicate pressure-cycling (yoyo tectonics) in a subduction channel (Rubatto et al. 2011). (B, C) Samples from the same unit display similar complex resorption and replacement textures in allanite core, with Y-epidote rim. Relic monazite can be preserved inside allanite aggregates. (Regis et al. 2012). (D, E) Compositions of growth zones visible in allanite from (C). Successive generations show decrease in REE contents and increase in ferric fraction ($\text{Fe}^{3+}/\text{Fe}_{\text{total}}$; labels along radial lines in diagram) (after Petrik et al. 1995). Clz = clinozoisite, Ep = epidote, Aln = allanite. (E, F) Minor and trace element compositions in overgrowth sequence shown in (C). REE patterns and the sequestration of the critical minor elements Sr, Y, Th and U indicate that monazite was the main precursor of allanite. While allanite grew at eclogite facies conditions, in the absence of feldspar, REE patterns of aln-I and aln-II reflect LREE enriched monazite composition and preserve its Eu-anomaly. Note strong Th/U fractionation. All data from Regis et al. (2014). Chondrite normalization based on Sun and McDonough (1989). BSE images courtesy of Daniele Regis.

¹ atoms per formula unit $\text{KAl}_{2-x}\text{Mg}_x[\text{Al}_{1-x}\text{Si}_{3+x}\text{O}_{10}](\text{OH})_2$

paragenetic sequence, and their geochemical characterization often allows estimates of P – T conditions (Regis et al. 2014; Mottram et al. 2015). However, textures within high-grade monazite (and less commonly allanite) tend to be complex, often patchy, and age relations are not always clear. Microstructural relations of allanite and monazite (and their inclusions) to metamorphic fabrics can be invaluable to relate P – T – t relations to deformation (Manzotti et al. 2012; Regis et al. 2012; Goswami-Banerjee and Robyr 2015; Wawrzenitz et al. 2015); considerable progress is being made relating monazite and allanite growth to deformation events (e.g., Ayers et al. 2002; Williams and Jercinovic 2002; Berman et al. 2005; Dahl et al. 2005; Simmat and Raith 2008; Kirkland et al. 2009; Cenki-Tok et al. 2011, 2014; Kelly et al. 2012; Wawrzenitz et al. 2012; Didier et al. 2013, 2014). Subsolvus retrograde growth of monazite ($\pm$ xenotime) at the expense of allanite or apatite + garnet has been documented in several instances; it is usually related to localized or pervasive fluid-influx, and such monazite has proven datable (Bollinger and Janots 2006; Tobgay et al. 2012). From similar environments, but also in retrograde corona formation from high-grade rocks, monazite breakdown to allanite + apatite has commonly been reported (Broska et al. 2005; Krenn et al. 2012; Ondrejka et al. 2016) and occasionally dated (Yi and Cho 2009).

Xenotime. Rasmussen et al. (2011) studied a metaclastic sequence (Mount Barren Group) in SW Australia and found xenotime closely associated with detrital zircon, commonly as syntaxial outgrowths. Up to $\sim 450^\circ\text{C}$, detrital and diagenetic xenotime is partly preserved, but wholly metamorphic grains largely replace these at higher temperatures. Dissolution–reprecipitation reactions produced compositionally distinct rims forming at greenschist and amphibolite facies conditions. As *in situ* U–Pb chronology of xenotime yielded at least four discrete age groups (2.0 to 1.2 Ga), a discontinuous sequence of reactions is likely to be responsible for the growth of metamorphic xenotime, at the expense of detrital and diagenetic precursors. A few specific reactions have been formulated so far (Table 2). Metamorphic xenotime shows distinctly lower Th and U contents, in some instances Th-rich annuli, and tiny U- and Th-rich product grains (e.g., Figs. 3 and 8 in Rasmussen et al. 2011). Similar phase relations were reported by Allaz et al. (2013) and, in eclogite facies metaclastics, by Regis et al. (2012). The latter study showed zircon to be one of the reactant precursors and identified thorite and aeschynite among the satellite products. In more calcic domains of the same samples, monazite and xenotime broke down to produce allanite. Phase relations (Fig. 11) calculated for metapelites from a thermodynamic basis (Spear and Pyle 2010) that includes (preliminary) data for the REE-phosphates, show approximate stability limits of xenotime in the subsolvus range. To distinguish different xenotime generations, REE are useful: compared to magmatic xenotime, which is typically HREE-enriched, at subsolvus conditions enrichment increases from LREE to MREE, and patterns from MREE to HREE are either flat or decrease.

Monazite–apatite–xenotime textural relations. Mutual inclusions and overgrowth relations are often observed among REE-phosphates (and allanite) and can be of great utility in relating ages to (partial) replacement reactions and metasomatic effects, e.g., related to ore formation. For instance, inclusions of monazite and/or xenotime commonly occur in apatite, and using chemical fingerprinting (halogens, Sr, Pb), it is possible to track fluid–rock interaction (Harlov and Förster 2003; Harlov et al. 2005; Broska et al. 2014; Shazia et al. 2015; Jonsson et al. 2016).

Effects of hydrous fluids

Apatite, monazite, and xenotime are commonly found in fluid-rich environments, both at low and high temperature (Harlov et al. 2008; Hetherington and Harlov 2008). The solubility of phosphate minerals in fluids is strongly composition-dependent, and substantial evidence from experimental studies (Harlov et al. 2005, 2007, 2011; Budzyń et al. 2011; Seydoux-Guillaume et al. 2012; Grand’Homme et al. 2016b) indicates that dissolution–reprecipitation processes are particularly effective when alkaline hydrous fluids are involved; in many cases F-apatite is a characteristic product phase, and xenotime as well as monazite are involved.

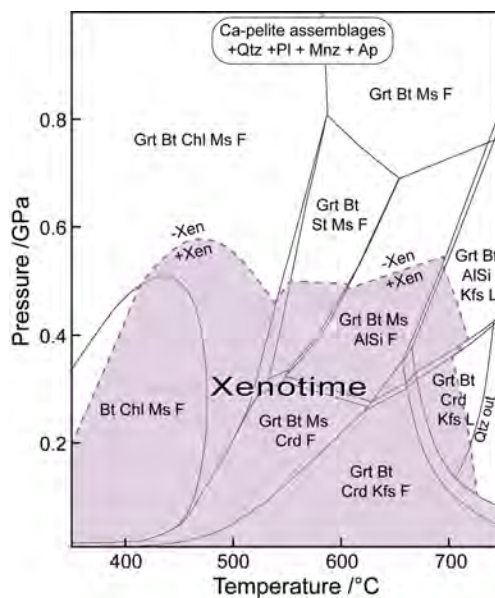


Figure 11. Phase relations calculated for a model pelite composition in $K_2O-Na_2O-CaO-MnO-MgO-FeO-Al_2O_3-SiO_2-H_2O-Y_2O_3-Ce_2O_3-P_2O_5$ -Fluid from Spear and Pyle (2010); the model is substantially founded on natural assemblages from a specific locality in Maine, includes data for pure xenotime and binary Ce-Y-monazite, but does not consider allanite. Stability limits for xenotime depend on bulk Y-contents; a realistic field is shown. Mineral abbreviations as in Figure 8, plus AlSi = kyanite or sillimanite, Crd = cordierite, St = staurolite.

For chronologic efforts, partial replacement by such processes can be a challenge (Williams et al. 2011), but interaction with pervasive fluid may be a most effective way to completely reset clocks in phosphate minerals (Harlov and Hetherington 2010; Harlov et al. 2011). These studies have spawned efforts to date hydrothermal systems (Williams et al. 2011; Shazia et al. 2015), and indeed several studies have thus investigated Alpine clefts (Janots et al. 2012; Grand'Homme et al. 2016a) and altered shear zones (Berger et al. 2013).

Particular geochemical characteristics of REE-minerals, e.g., the tetrad effect (Bau 1996) have long been attributed to effects of fluids, but Duc-Tin and Keppler (2015) showed convincingly that this effect can be explained by the orbital structure of particular LREE being particularly favorable for the irregular REE-coordination polyhedra in monazite and xenotime (Fig. 1). Their REE partitioning behavior—relative to melt, hydrous fluids or minerals with regular REE polyhedra—is thus different than expected solely from ionic radius considerations (Fig. 5). As a consequence, and contrary to previous work (Bau 1996), tetrad patterns may not directly indicate the effect of fluids but of crystal-structure dependent fractionation.

CHRONOLOGIC SYSTEMS

Owing to the elevated actinide contents of the REE-minerals, chronometry has been based on the $^{208}Pb/^{232}Th$, $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ (or $^{207}Pb/^{206}Pb$) ratios far more often than on alternative isotopic systems. As discussed above, the closure temperatures for these systems are not precisely known, but are certainly high enough for chronometry in many applications at subsolidus environments and, with caution, into the partial melting range. For apatite, U–Pb closure is estimated at lower temperature (350–550 °C; Cochrane et al. 2014; Chew and Spikings

2015), suitable only for dating crystallization conditions of upper crustal and blueschist facies samples. Lu–Hf (T_c 675–750°C) is an alternative for higher temperatures, but has been rarely applied so far (Barfod et al. 2003; Larsson and Söderlund 2005). And Sm–Nd dating has been applied to apatite based on intersectoral differences in partitioning (Rakovan et al. 1997).

Spatial resolution versus age resolution

Compared to ID-TIMS analysis, all *in situ* techniques have inferior age resolution and precision, but many studies focus on answering questions that demand high spatial resolution. For many samples and problems, finding grains of sufficient homogeneity and size for TIMS dating ranks somewhere between challenging and impossible. In other cases, the structural context can be preserved at least in part, with effort, by microdrilling (Kohn et al. 2005; Smye et al. 2011) or directly cutting monazite or allanite from a polished section. In this way, monazite has been successfully isolated and then analyzed with optimal precision using ID-TIMS (Hawkins and Bowring 1997; Baldwin et al. 2006). Allanite can also be separated into several age groups or magmatic generations based on the color and density of mineral fragments; precise ID-TIMS analysis of these then give a range of ages (Oberli et al. 2004). These indicate the timescale of plutonic evolution, though the specific significance of each age is not clear because no textural link to geochemical tracers is possible. So, precision is excellent in ID-TIMS studies, but context is sacrificed, and thus petrogenetically critical information for each fraction analyzed is missing.

Alternatives include a range of micro-analytical methods, some of which allow *in situ* dating of growth zones in polished sections. EPMA age mapping of monazite is a powerful way to resolve first-order geological problems, especially in polymetamorphic rocks with a complex evolution (Williams et al. 1999; Hermann 2002; Buick et al. 2010; Dumond et al. 2015; Johnson et al. 2015; Tucker et al. 2015) and in rocks that experienced extensive interaction with fluid (Shazia et al. 2015; Grand'Homme et al. 2016a; Kirkland et al. 2016). Allanite maps have similar potential, especially in high-pressure rocks and migmatites (Gregory et al. 2012; Regis et al. 2014), but have been much less utilized so far, since EPMA dating is not possible, and SIMS or laser-based analysis has lower spatial resolution and demands considerably more analytical effort.

U–Th–Pb

Monazite and xenotime. Monazite often contains several wt% Th, several thousand ppm U, and usually negligible initial lead (Montel et al. 1996). These high actinide concentrations result in high levels of radiogenic lead, except in very young samples. In xenotime Th and U contents are lower, but both monazite and xenotime are proven U–Th–Pb chronometers. Monazite and allanite normally contain both Th and U in concentrations sufficient to combine their decay systems for chronometry; for xenotime only U–Pb is possible. In both phosphates, REE contents are also high (e.g., 10^4 – 10^5 ppm Sm and Nd), and as tracer isotopes they add important geochemical constraints, especially combined with chronometry (Nemchin et al. 2013; Whitehouse et al. 2014).

The commonly high Th- and U-contents allow chemical U–Th–Pb dating of monazite and xenotime by EPMA (Suzuki and Adachi 1991; Montel et al. 1996; Williams and Jercinovic 2002; Pyle et al. 2005b; Williams et al. 2007; Hetherington et al. 2008; Spear et al. 2009). The power of the approach, its limits, technical aspects, and some applications are not reviewed here, as they are specifically addressed in this volume (Williams and Jercinovic 2017); similarly, isotopic dating by LA-ICP-MS and SIMS are covered separately (Kylander-Clark 2017; Schmitt and Vazquez 2017). Two developments are particularly suited to link ages with their geochemical and textural context: LASS ICP-MS (laser ablation split stream: Kylander-Clark et al. 2013; Goudie et al. 2014) and Scanning Ion Imaging using SIMS (Harrison et al. 2002).

In situ isotopic analysis by LA-ICP-MS or ion probe / SHRIMP involves particular concerns for each instrument, notably regarding standardization, fractionation, matrix correction, and

realistic error propagation. The magnitude of the effects varies for each type of mineral; in a general way, monazite and xenotime pose fewer problems in isotopic analysis than does allanite, but successful analytical protocols for all of them have been required. In particular, the question of matrix-matched⁸ standardization has been repeatedly raised (Kohn and Vervoort 2008), especially for allanite (Catlos et al. 2000), because of its large chemical variability. Since matrix-matching is more critical in ion probe analysis than in laser ablation analysis (Gregory et al. 2007; Darling et al. 2012), LA-ICP-MS may be the preferred method, given the paucity of suitable allanite standards (Smye et al. 2014). Fortunately, it now appears that the concerns over matrix-matching and standards in allanite analysis can be largely avoidable with carefully optimized LA-ICP-MS conditions (Burn et al. 2016; McFarlane 2016). However, matrix-matching remains essential in ion probe analysis (e.g., Fletcher et al. 2004).

Apatite

Apatite contains several thousand ppm REE and has typically high Lu/Hf ratios, making Lu–Hf dating possible (e.g., Barfod et al. 2005), with high closure temperatures similar to U–Pb in monazite (e.g., McFarlane and McCulloch 2007). Apatite also has relatively high U-contents, most useful in U–Pb thermochronometry (Chamberlain and Bowring 2001; Chew et al. 2011; Chew and Donelick 2012), often in conjunction with (U–Th)/He and/or fission track dating. These applications are beyond the scope of this review; for a short introduction consult Cochrane et al. (2014). Since metamorphic samples often contain more than one generation of apatite, U–Pb or Th–Pb isotopic analysis should be done by *in situ* methods allowing sufficient spatial resolution. Ion probe methods (Sano et al. 1999) or, more commonly, LA-ICP-MS (Willigers et al. 2002; Chew et al. 2011) has been used and is sufficiently precise to date low-U apatites, such as from mafic dykes (Pochon et al. 2016). Sr and Nd isotopes can be analyzed *in situ*, offering new possibilities of petrogenetic utility (Hammerli et al. 2014).

Allanite

Allanite usually contains 1,000–16,000 ppm Th and typically about a tenth that amount in U. Th/U > 2 is common, but shows substantial variation and may give genetic indications. Allanite has shown its potential as a robust Th/U–Pb chronometer, but several challenges remain, especially its high initial lead contents. Unlike monazite and xenotime, which commonly contain nearly 100% radiogenic lead, allanite (and apatite) have an affinity for Pb, and isotopic data used for dating must be corrected for this component. This is straightforward for ID-TIMS data using ²⁰⁴Pb where mass interferences are eliminated. In SHRIMP analysis, energy filtering effectively reduces isobaric interference (Rubatto et al. 2001) on mass 204, but spot analyses obtained by LA-ICP-MS combine ²⁰⁴Pb and ²⁰⁴Hg. Several methods are in use for estimating the composition of the initial lead component (Pb_{ini}), which includes inherited radiogenic and non-radiogenic lead; some are based on models, others on analysis of the sample being dated. As petrochronology typically aims to resolve local growth stages, and relics are the rule, not the exception, overall isotopic equilibration cannot be assumed, and methods relying on a single type of common lead (Wendt 1984) are not applicable in general⁹. If the fraction of non-radiogenic Pb is high—and in allanite (Gabudianu Radulescu et al. 2009a; Gregory et al. 2012) and apatite (Cochrane et al. 2014) it often is in the range 20–70%, but may be >90%—the common lead correction affects ages and their uncertainty very substantially. In addition, minerals with high Th/U contain excess ²⁰⁶Pb produced from excess ²³⁰Th (an intermediate daughter nuclide in the ²³⁸U chain) incorporated during growth, for which a correction is needed (Schärer 1984; Barth et al. 1994). These complications enlarge age uncertainties and make it difficult to check for possible Pb-loss, which may occur at temperatures above ~750–800 °C (Kamber et al. 1998).

⁸ Both structurally and chemically

⁹ This warning does not apply where the analytical uncertainty in the common Pb measurement exceeds the effect of potential variations in its composition.

Initial lead. A complete discussion of the issues and controversies surrounding common Pb is beyond the scope of this review, but data presented in the literature are commonly based on premises that have since been questioned. As these can affect ages substantially, one should understand the basic problem involved in estimating the composition (isotopic ratios) of the initial lead, know the approaches used to solve them, and consider at least some of the perils and implications. This is true for all chronometers containing high levels of non-radiogenic lead, notably Ca-rich minerals, where Pb can replace Ca. The specific situation for allanite is presented in Gregory et al. (2007, 2012). In essence, for both the Th–Pb and the U–Pb system, two approaches are used: A single-spot correction or an isochron method. The single-spot correction assumes a model Pb composition that does not change during allanite growth, and whose isotopic ratio is predicted by a global lead evolution model (Cumming and Richards 1975; Stacey and Kramers 1975). Even though local dissolution of accessory precursors are a likely staple on which allanite fed (Romer and Rötzler 2011), single spot correction has been widely used to treat allanite dates. An alternative practice is to determine Pb_{ini} composition from internal heterogeneity within an allanite crystal. This approach assumes a single growth stage with a common age but variable chemistry. Allanite commonly shows variable U/Th and common lead, so the isochron correction usually uses a Tera-Wasserburg diagram approach (plotting $^{207}Pb/^{206}Pb$ vs. $^{238}U/^{206}Pb$). Data showing variably non-radiogenic Pb (Fig. 12) are used to obtain the age (2007; Gregory et al. 2012). The common practice to determine common lead composition by analyzing both U-rich and coexisting U-poor minerals (e.g., feldspar) assumes isotopic equilibration in the same compositional domain as the mineral chronometer; within the context of an assumed single age, the isochron method allows this assumption to be tested. As pointed out by Burn (2016), it is advisable to combine these correction methods and use them to check the quality of data by first processing them in an uncorrected Tera-Wasserburg and a $^{206}Pb_c$ normalized isochron diagram (Fig. 12). Provided a dataset from different parts of a sample define a linear array in a Tera-Wasserburg diagram, the intercept with the y-axis defines the $^{207}Pb/^{206}Pb$ initial lead composition. Each diagram returns an estimate of the age and the initial lead composition of allanite (or any other mineral with high common lead contents, such as apatite; Chew et al. 2011). The concordance of these two age estimates is used to evaluate the quality of the data and estimate the age uncertainty.

During growth, both allanite and apatite may incorporate extraneous Pb; if growth is from a melt, isotopic equilibrium is often assumed, perhaps unjustly, as indicated by pre-melting relics in leucosomes from migmatites (Berger et al. 2009). At sub-solidus condition, metamorphic growth may occur in local domains or from isotopically inhomogeneous precursors (Lanari and Engi 2017), and local lead isotope ratios may be quite different from those of the bulk rock, let alone of a terrestrial evolution model (Stacey and Kramers 1975). Inheritance is of major concern in polymetamorphic basement rocks (Romer and Siegesmund 2003; Romer and Xiao 2005; Romer and Rötzler 2011), but since many metamorphic rocks contain relic accessory minerals, local variability should always be tested because local digestion of such relics may cause major deviations from bulk rock U/Pb, Th/Pb and $^{207}Pb/^{206}Pb$ (e.g., Wawrzenitz et al. 2015). Inheritance of this kind is evident in datasets as excessive scatter in the U/Pb or Th/Pb ages, i.e., scatter beyond the purely analytical uncertainty ($\sim 0.1\%$ for ID-TIMS, 2–3% for LA-ICP-MS or ion probe data). Major discrepancies between measured and model lead compositions have repeatedly been found in metamorphic allanite; e.g., Gabudianu Radulescu et al. (2009b) obtained a concordant U–Pb age 37.4 ± 0.9 Ma ($^{208}Pb/^{232}Th$: 38.3 ± 1.0 Ma) for allanite from micaschist (eclogite facies), in which the regressed $^{207}Pb/^{206}Pb$ was 0.498 ± 0.005 . According to Pb evolution models $^{207}Pb/^{206}Pb$ would be 0.838 and imply apparent ages > 200 Ma!

As emphasized by Janots and Rubatto (2014), for young samples (with low amounts of radiogenic lead) containing allanite with high Th/U and high initial Pb fraction $^{206}Pb_c$ -normalized Th–Pb isochron dating will yield the most reliable age and also provides an independent control on the isotopic composition of initial Pb.

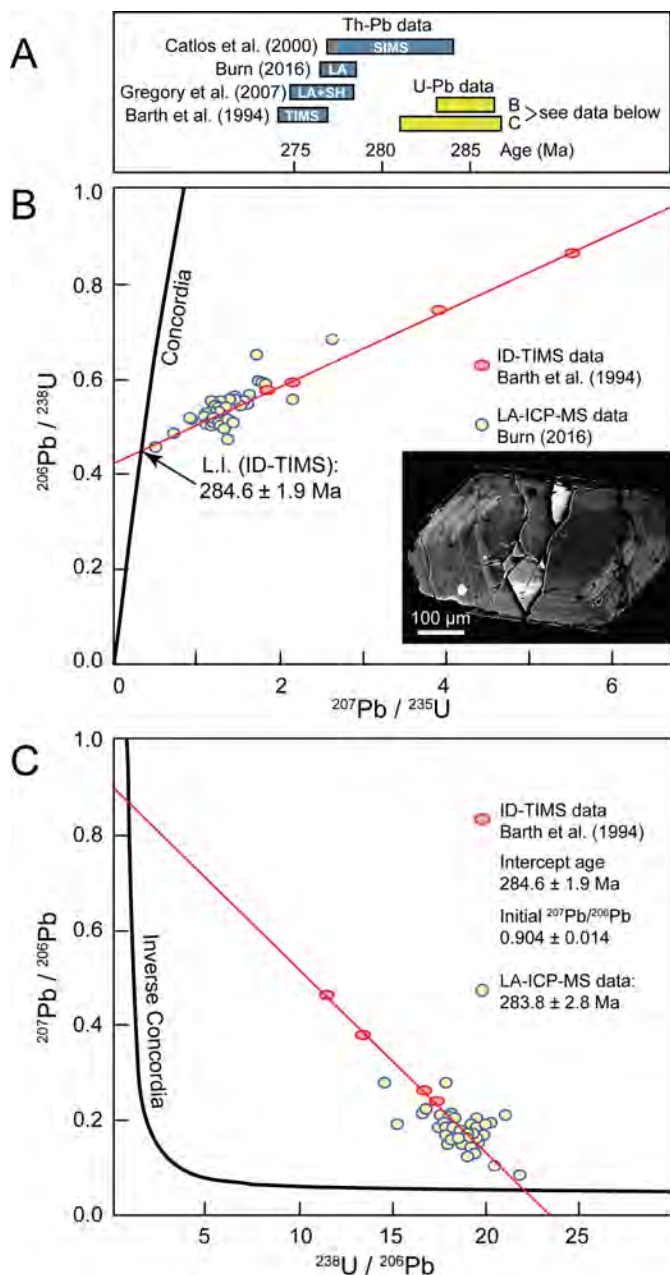


Figure 12. Allantite ages for CAP, a frequently used standard reference material from Permian granodiorite (Cima d'Asta Pluton, NE Italy). 6 datasets obtained by various techniques (ID-TIMS, SHRIMP, SIMS, LA-ICP-MS) are compared here. (A) As all datasets show, Th–Pb ages (weighted mean: $275.5 \pm 1.4 \text{ Ma}$) are lower than U–Pb ages, indicating that ^{206}Pb is partly thorogenic (from ^{230}Th); LA + SH for LA-ICP-MS + SHRIMP. (B, C) Concordia and Tera–Wasserburg (inverse Concordia) plots. TIMS and LA-ICP-MS data show agreement within error. Symbols of ID-TIMS data are larger than analytical uncertainty; the reverse is true for LA-ICP-MS data, and gives rise to apparent excess scatter. Common lead contents are 5–46%. Inset in (B) shows BSE image of CAP allanite illustrating oscillatory zoning typical of magmatic growth. Compare with Figure 6.

CASE STUDIES

Selection, purpose

With the wealth of studies—hundreds on monazite alone—it is quite impossible to do justice to so many and diverse results. Any selection of exemplary studies is necessarily subjective—for me, looking for balance seemed futile. Rather my goal is to focus on the understanding gained by combining petrogenetic analysis and chronology based on REE-minerals. Examples were chosen, in addition to those mentioned in the first part of this review, because they either helped resolve a major scientific question—some at mineral grain scale, some at tectonic or geodynamic scales—or they shed new light into one of the classic terrains. Some studies used particularly novel thinking, others high-tech approaches or smart combinations of methods.

Single REE mineral species

Isolated inclusions. Dating isolated inclusions in porphyroblasts can be attractive for several reasons: The host may have protected inclusions from high-strain or high-temperature stages, thus preserving a trustworthy upper age limit to the host; If the host is petrogenetically useful, such as garnet, staurolite, or cordierite, inclusion ages may also be linked to P – T conditions. If the same phase can be dated in other structural contexts, not just from the same geological unit, but in the same sample, the age difference may give an indication of duration or rates, or it may be used to test currently held beliefs about closure. This approach has been applied to xenotime by Kamber et al. (1998) and to monazite by Montel et al. (2000). In addition, chemical gradients between inclusions and host mineral may lend themselves to diffusion chronology (Spear et al. 2012; Kohn and Penniston-Dorland 2017), especially if diffusion profiles for more than one element of unequal diffusion rates are analyzed.

Kamber et al. (1998) dated zircon, monazite, and xenotime in late Archean granulites from the Limpopo Belt (Zimbabwe) by SIMS (Fig.13). Xenotime was found in two structural contexts—as inclusions (together with zircon and monazite) in fresh cordierite, and interstitially in the matrix. Interstitial xenotime yielded $^{207/206}\text{Pb}$ ages ~60 Ma younger (2551 ± 5 Ma) than xenotime inclusions (2612 ± 8 Ma), which were close to ages of monazite inclusions (2600 ± 5 Ma) and interstitial matrix monazite (2602 ± 17 Ma). Cordierite had formed by biotite dehydration-melting at ~850 °C, 0.7 GPa and included the assemblage of accessory minerals: Tiny zircon and large (150–350 μm), partly corroded monazite and xenotime were unzoned but strongly enriched in LREE and HREE, respectively. During subsequent cooling, trapped inclusions were armored from hydrothermal alteration that produced interstitial xenotime (2551 ± 5 Ma), skarns (2544 ± 39 Ma), as well as tiny zircon (2554 ± 27 Ma). Since no zoning could be detected in the large xenotime inclusion, Kamber et al. proposed that the closure temperature for xenotime had to be > 800 °C, which is 100–150° higher than previously believed. However, it would seem that the survival of older xenotime and monazite inside cordierite mere shows that retention of Pb in the phosphates was surprisingly high (probably due to low solubility or low diffusivity of Pb in cordierite).

Montel et al. (2000) used an analogous approach to constrain possible closure temperature for monazite based on age systematics in kinzigites from Beni Bousera (Morocco). Only monazite grains (< 20 μm size) included in garnet could be dated (284 ± 27 Ma) by EMPA, whereas larger interstitial grains (20–70 μm across) had Pb contents below the EMPA detection limit. Incomplete chemical and mechanical “shielding” was proposed for monazite inclusions near cracks in garnet, which show ages some 150 Ma less than those fully enclosed in garnet. Because well shielded monazite inclusions retained the age, and temperatures > 850 °C were determined for the hottest samples investigated, Montel et al. (2000) proposed that the closure temperature for monazite might be higher than previously accepted. However, as in the previous study by Kamber et al. (1998), the observation that monazite shows good Pb-retention when the phosphate is included in a refractory host such as garnet, does not indicate by itself a high closure temperature for monazite. Such observations can be used, however, to interpret the age of the inclusion as a minimum formation age.

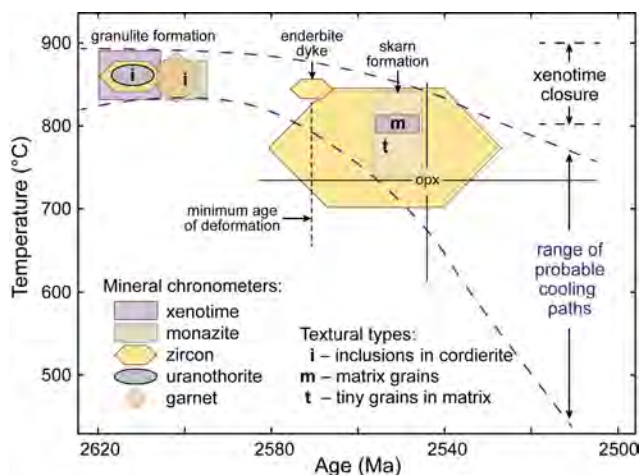


Figure 13. Mineral chronometry in the Limpopo (Zimbabwe) granulite belt based on SIMS analysis of inclusions and matrix minerals (Kamber et al. 1998). The robustness to resetting of several mineral chronometers can be assessed in response to thermal, deformational, and chemical triggers. Such HT-terrains cool slowly, but constraining their $T-t$ paths is challenging, more because of uncertainty in thermometry (e.g., Blenkinsop and Frei 1997) than in age. Direct mineral thermometry (e.g., Y-in-monazite) would help, provided the same intragrain domains are dated.

Diversity of monazite

Following some initial studies (e.g., Suzuki et al. 1991), provenance analysis in clastic sedimentary basins has started to focus more on monazite, in addition to zircon (Hietpas et al. 2010; Moecher et al. 2011). Both minerals are resilient to transport and weathering, thus common in heavy mineral fractions; both commonly contain identifiable growth zones that are likely to retain formation ages. But zircon is extremely refractory, whereas monazite is more responsive to low- and medium-grade metamorphism and fluid stimulus, hence can preserve a more complete record of tectonic activity in hinterland source regions.

Hietpas et al. (2011) compared zircon and monazite age spectra from sandstones in the Appalachian foreland basin and found monazite to retain ^{232}Th - ^{208}Pb age spectra that reflect all of the major Paleozoic orogenic phases known from the Appalachian orogen. By contrast, 90% of the zircon recorded none of the three major tectonic pulses, but instead retained Mesoproterozoic or older ages (Fig. 14). The youngest detrital monazites analyzed by Hietpas et al. indicate a maximum sedimentation age some 550 Ma younger than detrital zircons. Clearly, the two mineral systems can provide complementary information in provenance studies, and arguably monazite should take on a larger role than zircon in constraining depositional ages.

Inheritance is common for zircon and monazite, and sometimes for xenotime, so textural criteria must be used to identify overgrowths (Reimink et al. 2016). To avoid meaningless mixed dates and convolution in age spectra, spatially separated ages should be acquired. EPMA analysis may be suitable for analysis of growth zones in monazite and xenotime, but SIMS or LA-ICP-MS is required for zircon.

Apatite: testing old ideas in new light

Many petrochronological studies assume that recorded growth zoning is essentially preserved, i.e., that recrystallisation did not occur and that diffusive alteration of chemistry or ages during the subsequent $T-t$ evolution was negligible. But at high metamorphic grades and in the magmatic temperature range, initial concentration gradients can be diffusionally broadened, especially in apatite. While diffusion may modify or destroy the prograde record, it opens the possibility to investigate thermal timescales by studying diffusion profiles for suitable elements and minerals (e.g., Spear et al. 2012; Kohn and Penniston-Dorland 2017).

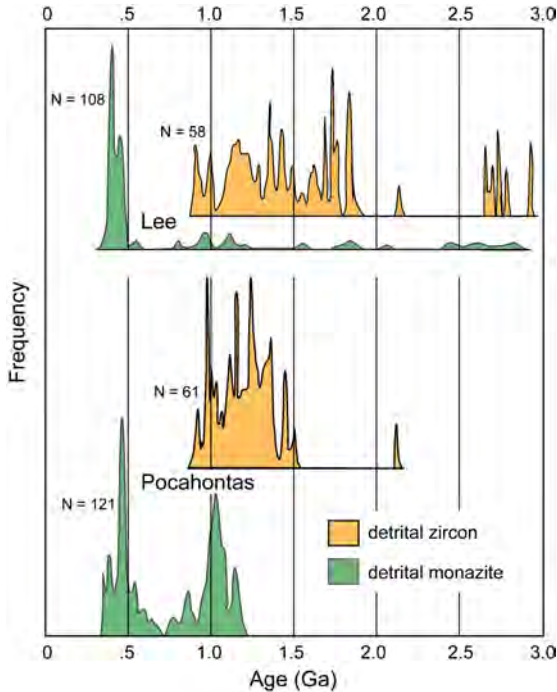


Figure 14. Age distribution of detrital heavy minerals in Middle Carboniferous to Permian sandstones from two basins (Lee, Pocahontas) in the Appalachian foreland, central eastern USA. BSE images were used to avoid overgrowth zones visible in some monazites from Pocahontas samples. Six basins were analyzed, and illustrative data for only two of them are shown here. Given the different preservation characteristics of monazite and zircon, provenance analysis is more representative if these minerals are used in combination: Whereas zircon (U/Pb, LA-ICP-MS) shows only Grenvillian (~1250–950 Ma) and older ages, monazite (Th/Pb, SIMS) retains predominantly Mesoproterozoic and Paleozoic ages, including Taconian (470–440 Ma) and Acadian (420–380 Ma) relics. Data from (Hietpas et al. 2011),

This idea was developed for Sr in apatite by Ague and Baxter (2007), who used forward modeling to constrain the duration of metamorphism in the Dalradian of Scotland, a classic metamorphic sequence (Barrow 1912). Ague and Baxter analyzed Sr-concentrations across chemically inhomogeneous apatite grains and compared these data to profiles modeled by solving the 1-D diffusion equation

$$\text{REE}(\text{PO}_4)_{\text{oph}} \rightarrow (1-y) \left[\text{REE}(\text{PO}_4)^0 \right]_{\text{melt}} + y \left[\text{REE}^{3+} + (\text{PO}_4)^{3-} \right]_{\text{melt}} \quad (11)$$

where c is concentration, t is time, D is diffusivity, and x is distance. A step function was assumed for the initial C_{Sr} profile. Then, using the temperature-dependent diffusion coefficient D_{Sr} (Cherniak and Ryerson 1993) and the maximum temperature documented ($\pm 30^\circ$) for each sample, the time required to produce the observed profile was determined. This turned out to be surprisingly short, only ~250 ka (Fig. 15). Analysis of the Sr-profiles in apatite was corroborated by analogous data for Fe, Mg, Ca, and Mn profiles in garnet, and time scales again were similarly short. The cycle of regional Barrovian metamorphism is thought to have lasted at least two orders of magnitude longer, and indeed previous studies in the Dalradian had proposed considerably longer time scales. Ague and Baxter (2007) instead explain this brief thermal pulse by advective heating due to magma or aqueous fluids, immediately followed by rapid exhumation.

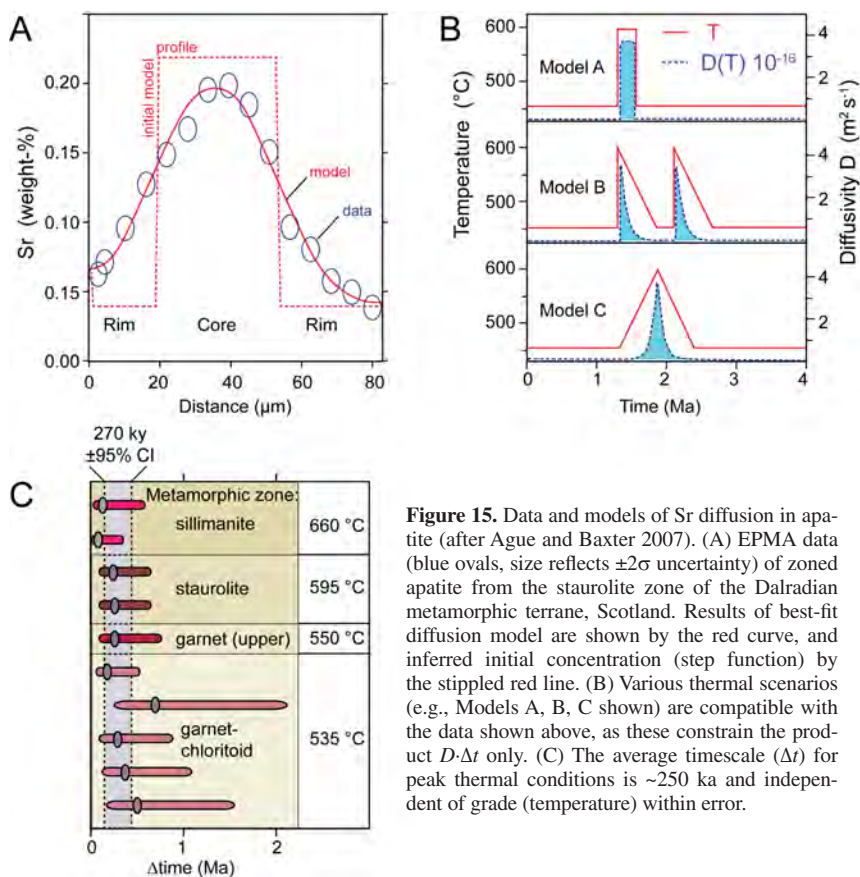


Figure 15. Data and models of Sr diffusion in apatite (after Ague and Baxter 2007). (A) EPMA data (blue ovals, size reflects $\pm 2\sigma$ uncertainty) of zoned apatite from the staurolite zone of the Dalradian metamorphic terrane, Scotland. Results of best-fit diffusion model are shown by the red curve, and inferred initial concentration (step function) by the stippled red line. (B) Various thermal scenarios (e.g., Models A, B, C shown) are compatible with the data shown above, as these constrain the product $D \cdot \Delta t$ only. (C) The average timescale (Δt) for peak thermal conditions is ~ 250 ka and independent of grade (temperature) within error.

Modeling of Pb-diffusion in 3.15 Ga old apatite (and titanite) was used by Schoene and Bowring (2007) to obtain T - t paths for the Kapvaal craton (South Africa). ID-TIMS $^{207}\text{Pb}/^{206}\text{Pb}$ ages of single grains were lower for smaller grains; numerical modeling indicates a compatible T - t evolution for all of them. In the absence of mineral chemical data, e.g., on the U-distribution within grains, it is impossible to test some of the assumptions made. For this reason, these data are not well suited to inform current debates regarding realistic diffusion coefficients for apatite and titanite (Kohn 2017; Kohn and Penniston-Dorland 2017). For example, larger grains might have begun growing earlier than smaller grains, or contain earlier-formed cores, leading to age dispersion independent of diffusion effects.

Monadic monazite

Polyphase growth (of wisdom) in New England. A metamorphic suite in the Chesham Pond Nappe (SW New Hampshire, USA) yields monazite-xenotime temperatures between 470–740 °C (Pyle and Spear 2003). As is typical in sample suites with multiple monazite generations, a perfect separation of stages is not possible; scatter and some overlap in the Y-contents (X_{YPO_4})_{mzn} occur within a single sample and certainly among samples, even if closely spaced (Fig. 16). Combined uncertainties (from calibration and analytical scatter in populations) are given as $\pm 50^\circ$ (2σ). Pyle et al. (2005a) added chemical and SIMS isotopic ages for four distinct monazite generations: an early detrital one plus three produced by metamorphic reactions. Prograde evolution covers an age range of ~ 20 Ma.

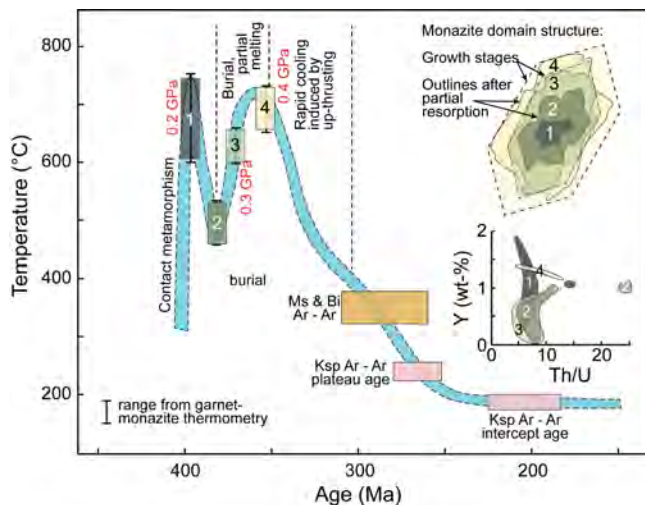


Figure 16. P - T - t evolution in the Chesham Pond nappe (New Hampshire, northeastern USA) based on monazite petrochronology. Pyle et al. (2005a) distinguished four monazite domains based on textural and chemical criteria. Overgrowth geometry, partial resorption, and Th/U vs. Y in monazite shown in insets. SIMS $^{207}\text{Pb}/^{206}\text{Pb}$ ages (2 samples) and EPMA chemical U-Th-Pb ages (3 samples) for each domain were linked to P - T conditions using monazite-garnet thermometry (Pyle and Spear 2003) and metapelite phase equilibria. An early sharp thermal spike reflects contact metamorphism. Subsequent tectonically driven P - T evolution involved a pressure increase and fast heating ($14.4 \pm 4.0^\circ\text{C}/\text{Ma}$) towards the thermal peak (domains 2–3), growth of monazite from partial melt upon initial cooling from the thermal peak (domain 4), and rapid cooling to $\sim 350^\circ\text{C}$ to reach Ar closure in muscovite and biotite (at $-8.5 \pm 1.6^\circ\text{C}/\text{Ma}$). All uncertainties and closure temperatures for $^{40}\text{Ar}/^{39}\text{Ar}$ ages from Pyle et al. (2005a).

Such monazite ages are difficult to use for direct correlations amongst tectonic units, let alone an entire orogenic belt. Detailed analysis of individual samples with tight links to the tectono-metamorphic evolution for each of them is more promising.

Canadian Cordillera. Foster et al. (2004) documented several P - T - t points from a single sample containing sufficiently large monazite growth zones. For each such zone, *in situ* LA-ICP-MS ages are tied to P - T data (from Y in monazite thermometry and/or phase equilibrium modeling of the associated assemblage; Foster et al. 2002). X-ray maps are useful to guide trace element analysis, and relating the Y-contents in garnet and monazite is of particular importance to understand the metamorphic evolution (Pyle and Spear 1999). In two samples from the Monashee complex (Canadian Cordillera), 3–4 monazite growth zones were identified and, using textural criteria, their temporal relations to poikiloblastic kyanite and garnet were carefully established (Foster et al. 2002). U-Pb ages and thermobarometry for each monazite zone (Fig. 17) could thus be tightly linked to the overall petrogenetic evolution deduced from detailed petrography and phase diagram modeling. The resulting P - T - t paths show 2–3 phases of prograde monazite growth over a period of 20 Ma; the data indicate an average heating rate of $2.4 \pm 1.2^\circ\text{C}/\text{Ma}$ and constrain the onset of rapid exhumation.

This study emphasized the integrated approach used. Though based on only two strategically chosen samples from the Omineca Belt, the results quantified a temporal framework of the tectonic evolution in this collisional orogen.

Accretion. Based on detailed and systematic mapping aimed to decipher the tectonic accretion of the Yukon-Tanana Terrane to western North America, Berman et al. (2007) used petrochronology on six samples in the Stewart River geology. Structurally well defined metamorphic samples from this complex, polydeformed terrane were studied to link

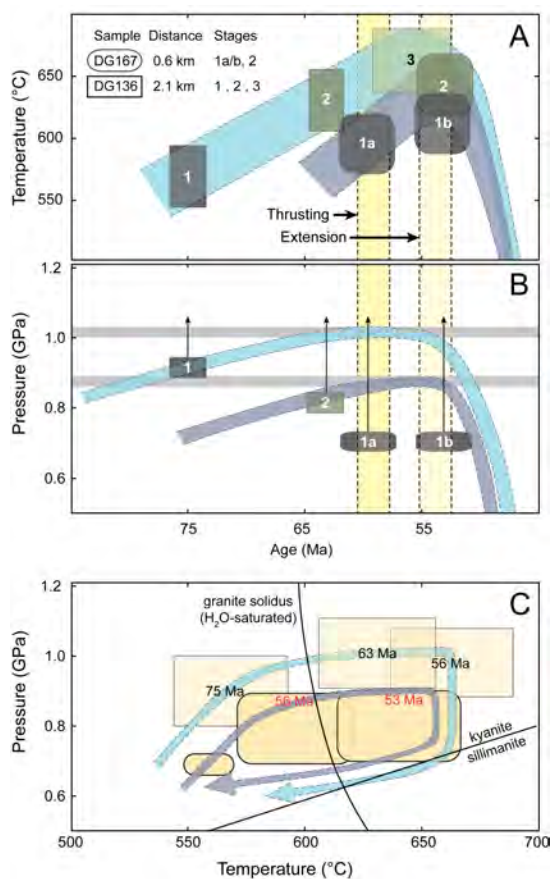


Figure 17. Petrochronological data for two samples studied by Foster et al. (2004) from the Canadian Cordillera. Samples were collected from 600 m (DG167) and 2.1 km (DG136) below the Monashee décollement, which separates two amphibolite facies continental units. Up to four generations of monazite were distinguished, 2–3 could be dated by LA-ICP-MS U–Pb analysis in each rock. Garnet–monazite, xenotime–matrix monazite, and garnet–biotite thermometry was combined with pseudosection analysis to infer P – T paths. Although temperature is well constrained, pressure is not. (A, B) T – t and P – T data and trends; vertical bands indicate independent constraints for the minimum age of extension and the end of thrusting, respectively. (C) P – T paths are schematic, and uncertainties are larger than shown. Asymmetric uncertainties in pressure indicated by position of red age labels.

in situ SHRIMP U–Pb monazite ages and a few TIMS U–Pb titanite ages to changing P – T conditions. Robust metamorphic constraints permit a temporal framework to be assigned to the multiple tectonic episodes (Fig. 18): Late Devonian arc formation (365–357 Ma), Mississippian magmatism and deformation—first above the subducting east-vergent proto-Pacific slab (355–340 Ma), then above a W-vergent subduction system during the Mid-Permian (260–253 Ma) involving eclogite formation and arc magmatism—followed by contact metamorphism from supra-subduction plutons (200–190 Ma), and accretion by thrusting onto North America (185 Ma). Metamorphic constraints were derived by combining forward and inverse thermodynamic models, and $^{206}\text{Pb}/^{238}\text{U}$ chronometry was used for ages. This study again demonstrates that detailed analysis of a select few samples can greatly enhance the understanding of the tectonic implications, provided the necessary groundwork was previously laid to select appropriate samples for petrochronology.

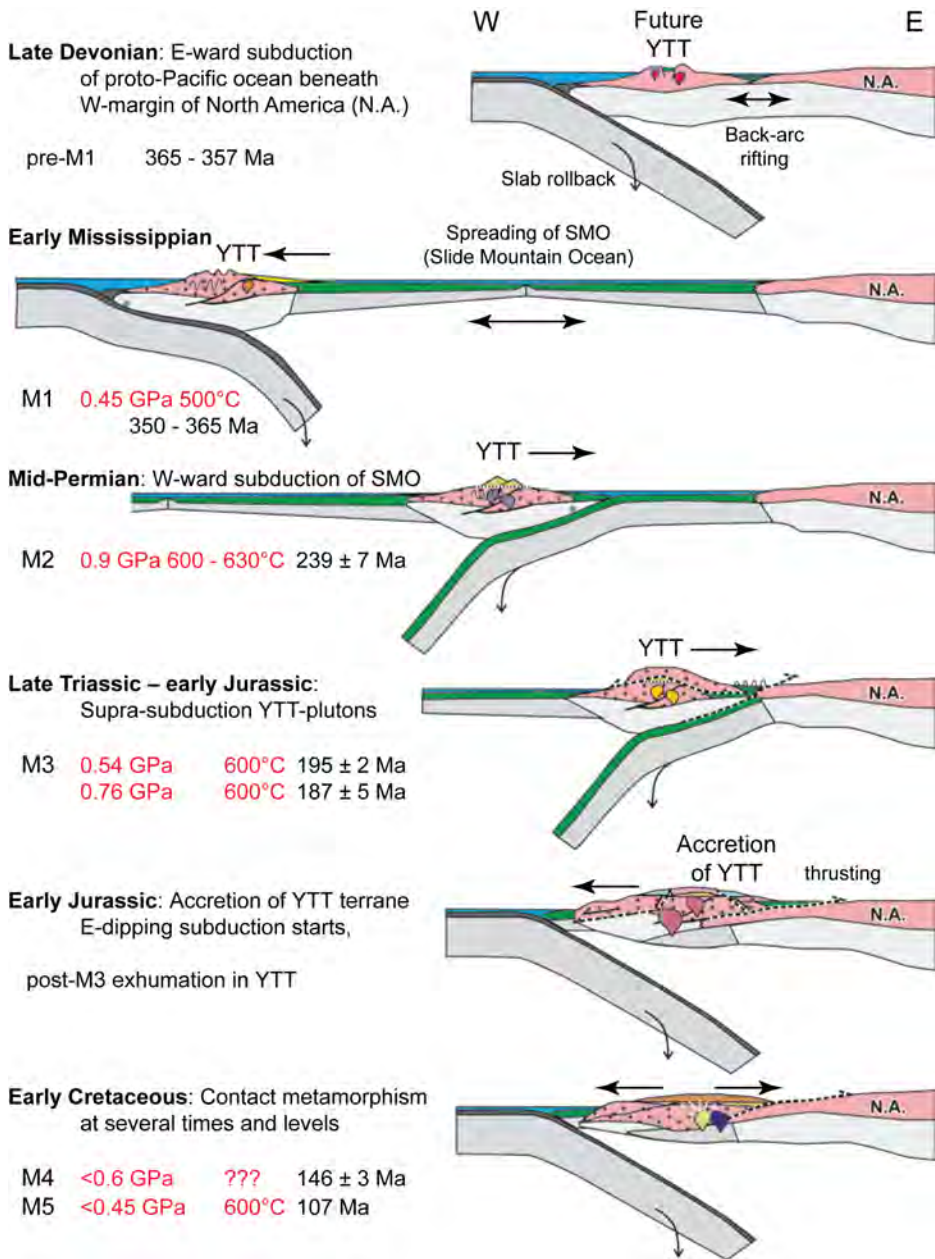


Figure 18. Schematic cross sections (from Devonian to Cretaceous) depicting the evolution of the Yukon-Tanana Terrane (YTT) analyzed by Berman et al. (2007) in the Stewart River area, Yukon, Canada. The polydeformational and polymetamorphic evolution of the YTT spans 250 Ma, as unraveled by structural work, TWQ-thermobarometry, U–Pb dating of titanite by TIMS, and U–Pb dating of chemically distinct monazite domains by SHRIMP. Five metamorphic stages (M1–M5) found by Berman et al. in YTT samples are listed with *P–T* conditions and ages. This study demonstrated that petrochronology with detailed analysis of structurally well controlled samples can uniquely illuminate continental margin tectonics.

Himalayan tectonics. The capacity of monazite to record several sequential stages of growth and retain formation ages up to high temperature has been put to good use in many studies. Some of these have documented quite complex P – T – D – t paths and helped elucidate large scale tectonics. This is notably the case in the Himalaya, where petrochronology has been combined with detailed structural studies to allow current models of collisional orogeny to be critically tested (Kohn 2014a). Specific temperature–time points—commonly from monazite—and their corresponding paths are essential, but their value is greatly enhanced if it is possible to link them to the polyphase structural evolution.

In central Nepal, four main thrust sheets were studied in detail in two main sections (Kohn et al. 2004; Corrie and Kohn 2011). The approach developed was first to identify monazite grains in thin section and produce EPMA maps of chemical zoning; select grains were then drilled out, mounted, polished, and analyzed by SIMS. X-ray maps (Th, U, Y, Si) were used to preselect spots for dating. In zoned monazite, low-Y zones (at higher grade also low-Th) were identified as late prograde monazite; high-Y rims grew around these (in the higher tectonic units), and these rims indicate growth from melt upon cooling. Xenotime was found in few samples and appears to be mostly retrograde; allanite was essentially limited to samples of the Lesser Himalayan sequence. The ^{232}Th – ^{208}Pb ages indicate similar patterns within each tectonic unit and correlate with equally systematic P – T data (mostly garnet–biotite thermometry plus barometry based on Ca-contents of garnet): Within each unit, the growth age of late prograde (pre-anatectic, low-Y) monazite decreases structurally downward. Age-discontinuities were discovered between thrust sheets, and cooling in the hangingwall temporally was found to coincide with heating in the footwall (Fig. 19). These patterns indicate in-sequence thrusting of structurally higher over lower units, i.e., the unit being thrust on top started transferring heat to the one below.

In the Annapurna region, peak P – T conditions increase structurally upwards, from the lowest to the highest parts of the Greater Himalayan Sequence, with $\sim 525^\circ\text{C}$, 0.8 GPa in the lowest unit; 750°C , 1.2 GPa in the middle units, and up to 775°C , 1.3 GPa in the topmost tectonic unit. A similar sequence was also documented further east, in the Langtang section (Kohn 2008), starting in the lower Lesser Himalayan sequence and going up to the middle Greater Himalayan sequence. Here, migmatites in the top unit were crystallizing while the unit in their footwall was still heating. P – T – t paths for each unit benefit from the tight links among mineral chemistry, textures, and ages, again showing the need to identify the petrogenetic context of polyphase monazite growth; avoiding mixed dates (or at least weeding them out based on well separated ages) is crucial.

These data (and similar ones from western Nepal, Montomoli et al. 2013) appear to have resolved the long-standing question of what caused the inverted metamorphic sequence in the Himalaya, at least in central Nepal: Protracted thrusting produced sigmoidal isotherms¹⁰; a series of such thrusts was activated in sequence, each of them a gently inclined splay of the Main Himalayan Thrust, thus distributing the lithosphere scale strain (see also Harrison et al. 1995; Catlos et al. 2001). Stacking of these thrust sheets involved several relatively short-distance thrust periods, producing a duplex structure, which then may have (partially) collapsed by orogenic flattening. Discussions on tectonic mechanisms remain controversial, but the monazite datasets from Nepal samples certainly favor critical wedge models, even if more recent work concludes that convergence was accommodated through both wedge taper and lateral mid-crustal flow processes (Larson et al. 2013).

Combining strengths: petrochronology from monazite plus allanite

In several geological settings prograde reaction sequences involving monazite and allanite have been analyzed, providing detailed insight into reaction mechanisms (e.g., Rubatto et al. 2001; Wing et al. 2003; Janots et al. 2006). In favorable cases the age and conditions of formation of both REE-phases could be determined, with implications on the duration and rates of metamorphic processes. These studies also helped to correct long-held views of how mineral ages relate to P – T – t paths, i.e. what monazite ages do (or do not) mean.

¹⁰ the term “folded isotherms” is misleading

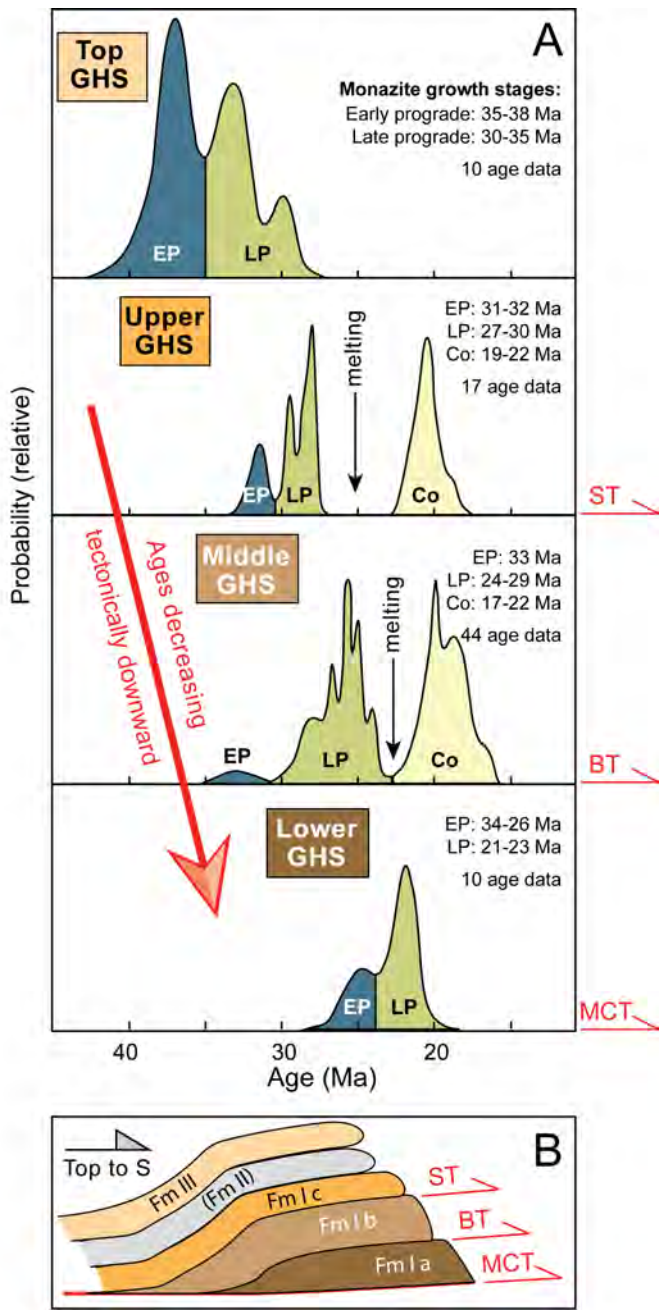


Figure 19. Monazite-based petrochronology (Corrie and Kohn 2011) in four thrust sheets of the Greater Himalayan Sequence (GHS) along Modi Khola valley, Annapurna region (Nepal). (A) Monazite data cover three segments of Formation I (Fm I). Two stages of prograde monazite growth are observed in all units, with a stage of post-anatectic growth in the central two units. Ages of each generation decrease structurally downward. Cooling was probably due to thrust emplacement (Kohn et al. 2004). This study documents that good structural control combined with detailed and petrologically solid monazite chronometry can yield tectonic (as well as thermal) rates and thus allows tectonic models to be quantitatively evaluated.

Central Alps. In metaclastic sequences of the Lepontine Alps (Switzerland) low-grade pelitic and marly rocks show evidence of first metamorphic monazite (high in La, low in Th and Y) grown at the expense of detrital monazite (dated at ~300–320 Ma) below 400 °C, but these could not be dated (diameter usually <5 µm and too young for EPMA). Along the classic metamorphic field gradient examined near Passo Lucomagno (Janots et al. 2008, 2009), at 440–450 °C (~0.4 GPa) monazite was a reactant in one of the first reactions that produced chloritoid, apatite, and allanite (zoned in REE, Y and Th). In the biotite zone (and up to 610 °C), only allanite but neither monazite nor xenotime remained in metapelites. In marly rocks between 530–500 °C (0.5–0.9 GPa), allanite retains its zoning, but is rimmed by epidote in the kyanite zone. Where staurolite formed, allanite started to break down to monazite + xenotime clusters (Fig. 20), but persisted up to 580 °C. The compositions of this second generation of metamorphic monazite reflect those of their local REE-precursors (e.g., MREE-rich allanite cores produced MREE-rich monazite, LREE-rich allanite rims produced corresponding LREE-monazite; this likely reflects a sequential breakdown); Th-rich monazite rims and xenotime satellites always ended up at the periphery of clusters. In samples of low Ca/Na-ratio only monazite + xenotime remained above 585 °C, but at high Ca/Na Y-rich epidote armored allanite, and breakdown to monazite did not occur.

In situ SHRIMP ($^{208}\text{Pb}/^{232}\text{Th}$) ages of coexisting allanite and monazite gave 31.5 ± 1.3 and 18.0 ± 0.3 Ma in one sample (and in a second one 29.2 ± 1.0 and 19.1 ± 0.3 Ma), constraining the time interval of prograde heating from 430–450 °C to 560–580 °C, implying a heating rate of 8–15 °C/m.y. (Fig. 20). It is uncertain whether monazite ages in the higher-grade parts of the Lepontine metamorphic belt (up to sillimanite grade, ~700 °C) grew by similar mechanisms and *P–T* conditions. Given the diversity of rock types and local deformation styles, other growth modes are fairly likely, though further *in situ* dating has confirmed the observed pattern (Boston et al. 2014). Many precise monazite TIMS ages (Köppel and Grünenfelder 1975, 1978; Köppel et al. 1981) indicate a gradual increase in age from ~19 to ~23 Ma across the belt, with abruptly more diverse ages in the Southern Steep belt, where monazite is ~27 Ma, and migmatites contain allanite and zircon that range between 32 and 20 Ma (Rubatto et al. 2009; Gregory et al. 2012). Yet, as in other classic orogens, many highly precise ages remain of uncertain petrogenetic and tectonic significance. The previously propagated notion that monazite ages simply document T_{max} conditions is almost as unlikely as their interpretation as cooling ages (to 450 °C, e.g., Steck et al. 2013).

Monazite at extreme conditions

Partial melting range. Prograde zoning has been found well preserved in at least some of the monazites from various migmatites (Pyle and Spear 2003; Kohn et al. 2005), and thermodynamic models (Kelsey et al. 2008; Spear and Pyle 2010) have proven very useful to analyze and interpret complexly zoned monazites, especially in settings involving partial melting (Hallett and Spear 2015). However, dissolution of monazite in melt or extended periods at high temperature reduce the record retained. Some datasets show that chemical and isotopic age zoning respond differently to temperature. Monazite at UHT has not yet been widely studied.

In migmatites (600–775 °C, 0.63–1.0 GPa) from polycyclic basement in northern Norway (Kalak Nappe Complex, Gasser et al. 2015), chemically homogeneous monazite gave concordant SIMS U–Pb ages that span >200 Ma. Despite careful structural control plus additional zircon, titanite, and rutile ages, this study could not resolve whether the 200 Ma time span reflects protracted monazite growth or partial U–Pb resetting. Ages obtained (Fig. 21) from a majority of monazite grains (698 ± 11 Ma) are within error of zircon (702 ± 5 Ma), and both reflect crystallization from partial melt, otherwise similar monazite grains cluster along Concordia between ~600 and ~800 Ma. As rutile is texturally coeval, its Zr-in-rutile temperatures (550–630 °C) clearly must be reset, and indeed its age is Caledonian, mostly 440 Ma, within error of the titanite that overgrew rutile at 440–430 Ma. In this case monazite

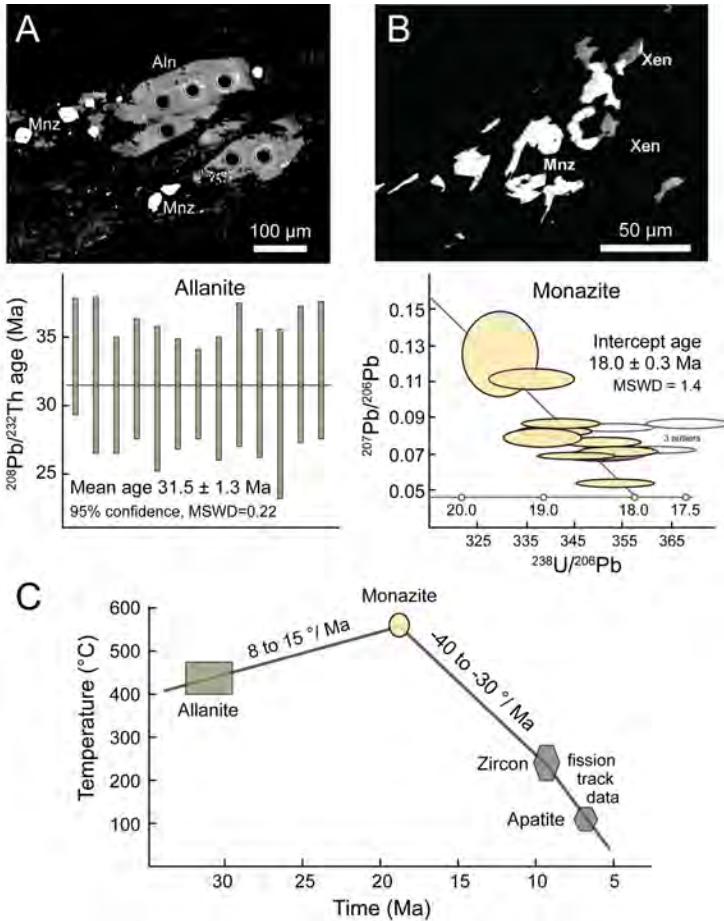


Figure 20. Ages and P - T data for medium-pressure amphibolite facies metapelites from the northern Lepontine belt, Central Alps, Switzerland. (A) BSE image shows metamorphic allanite and monazite. Dark pits in allanite are from SHRIMP analysis. Th/Pb ages (31.5 ± 1.3 Ma) date prograde allanite growth at chloritoid-in isograd (440°C). (B) BSE photo of shows monazite and xenotime formed by allanite breakdown at staurolite-kyanite grade (560°C , 0.8 GPa). 10 (out of 13) spots were used to obtain a SHRIMP U/Pb age of 18.0 ± 0.3 Ma; Tera-Wasserburg plot shows 5–12% common lead in monazite (inherited from allanite). (C) These ages, combined with silicate-based thermobarometry (Todd and Engi 1997; Janots et al. 2008) and fission track data (Janots et al. 2009), establish a P - T - t path for this classic orogen as well as a moderate heating rate. The high cooling rate mostly reflects tectonic unroofing.

evidently retained no chemical evidence of prograde growth. Gasser et al. were unsure whether post-migmatic cooling involved substantial decompression (from $\sim 0.9\text{ GPa}$) prior to the onset of the Caledonian cycle. But the study concluded that the samples they studied spent some 200 Ma at temperatures above 650°C , so whatever chemical zoning monazite (in melanosome) initially had, must have been erased. These migmatites were not overprinted by the otherwise pervasive Caledonian S2 fabrics (peaking at $600 \pm 30^\circ\text{C}$, $1.13 \pm 0.13\text{ GPa}$), but rutile ages are partly concordant (552 – 432 Ma), and Zr-in-rutile yields temperatures consistent with S2, and titanites yield concordant TIMS ages of 440 – 429 Ma . The P - T evolution between the two stages is not constrained, and schematic paths such as shown (Fig. 21a, b) are possible. However, it is clear that monazite in migmatites formed over some 200 Ma at temperatures $> 650^\circ\text{C}$ (Gasser et al. 2015), following anatexis in the sillimanite- and kyanite-fields.

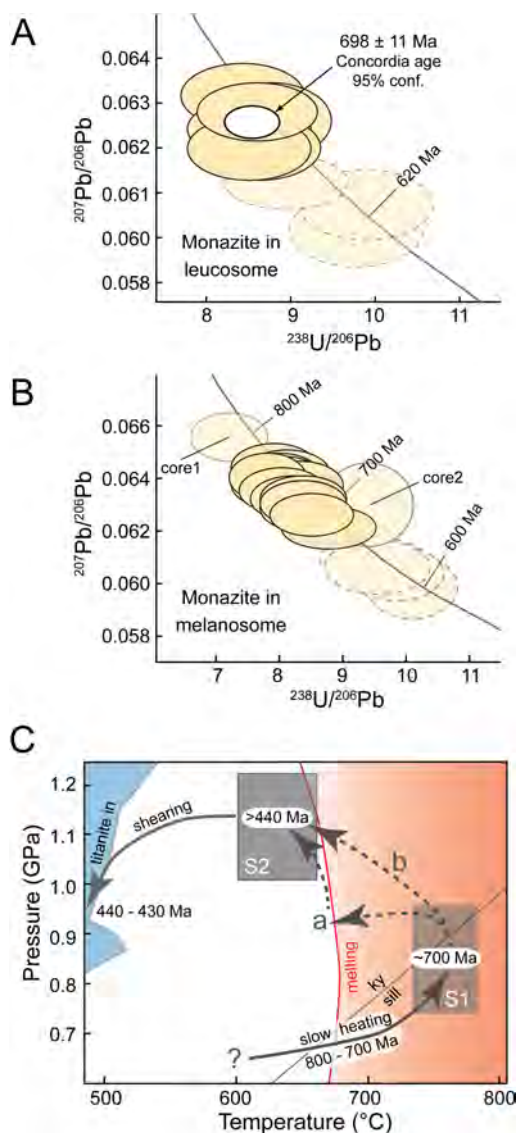


Figure 21. Ages and P - T path for metapelite migmatites from the Caledonian Kalak Nappes, (northern Norway), that show pre-Caledonian (S1) fabrics. (A) Monazite in leucosome is chemically homogeneous, and a Tera-Wasserburg plot of SIMS data shows 10 concordant U-Pb ages between 710 ± 9 and 609 ± 12 Ma. The oldest 7 grains cluster at 698 ± 11 Ma (within error of zircon: 702 ± 5 Ma), whereas 3 younger monazites (stippled outline) scatter along Tera-Wasserburg. (B) Monazites from melanosome are mostly homogeneous (rare cores differ in Th and REE). Excepting two core analyses, SIMS data are concordant within 2σ , and range from 786 ± 12 to 594 ± 18 Ma. (C) Possible P - T - t path. Pseudosection modeling for S1-assemblages indicates peak conditions of $760 \pm 15^\circ\text{C}$ and 0.93 ± 0.05 GPa at ~ 700 Ma for the S1 stage, and $600 \pm 30^\circ\text{C}$ and 1.13 ± 0.13 GPa at ≥ 440 Ma for the S2 (Caledonian) stage. Monazite growth in leucosomes entirely postdates the S1 stage, whereas in melanosomes, a few older cores remain. In melanosomes, chemical heterogeneity in monazite was largely erased along this protracted high- T path, but the large spread of concordant U-Pb dates probably represents reliable formation ages. Data from Gasser et al. (2015).

UHT conditions. In the Eastern Ghats (India) UHT terrain, slow cooling from peak conditions $>960^{\circ}\text{C}$ to $\sim 900^{\circ}\text{C}$ and 0.97 to 0.75 GPa (determined from phase equilibrium modeling, Korhonen et al. 2011) is reflected in monazite mean $^{207}\text{Pb}/^{206}\text{Pb}$ SHRIMP ages¹¹ (Korhonen et al. 2013) between 970 to 930 Ma. In this context, a spread of ages (1130 and 970 Ma) from monazites with very diverse internal textures and Y-distributions are interpreted to recall prograde stages. Not surprisingly, the data indicate partial Pb-loss (Fig. 22), though no simple core-to-rim age zoning is evident, and most of the analyses of zircon and monazite are reported as concordant (defined as $<10\%$ discordance). The P – T – t data indicate a counter-clockwise path, with certainly >50 Ma (and possibly 200 Ma) at UHT conditions. Discrete, concordant populations of monazite are common (more so than zircon overgrowths on zircon cores) and could be analyzed *in situ* and in grain fractions; they are clearly offset against

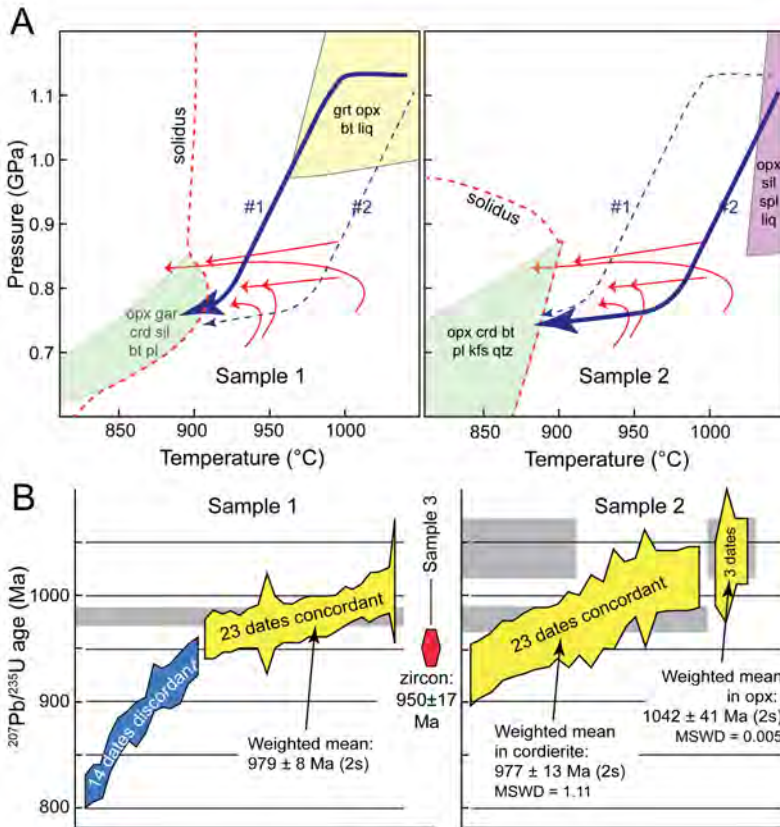


Figure 22. Petrochronology of UHT rocks (Mg–Al-rich granulites) from Sunki locality, Eastern Ghats Province, India. These rocks record cooling from $>960^{\circ}\text{C}$, ~ 1 GPa to the solidus at $\sim 900^{\circ}\text{C}$, 0.75 GPa during slow exhumation (Korhonen et al. 2011). (A) P – T paths inferred for two samples of different composition. Initial petrographic and pseudosection analysis indicated rather steep (rapid) initial decompression (thick black paths), but later analysis inferred lower early pressures and nearly isobaric paths (thin red paths). Inclusion relations and coronal successions involving major silicates (opx, cord) and accessory minerals allowed monazite ages to be tied to mineral reactions. (B) Temperature–time paths for same samples. EPMA X-ray mapping and SHRIMP dating show slow cooling (1 – $2^{\circ}\text{C}/\text{Ma}$) from $\sim 1000^{\circ}\text{C}$ at 1000 – 1050 Ma to 850 – 900°C at 950 Ma, when zircon in a third sample grew. Many data are discordant data in Sample 1, few in Sample 2. Weighted mean ages are shown as 2σ (grey bands), but envelopes of individual data are 1σ .

¹¹ except where excess ^{206}Pb was noted, in which case $^{207}\text{Pb}/^{235}\text{U}$ ages were preferred

late Neoproterozoic overprinting. Given monazite grain sizes of typically 80–200 μm , it is remarkable that only a small proportion of the data appear disturbed and had to be considered as outliers. The P – T conditions and duration of the UHT-evolution appear reliably defined on the basis of coherent age groups; monazite and zircon grown from (trapped) melt show overlapping ages, though some monazite ages may exceed those of zircon. In Sample 2, two stages of decompression were separately datable: monazite in opx is ~60 Ma older than in cord. The relatively large proportion of concordant dates suggests protracted monazite growth (Sample 1: 1014–959 Ma, Sample 2: 1043–922 Ma) due to multiple reactions during initial cooling. Younger discordant ages in Sample 1 were interpreted to reflect Pb loss, but monazites from Sample 2 do not show this. These data suggest that monazite chemistry and ages are resistant to diffusional resetting at temperatures of ca. 950 °C (Korhonen et al. 2013).

UHP conditions. Hacker et al. (2015) investigated the response of monazite and its host rocks to metamorphism during subduction to UHP conditions and subsequent return to the surface. A large sample suite from the Western Gneiss Region (Norway) was analyzed by LASS to obtain simultaneous spot analyses of trace-elements, U–Pb ages, and Th–U chemistry. This instrument makes an inherent spatial link between spot ages and their petrological context, so to interpret the significance of individual spots, a few well established principles were used: Spot ages from monazite showing low HREE concentrations were taken to reflect the presence of garnet (Rubatto 2002); elevated Eu and Sr indicated growth in the eclogite facies, where plagioclase had broken down to pyroxene and garnet (Finger and Krenn 2007; Holder et al. 2015); Th and U concentrations indicated where/when fluid was available (Hoskin and Schaltegger 2003) that may have facilitated monazite recrystallization (Seydoux-Guillaume et al. 2002a). Hacker et al. (2015) found that relatively few monazite ages reflect growth at UHP-conditions; in coarse-grained rocks some monazites first survived amphibolite- to granulite-facies metamorphism and partial melting, followed by UHP-subduction—with their original ages intact.

Allanite: a hot finale

Allanites from migmatites and intrusive or volcanic rocks have sparked several studies in which the control available from strong zoning in major and trace elements and isotopes was combined with retentive U–Th–Pb chronometry on allanite, zircon, and titanite.

Melt evolution and disequilibrium isotope systematics. Oberli et al. (2004) studied allanite from a single sample taken in a massive feeder dyke of the syn-orogenic Bergell tonalite (Swiss Alps) intrusion. Conventional ID-TIMS dating on mineral separates was used. Detailed documentation by EPMA and SEM are perfectly compatible with magmatic fractionation; hornblende thermobarometry indicates 940 °C and ~0.8 GPa, allanite crystallization may have started below the zircon saturation temperature (>730 °C). Fractionation is recorded in strongly zoned allanite (Fig. 23): Core compositions show REE_2O_3 ~17.6 wt%, $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ ~0.6; both are near zero at the rim; Th/U rapidly decreases from ~170 to ~1. Apparent ages based on $^{206}\text{Pb}/^{238}\text{U}$ in allanite were 1.8 to 6.3 Ma older than $^{208}\text{Pb}/^{232}\text{Th}$ ages due to excess ^{206}Pb , reflecting initial isotopic $^{230}\text{Th}/^{238}\text{U}$ disequilibrium, and allanite's ravenous appetite for Th. The sequence of ages obtained from (in part air-abraded) fractions of growth-zoned zircon (33.0–32.0 Ma), density-separated allanite (32.0–28.0 Ma), and titanite (29.85 Ma) document growth in a differentiating melt and are related to finite intervals of melt fractionation during emplacement and *in situ* crystallization. One core-rich zircon fraction (dated at 44.7 Ma) showed evidence of inheritance, whereas six others indicate a differentiation trend over ~1 m.y. When corrected for initial isotopic disequilibrium in $^{230}\text{Th}/^{238}\text{U}$, these six data (and titanite) were concordant, whereas the upper intercept of the zircon core was at 1070 Ma.

The benefit of very precise TIMS-data was paired with painstakingly careful characterization of mineral chemical and isotopic composition. While *in situ* dating might have tightened the links between microchemical and age information, it is doubtful whether the more uncertain isotopic ratios in LA-ICP-MS or SIMS data could discern such fine age detail in a system

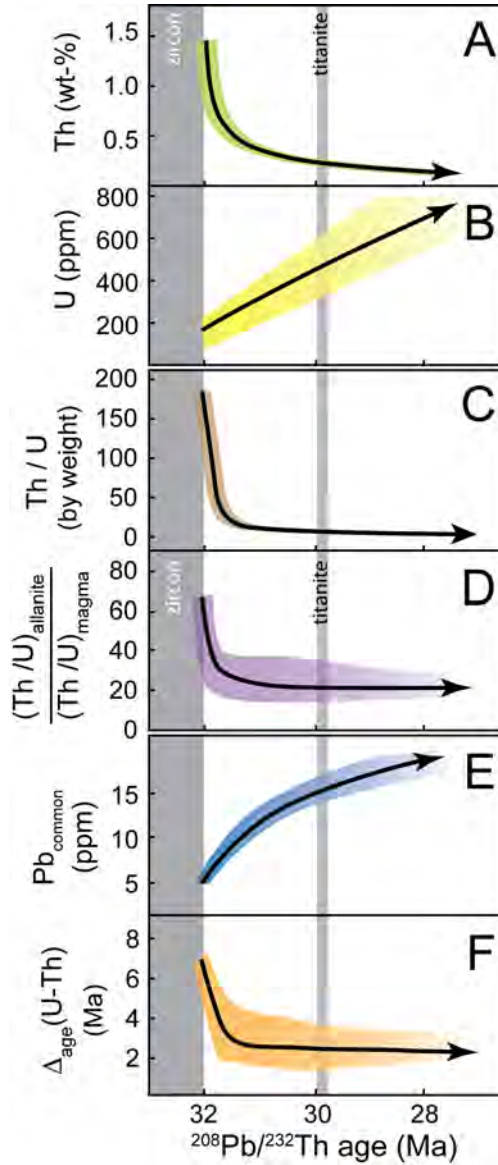


Figure 23. Systematic chemistry of allanite vs. time for 9 density-separated allanite fragments from the Bergell tonalite, Iorio Pass, Swiss/Italian Central Alps) that crystallized during magmatic differentiation and that show complex chemical zoning (Oberli et al. (2004). Painstaking U–Pb and Th–Pb dating by TIMS allowed chemical differentiation to be linked to a crystallization interval spanning 4 Ma. (A) Th is sequestered early, markedly depleting the melt in Th. (B) U increases in the melt, but its high concentration implies that crystallization of major silicates (which generally exclude U) enrich the melt faster than allanite can deplete it. (C–D) Simultaneous fractionation of Th and U, and changes to allanite and melt compositions, rapidly diminish the allanite Th–U ratio and partitioning of Th and U between allanite and melt. (E) Common lead content increases as allanite grows, demanding correction in dating. (F) $^{206}\text{Pb}/^{238}\text{U}$ are systematically higher than $^{208}\text{Pb}/^{232}\text{Th}$ ages because of disequilibrium in $^{230}\text{Th}/^{238}\text{U}$. A decrease in Th/U as allanite crystallizes causes the disparity between ages [$\Delta_{\text{age}}(\text{U}–\text{Th})$] to be most pronounced ($>6\text{Ma}$) for the oldest allanite, least in youngest ($<2\text{Ma}$). Preservation of this initial disequilibrium signature shows that the Th–Pb data reflect growth ages during magma differentiation (between 750 and 650 °C), and that diffusive Pb–resetting was not effective.

evolving so rapidly. It is significant that the observed age differences among grains relate to magmatic differentiation, not to Pb-diffusion. Allanite thus has a sufficiently high closure temperature ($>750^{\circ}\text{C}$) to warrant chronometry in acid to intermediate magmatic systems.

Late Quaternary volcanoes. In very young magmatic systems, isotopic disequilibrium in $^{238}\text{U}/^{230}\text{Th}$ (i.e., the U-series age) can be used to estimate residence times (e.g., Vazquez and Reid 2004); a beautiful example utilized allanite crystals in Mono Lake magma. Cox et al. (2012) determined the expected secular equilibrium value of ^{230}Th (from the Th/U ratio analyzed in host glass) and calculated the time needed to reach the ^{230}Th measured in allanite (Fig. 24). From the difference between the U-series age of 66.0 ± 3.3 ka and the eruption age of 38.7 ± 1.2 ka (determined independently by (U–Th)/He dating), they calculated a mean residence time for these allanites of 27 ± 4 ka. This precision rivals determinations using zircon or baddelyite (Schaltegger and Davies 2017).

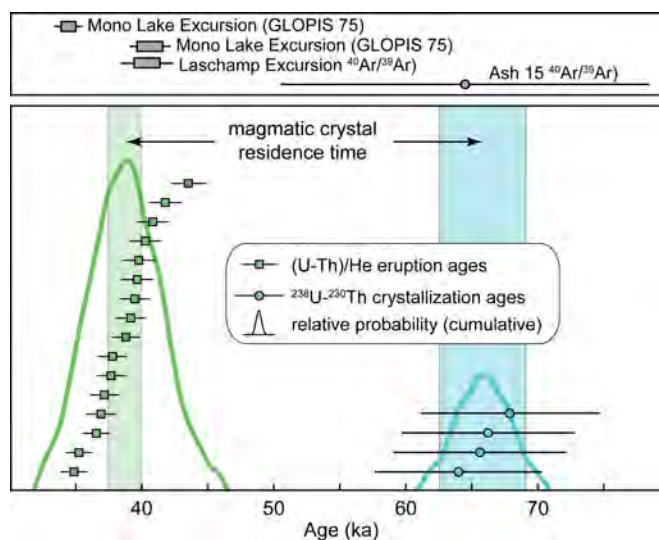


Figure 24. U-series ages from allanite and (U–Th)/He ages of eruption from ash layer 15, Mono Lake, eastern Sierra Nevada, California, USA. The U-series date (66.0 ± 3.3 ka, 2σ) was determined using ICP-MS (Cox et al. 2012) and reflects the average crystallization age in the magma. The (U–Th)/He date (38.7 ± 1.2 ka, 2σ) is the (helium) eruption age. These data yield a 27 ± 4 ka average residence time of allanite in the rhyolitic magma. Shown for comparison are $^{40}\text{Ar}/^{39}\text{Ar}$ data for Ash 15 and ages for two prominent magnetic excursions (Mono Lake and Laschamp).

FUTURE DIRECTIONS

- Further analytical developments will undoubtedly allow dating ever smaller volumes at higher precision. Of equal importance is sharpening and wielding tools that provide textural and microchemical context to these ages: X-ray maps from EPMA need to be combined with trace element maps from laser ablation methods, prior to spot dating.

- Thermodynamic models are needed for the main REE-minerals to make reliable prediction of the reaction relations involving major and accessory minerals and to enhance thermobarometry based on their composition. The lead taken by Janots et al. (2007), Spear (2010), and Spear and Pyle (2010) should be expanded, and for this purpose experimentally determined phase equilibria—ideally reaction reversals—are required that involve REE-phases and fully documented natural assemblages from well known P – T conditions.

• Pressure estimates need improving to link chronologic data, especially based on monazite and allanite. Since allanite frequently contains quartz inclusions, Raman micropiezometry (Kohn 2014b) on these might be attempted, though shear modulus data for epidote (Hacker et al. 2003) are but approximately valid for allanite. Radiation softening may also prove problematica. Elastic properties for the REE-phosphates were compiled by Mogilevsky (2007).

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