

CHAPTER 6: Th-Pb ion microprobe dating of allanite.

6.1. Introduction

Allanite, a member of the epidote group $[A_2M_3Si_3O_{12}(OH)]$, occurs primarily in regionally metamorphosed pelites and felsic igneous rocks. The mineral preferentially incorporates Th and U into its structure, and has been the subject of isotope dilution U-Th-Pb dating studies (Mezger et al., 1989; von Blackenburg, 1992; Barth et al., 1994a; Davis et al., 1994; Oberli et al., 1999). Using an ion microprobe to determine allanite ages has several advantages over conventional methods: dating of small grains ($\sim 15 \mu\text{m}$) is feasible and mineral separation is unnecessary, preserving rock textures and permitting appraisal of inclusion/host relationships. In addition, the ion microprobe has the capability to analyze small areas on grains unaffected by radiation damage and subsequent alteration.

In the allanite structure, the A-sites (A1 and A2) typically contain large, highly coordinated cations, such as Ca^{2+} , Sr^{2+} , or REE^{3+} , whereas the M-sites (M1, M2, and M3) admit octahedrally coordinated cations, including Al^{3+} , Fe^{3+} , Mn^{3+} , Fe^{2+} , or Mg^{2+} (Dollase, 1971). However, large amounts of additional elements (Th^{4+} , U^{4+} , Zr^{4+} , P^{5+} , Ba^{2+} , Cr^{3+} , and others) may be present in the mineral (see Deer et al., 1993). The variability makes allanite a challenging phase for ion microprobe analysis because significant matrix effects on the ionization efficiency of U, Th, and Pb could limit the use of even well characterized standards to a narrow compositional range. For example, U-Pb ages are routinely determined for zircon $[\text{Zr}(\text{SiO}_4)]$ with a precision of $\pm 1\%$ (Compston, 1999), whereas the precision of Th-Pb ages of monazite $[(\text{LREE,Th})\text{PO}_4]$ is

lower at $\pm 2\%$ (Harrison et al., 1995), and may reflect the greater potential for compositional substitution in monazite (e.g., 0-15 wt% ThO₂; Deer et al., 1993).

In this chapter, the use of a conventional ion microprobe calibration plot (e.g., ThO₂⁺/Th⁺ vs. ²⁰⁸Pb*/Th⁺) to determine Th-Pb allanite ages is shown to be restricted by matrix effects imposed on the ionization of Th⁺ and Pb⁺. However, involving FeO⁺/SiO⁺ as a proxy control permits the determination of Th-Pb ages of compositionally characterized allanite to approximately $\pm 10\%$ accuracy. The application of the method is illustrated by dating metamorphic allanite from the Nepal Himalaya and igneous allanite from a Californian pegmatite.

6.2. Review of allanite petrogenesis and mineral chemistry

The chemistry of epidote group minerals varies mainly in the A2 and M3 sites. Coupled substitution of REE³⁺ and Fe²⁺ for Ca²⁺ and Fe³⁺ relate allanite to epidote, and the major difference between the minerals is that ideal allanite contains only Fe²⁺ in the M-sites, whereas end-member epidote contains Fe³⁺ (Burt, 1989). The coupled substitution can be inferred from allanite electron microprobe analyses from a variety of rocks, including garnet amphibolite from the Catalina Schist, southern California (Sorensen, 1991), granitoids from the Western Carpathians, Slovakia (Petřík et al., 1995), and igneous, metamorphic, and hydrothermally altered rocks from the Isle of Skye, Scotland (Exley, 1980).

Backscattered-electron (BSE) images of allanite grains typically show zoning controlled by the abundance of light rare-earth elements (LREE), Fe, Th, and U (for

examples see Sorensen, 1991; Buda and Nagy, 1995; Petřík et al., 1995; and figures in this chapter). LREE zoning in allanite has been attributed to a complex interplay between coupled substitutions, mineral-structure constraints, and geochemical environment. For example, Affholter (1987) synthesized allanite under controlled pressure, temperature, and oxygen fugacity, and found Fe^{2+} in the M3 site expands its structure to accommodate LREE in the A2 site. Affholter (1987) concluded that natural allanite with epidote rims reflect a REE control indirectly related to oxygen fugacity, and if the environment were to become more oxidizing at a fixed pressure and temperature, epidote could form rather than allanite. In some hydrothermal allanite grains, $\text{Fe}^{2+}/\text{Fe}^{3+}$ decreases from LREE-rich cores to LREE-depleted, heavy REE-enriched rims (see Exley, 1980), and variations in LREE abundance in hydrothermal LREE-epidote grains are thought to reflect changes in fluid content (Sorensen, 1991). Sawka et al. (1984) interpreted similar zoning of granitoid allanite grains as the result of an evolving melt composition during differentiation and solidification.

Several investigators explored the significance of epidote as an indicator of minimum intrusion pressure of granodioritic and tonalitic magmas (Zen and Hammarstrom, 1984; Dawes and Evans, 1991; Schmidt and Thompson, 1996). Magmatic allanite, commonly found in cores of epidote, may be stable to higher temperatures than epidote (Schmidt and Thompson, 1996). Gieré et al. (1999) speculate that the stability of allanite in magmatic environments is closely related to temperature and H_2 fugacity rather than to the melt REE content or a threshold pressure. Franz et al. (1986) showed allanite is present under conditions of eclogite formation. Experiments

using basaltic-andesite, andesite, and rhyodacite glasses doped with REE contained stable allanite at 1050°C and 30 kbar (Green and Pearson, 1983). Crystalline allanite also formed in experiments run with trondhjemite glass + 50% H₂O at 900°C and 20 kbar (Adams et al., 1996). Hydrothermally synthesized, end-member Ce-allanite decomposes to britholite, anorthite, magnetite, quartz, and a Ce-silicate at 800°C, 1 kbar, and 0.25 X_{H₂O} (Affholter, 1987).

Although allanite appears more common in greenschist facies than at higher grades (Overstreet, 1967), its pressure and temperature stability in metamorphic rocks remains estimated from its textural relationship with monazite (Smith and Barreiro, 1990; Finger et al., 1998). For example, petrologic observations suggest monazite forms at ~500°C in pelitic rocks from allanite breakdown (Smith and Barreiro, 1990; Kingsbury et al., 1993; Wing et al., 1999). In metaluminous orthogneisses, magmatic allanite destabilizes to monazite and thorite at higher temperatures (700-760°C; Bingen et al., 1996). Monazite is typical in peraluminous granitoid rocks, whereas allanite is a common accessory mineral in CaO-rich metaluminous granitoid rocks (Broska and Siman, 1998). Lee and Bastron (1967) observed monazite-bearing granites with <0.7 wt% CaO, whereas allanite-bearing granites had >1.8 wt% CaO. Allanite and monazite coexist in pelitic schists with <0.5 wt% CaO (Smith and Barreiro, 1990).

6.3. Methods of analysis

6.3.1. Details of the ion microprobe dating technique

The CAMECA ims 1270 ion microprobe determines zircon U-Pb ages and monazite Th-Pb ages with 1-2% precision at ~15 μm spatial resolution (see Harrison et al., 1995; Quidelleur et al., 1997; Harrison et al., 1999b). Like monazite, allanite preferentially incorporates Th during growth, which results in relatively high radiogenic ^{208}Pb contents. The allanite grains in this study have ThO_2 concentrations up to 1.8 wt% and low common Pb, suggesting the mineral is a promising candidate for ion microprobe dating. However, allanite poses a challenge because Th^+ and Pb^+ ionization efficiencies may be highly sensitive to its variable composition (see Reed, 1985, 1986). Matrix effects associated with Fe-bearing minerals have been previously reported (Havette, 1985). The sputtering yields of Mg^+ in both olivine and Ca-poor pyroxene (Shimizu et al., 1978) and the Ca^+/Si^+ ratio of pyroxene increases as a function of Fe^+ intensity (Shimizu and LeRoex, 1986).

Individual allanite grains were mounted in epoxy, polished using 0.3 μm alumina, and carbon coated. A 2-4 nA primary O^- beam focused to a 15 x 20 μm spot produced a high ionization efficiency of Pb from allanite. These analyses were done using a 50 eV energy window and a ~10 eV offset for Th^+ . At a mass resolving power of ~6000, all Pb and Th isotopes were resolved from any significant molecular interferences (Fig. 6.1). Figure 6.2 shows the energy distributions for $^{232}\text{Th}^+$, $^{248}\text{ThO}^+$, $^{264}\text{ThO}_2^+$, and $^{208}\text{Pb}^+$ ions sputtered from the allanite are similar to those of monazite (see Harrison et al., 1995).

Th-Pb ion microprobe dating takes advantage of the kinetic energy distribution of the sputtered ions of Th and Pb (Harrison et al., 1995). Three isotope ratios are measured: $^{264}\text{ThO}_2^+ / ^{232}\text{Th}^+$, $^{208}\text{Pb}^+ / ^{232}\text{Th}^+$, and $^{204}\text{Pb}^+ / ^{208}\text{Pb}^+$. The $^{208}\text{Pb}^+ / \text{Th}^+$ is corrected

for common Pb using the relationship $^{208}\text{Pb}^*/\text{Th}^+ = (^{208}\text{Pb}^+/\text{Th}^+)\{1 - [(^{208}\text{Pb}/^{204}\text{Pb})_s(^{204}\text{Pb}^+/\text{Pb}^+)]\}$, where $(^{208}\text{Pb}/^{204}\text{Pb})_s$ is the known ratio of the standard. (The asterisk indicates the species is corrected for common Pb.) A linear relationship between $^{208}\text{Pb}^*/\text{Th}^+$ versus $\text{ThO}_2^+/\text{Th}^+$ is typically observed for monazite grains with known uniform Pb/Th ratio (Harrison et al., 1995). Isotopic data collected from several ion microprobe spots on the age standard define this linear relationship, and allow a correction factor to be derived by dividing the measured $^{208}\text{Pb}^+/\text{Th}^+$ of a standard grain at a reference $^{264}\text{ThO}_2/\text{Th}^+$ value by its known daughter-to-parent ratio. This correction factor permits the determination of Pb/Th ratios of unknown grains measured under the same instrumental conditions. For ion microprobe analyses of 20 Ma monazite, the precision of the 2-D calibration method is not limited by counting statistics, but by the reproducibility of the calibration curve (typically $\pm 2\%$; Harrison et al., 1995).

In this study, three materials are used as allanite Th-Pb dating standards. Two of the three, the Cima d'Asta Pluton (CAP) and Atesina Volcanic Complex (AVC) allanite, are from a calc-alkaline, volcanoplutonic association in the Southern Alpine domain, northern Italy. Using U-Th-Pb isotope dilution methods, Barth et al. (1994a) dated single grains of these samples and Barth et al. (1994b) found that no Pb was lost from these grains since they crystallized. Monazite inclusions within the CAP and AVC allanite grains were also dated with the ion microprobe (Fig. 6.3). Two allanite grains from the AVC rhyolite yielded an isotope dilution age of 276 ± 2 Ma (2σ ; Barth et al., 1994a). Using the ion microprobe, the monazite inclusion within an AVC allanite yielded a Th-Pb age of 254 ± 26 Ma (2σ ; assuming a common $^{208}\text{Pb}/^{204}\text{Pb}$ of 38.34). Although imprecise,

this date is within analytical uncertainty of the isotope dilution age. Four single grains of the CAP allanite yielded 276 ± 2 Ma, and a monazite inclusion within this allanite analyzed by the ion microprobe was consistent with the isotope dilution result at 266 ± 12 Ma (2σ).

The third allanite is from the La Posta Pluton (LPP), eastern Peninsular Ranges batholith, southern California. This pluton has a 94 ± 2 Ma (2σ) U-Pb zircon age (Walawender et al., 1990). Although no Th-Pb age on the coexisting allanite exists, this rock cooled relatively rapidly following emplacement, and concordance can be assumed between the U-Pb zircon and Th-Pb allanite ages. The LPP allanite grains show complex zoning (Fig. 6.4), but the pluton experienced little subsolidus deformation or alteration, and thus provides an excellent opportunity to examine silicate minerals that retain their primary magmatic character (Clinkenbeard and Walawender, 1989).

6.3.2. Details of allanite composition and zoning

Knowing the compositional variability within allanite grains analyzed with the ion microprobe is important because matrix effects may significantly alter the ionization efficiency of Th^+ and Pb^+ during sputtering. For example, Reed (1985) analyzed the REE content of allanite grains with the ion microprobe and determined a higher REE-oxide/REE secondary-ion ratio in the mineral compared to a standard glass. Reed (1985) attributed this difference to a matrix effect, and concluded that a compositionally characterized allanite rather than a synthetic glass should be used as a standard. To evaluate the role of allanite composition for ion-microprobe age determinations, detailed information about the standard and unknown grains is required.

Allanite grains from a variety of geologic settings were analyzed using the JEOL electron microprobe at the Smithsonian Institution's National Museum of Natural History operating at an accelerating potential of 15 kV and a probe current of 3.1×10^{-8} A. Corning synthetic standard glasses were used for Th (W glass) and U (X glass), and synthetic phosphates from Jarosewich and Boatner (1991) for Y and LREE. Since each REE produces at least 12 X-ray lines in the L spectrum, finding interference-free regions for background measurements and peak intensities can be difficult (see Exley, 1980; Williams, 1996; Reed and Buckley, 1998). For these analyses, the LREE peak positions recommended by Exley (1980) were used. Peak count times were 10 seconds with 5-second backgrounds for all elements, except for Th, U, and P in which 30 second count times and 10 second backgrounds were used. Background and dead-time apparent concentrations were corrected for matrix effects by standard ZAF procedures. To check for systematic errors, four Drake and Weill (1972) glasses were analyzed after every six allanite measurements. Table 6.1 lists the approximate detection limits and relative errors in the electron microprobe determinations.

BSE images and electron microprobe analyses reveal zoning in LREE, Fe, Th, and U within individual grains (see Figs. 6.3-6.6; and Tables 6.2-6.8). For all electron microprobe compositions reported here, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ was determined using the computer program LAG (Dollase and Newman, 1984), based on 8 cations and 12.5 oxygen atoms. The LPP analyses indicate that allanite may exhibit some substitution of Al for Si. Some BSE images show cryptically altered areas within single grains. Locations that had compositional information inconsistent with allanite's mineral formula may be altered by

radiation damage, fluid-mineral interaction, or subsolidus reactions with adjacent phases, and were avoided during *in situ* ion microprobe analysis.

6.4. Results

6.4.1. Electron microprobe analysis

The FeO contents of allanite grains vary from 11.1 to 14.4 wt% for AVC, 9.6 to 12.5 wt% for CAP, and 4.3 to 10.4 wt% for the LPP. Overall, Ce was the most abundant LREE in the allanite grains analyzed in this study. The Ce₂O₃ contents vary from 9.8 to 13.3 wt% for AVC, 9.3 to 13.4 wt% for the CAP, and 6.0 to 12.0 wt% for the LPP. The relative order of LREE content in these allanite grains is Ce > La > Nd > Pr > Sm > Gd and a chondrite-normalized plot shows these allanite grains are LREE enriched (Fig. 6.7). The general LREE patterns of the standard allanite grains are similar to those analyzed as unknowns, and to some LREE patterns in allanite reported from other locations (see Lee and Barston, 1967; Exley, 1980; Ward et al., 1992).

More than 150 analyses of 26 allanite grains are compared to those reported in the literature by assigning elements to sites and displaying the results by geologic setting (Fig. 6.8). The A-site elements are REE, Ca, Sr, Th, and U, whereas Fe, Al, Mg, Cr, Mn and Ti are assigned to the M-sites. Analyses done for this dissertation include the standard grains in this study (Tables 6.2-6.4) and allanite from the Pacoima Canyon pegmatite in southern California (Table 6.5), pelites and gneisses from central Nepal (Table 6.6), granulite facies rocks near Cauchon Lake in Canada (Table 6.7), and Long Valley rhyolite in central California (Table 6.8). These data have Si between 2.97 and

3.01 atoms per formula unit and weight percent totals between 97% and 100%. By plotting the excess of elements in the A-sites versus excess in the M-sites, we find a consistent A-site deficiency and M-site excess (Fig. 6.8). The lines in Figure 6.8 show how the data should plot if both A-site deficiency and M-site excess exist, as would be the case if some cation (or portion thereof) was assigned to the M-site instead of the A-site. Peterson and MacFarlane (1993) interpreted A-site deficiency in allanite to result from a vacancy substitution of the form: $3\text{Ca}^{2+} \leftrightarrow 2\text{REE}^{3+} + \text{vacancy}$. Most of the data in Figure 6.8, however, lie along the line, indicating A-site deficiency = M-site excess. A simple explanation is that some Fe^{2+} was incorporated into the A-sites, substituting for Ca^{2+} . The presence of Fe^{2+} in the A-sites has implications for the calculation of oxygen fugacity from allanite compositional data (e.g., Petrík et al., 1995).

6.4.2. Ion microprobe analyses

For dating monazite using the Th-Pb ion microprobe method, a linear relationship between $^{208}\text{Pb}^*/\text{Th}^+$ versus $\text{ThO}_2^+/\text{Th}^+$ is typically observed for multiple spot analyses on grains used as age standards (Harrison et al., 1995, 1999b). The CAP and AVC allanite grains are of similar age [276 ± 2 Ma (2σ); Barth et al., 1994a], and by analogy to monazite, the same linear relationship for the allanite is expected. However, the ThO_2^+ sputtering yield is enhanced in allanite from the AVC relative to CAP (Fig. 6.9). Using the conventional 2-D calibration, the age of AVC allanite cannot be reproduced accurately using the CAP allanite as a standard with a defined 276 Ma age (Table 6.9). Thirteen ion microprobe spots on two Cima d'Asta allanite grains yielded a poor linear correlation coefficient of 0.41 between $^{208}\text{Pb}^*/\text{Th}^+$ versus $\text{ThO}_2^+/\text{Th}^+$. Using this

calibration line, seventeen ion microprobe spots on two of the AVC allanite grains yielded a significantly younger apparent age [137 ± 20 Ma (2σ)] than reported by Barth et al. (1994a).

Electron microprobe analyses show the two allanite populations differ by 4 to 7 wt% FeO. Fe is a major constituent of allanite and previous studies documented matrix effects associated with Fe-bearing minerals (Shimizu et al., 1978; Ray and Hart, 1982; Havette, 1985; Shimizu and LeRoex, 1986), so Fe is used as a proxy to examine the relative ionization efficiencies. On a plot $\text{FeO}^+/\text{SiO}^+$ versus $\text{ThO}_2^+/\text{Th}^+$, spots on allanite grains from five different localities and having different Fe contents yield a roughly linear relationship (Fig. 6.10).

By adding Fe content as a third dimension to the typical calibration plot, an internally consistent set of ages that agree within uncertainty with results from single-grain, isotope-dilution measurements is obtained. Initially, the Fe-content measured with the electron microprobe was used at the spot from which the isotopic data were obtained. For the data reported in this dissertation, an ion microprobe measurement of the $\text{FeO}^+/\text{SiO}^+$ ratio was collected on the same spot used for the Pb^+ and Th^+ analyses.

Plotted in the three-dimensional space as described above, the CAP and AVC allanite grains lie on the same calibration plane, whereas the LPP allanite grains are younger and define a separate, internally consistent, calibration (Figs. 6.11-6.13; Tables 6.10-6.13). The plane may be described by the equation $^{208}\text{Pb}^*/\text{Th}^+ = A(\text{FeO}^+/\text{SiO}^+) + B(\text{ThO}_2^+/\text{Th}^+) + C$, where A, B, and C are constants derived by multivariate regression of several ion microprobe analyses of the allanite age standard. The age of an unknown is

given by $(\ln \{1 + [({}^{208}\text{Pb}^*/\text{Th})_s({}^{208}\text{Pb}^*/\text{Th}^+)_{\text{unk}}] / [A(\text{FeO}^+/\text{SiO}^+) + B(\text{ThO}_2^+/\text{Th}^+) + C]\}) / \lambda$ where $({}^{208}\text{Pb}^*/\text{Th})_s$ is the known ratio for the standard corrected for common Pb, $({}^{208}\text{Pb}^*/\text{Th}^+)_{\text{unk}}$ is the ion microprobe ratio corrected for common Pb for an allanite grain of unknown age, and λ is the decay constant of ${}^{232}\text{Th}$ in years. If the system remained closed from Pb loss, a 276 Ma allanite grain should have a $({}^{208}\text{Pb}^*/\text{Th})_s = 1.37 \times 10^{-2}$ and a 94 Ma allanite grain should have a $({}^{208}\text{Pb}^*/\text{Th})_s = 4.66 \times 10^{-3}$.

Using the AVC allanite as the 276 Ma age standard (Table 6.10 and Fig. 6.11), this method yields an age of 288 ± 6 Ma (1σ) for nine spots on three CAP allanite grains. If the 2-D calibration was used, the same spots yield an older, more uncertain age of 324 ± 24 Ma (1σ). In Table 6.11 and Figure 6.12, the LPP allanite is used as the 94 Ma age standard to reproduce the CAP and AVC allanite ages. Twelve spots on three LPP allanite grains define the plane, which yielded an age of 250 ± 17 Ma (1σ) for both the AVC and CAP allanite samples. Although the ages show a wide range (i.e., from 180 ± 11 Ma to 299 ± 17 Ma for the CAP allanite in Table 6.11), the average age of all the results are within 2σ of the single grain isotope dilution ages reported (Barth et al., 1994a).

Table 6.12 summarizes the ion microprobe results from the CAP, AVC, and LPP allanite grains analyzed in this study. Typically, the CAP and AVC allanite grains produce a 3-D calibration curve that reproduces the 276 Ma age with an accuracy of 2-5%, whereas the LPP allanite calibration curve yields the 94 Ma age with an accuracy of 6-12%. The less accurate LPP results may relate to the amount of ${}^{208}\text{Pb}^*$, as the AVC and CAP allanite grains are highly radiogenic ($97 \pm 2\%$) whereas the LPP allanite grains are somewhat less so ($73 \pm 15\%$), or reflect additional matrix effects.

The data in Table 6.12 indicate that the 3-D calibration method significantly improves the precision and accuracy of age determinations for allanite grains with different Fe contents over the conventional 2-D calibration method. In this study, the 3-D calibration method specifically applies to allanite grains with different Fe contents. If the allanite contained similar amounts of Fe, the 2-D calibration has the potential for better results because the sputtering yield of Pb^+ and Th^+ from both standard and unknown would be similarly affected. The 3-D calibration method is intended for ion microprobe analysis of allanite grains that differ by more than about 1 wt% FeO from the allanite standard. The matrix effects on the ionization efficiency of Pb^+ and Th^+ restrict the use of the 2-D calibration to compositionally well-characterized standards and unknowns with essentially the same Fe content.

The accuracy of the 3-D calibration method for Th-Pb allanite analyses is less than routinely expected from U-Th-Pb analyses of zircon or monazite and is probably due to enormous compositional variability in allanite relative to the other phases. However, a number of important geologic problems can still be addressed using this dating method.

6.5. Discussion: Applications of the method

The 3-D Th-Pb calibration method was applied to allanite grains from different geologic environments: metamorphic allanite from the footwall of a major thrust fault in central Nepal and allanite from the Pacoima Canyon pegmatite in southern California.

Garnet-bearing schist samples MA27 and MA33 were collected beneath the Main Central Thrust (MCT) along the Marysandi River in central Nepal. The MCT is one of

the major tectonic structures that formed as the result of the collision that telescoped the Indian margin (e.g., Le Fort, 1996). The fault marks the base of the sharp change in elevation of the present-day Himalayas and accommodated several hundred kilometers of slip (e.g., Srivastava and Mitra, 1994). There is no break in metamorphic facies across the MCT and metamorphism within the footwall increases up-section (i.e., is 'inverted') towards the fault from zeolite to kyanite grade over a N-S distance of ~20 km (e.g., Colchen et al., 1980). MCT slip has been linked to the origin of the apparent inverted metamorphic sequence (e.g., Le Fort, 1996), and proposed to occur simultaneously with extension within the range (e.g., Hodges et al., 1992, 1998). Knowing the slip history of the thrust is important to deciphering the evolution of the Himalayan range, but significant gaps exist in our understanding.

Geochronologic studies show the hanging wall was deforming at ~22 Ma (e.g., Hodges et al., 1996). Th-Pb ion microprobe analyses of monazite inclusions in garnets from rocks of the inverted metamorphic sequence indicate the footwall shear zone was active at ~6 Ma (e.g., Harrison et al., 1997b). Petrographic observations of pelitic rocks indicate monazite first appears in the garnet zone, whereas allanite is the principal host of LREE in chlorite- and biotite-zone rocks. To determine if the allanite grains record Late Miocene MCT activity, ion microprobe measurements of coexisting monazite and allanite grains from rocks collected from the thrust's footwall were made.

Sample MA27 is structurally closer to the hanging wall (~0.2 km), whereas sample MA33 is ~8 km further south. The mineral assemblage for both samples is garnet + biotite + muscovite + chlorite + plagioclase + rutile + ilmenite. Sample MA27 contains

matrix monazite and allanite inclusions in garnet, and sample MA33 contains monazite in both the matrix and garnet rims, but allanite only in garnet cores. Matrix monazites from sample MA27 yield a Th-Pb age of 17.7 ± 0.8 Ma (1σ), whereas MA33 matrix monazite and garnet rim inclusions record Late Miocene crystallization at 6.7 ± 0.3 Ma (1σ).

Garnet-biotite thermometry (Ferry and Spear, 1978; Berman, 1990) and garnet-biotite-muscovite-plagioclase barometry (Powell and Holland, 1988; Hodges and Spear, 1982) result in temperatures and pressures of the garnet rim in MA27 of $640 \pm 30^\circ\text{C}$ and 8.7 ± 0.8 kbar. The garnet rim of sample MA33 yielded lower pressures and temperatures of $570 \pm 20^\circ\text{C}$ and 6.2 ± 0.4 kbar. Compositional traverses of Mn, Mg, Ca, and Fe in garnets from these rocks were made to discern their zoning patterns. Sample MA27 garnets exhibit zoning in Mn, Mg, Ca, and Fe consistent with diffusion, whereas garnet zoning in sample MA33 is consistent with either a polymetamorphic history or a significant change in mineral assemblage. The MA33 garnet sharply decreases in Ca and Mn, and increases in Mg and Fe within 0.2 mm of the rim. The ~ 7 Ma monazite grains are only found within this garnet rim.

Allanite inclusions in garnet from samples MA27 (445 ± 16 Ma, 1σ ; Table 6.13) and MA33 (252 ± 7 Ma, 1σ) gave significantly older ages than coexisting monazite. These results indicate allanite formation in these rocks is unrelated to MCT slip, but may represent variable Pb loss from a grain associated with the older Pan-African orogeny (Le Fort et al., 1986). The result for MA33 is consistent with two-stage garnet growth and has implications for the timing and evolution of the inverted metamorphism that affected the MCT footwall.

The 3-D calibration method is also applied to the analysis of an allanite grain from the Pacoima Canyon pegmatite, southern California, known informally as the “allanite pegmatite” (Silver et al., 1963) because of its high abundance. This allanite is well known in mineralogical circles because it has been the subject of detailed structural studies (e.g., Dollase, 1971). The Pacoima Canyon pegmatite contains large (several mm sized) euhedral allanite grains that appear unaffected by alteration. This allanite sample was obtained from the Smithsonian Institution’s National Museum of Natural History. Electron microprobe analyses indicate the mineral contains ~1.1 wt% ThO₂. Isotope dilution U-Pb zircon ages from the pegmatite yield an age of 1191±4 Ma (Silver et al., 1963; Barth et al., 1995). Using the LPP allanite as a standard, a Th-Pb age of 1006±37 Ma (1σ; 2 spots on 1 grain) is obtained. Although the uncertainty is relatively large, these ages suggest cooling below the closure temperature of Pb in allanite occurred more than 100 million years following crystallization of the pegmatite.

The data suggest *in situ* Th-Pb ion microprobe dating of allanite can be used to address geologic questions with an age accuracy of ±10%. This method permits *in situ* dating of small (~15 μm) grains and those included in phases such as garnet, with the spatial selectivity to analyze areas unaffected by alteration. Although the extreme compositional variability of the phase poses a challenge for ion microprobe analysis, a 3-D calibration plot (²⁰⁸Pb*/Th⁺ vs. ThO₂⁺/Th⁺ vs. FeO⁺/SiO⁺) overcomes the problem at a level of accuracy of about ±10%.

6.6. Conclusions

Allanite, which is a common accessory mineral in a variety of rock types, typically contains high Th and U concentrations; thus, an *in situ* method of U-Th-Pb dating of this phase has broad application. This chapter describes a technique to obtain Th-Pb ages of allanite with approximately $\pm 10\%$ accuracy using a high-resolution ion microprobe. Knowledge of the composition and substitution mechanisms of this complex mineral is essential to understanding the relative ionization efficiencies of Th^+ and Pb^+ . The chemical compositions of three allanite samples used as age standards (CAP, 275.5 ± 1.5 Ma; AVC, 276.3 ± 2.2 Ma; LPP, 94 ± 2 Ma) were determined using an electron microprobe, permitting an assessment of matrix effects on ionization. An ion microprobe calibration curve involving elemental and oxide species of Th and Pb (i.e., $^{208}\text{Pb}^*/\text{Th}^+$ vs. $\text{ThO}_2^+/\text{Th}^+$) yields highly scattered apparent ages when allanite age standards with different Fe-content are used. However, a three-dimensional plot of $^{208}\text{Pb}^*/\text{Th}^+$ vs. $\text{ThO}_2^+/\text{Th}^+$ vs. $\text{FeO}^+/\text{SiO}^+$ improves the calibration accuracy to about $\pm 10\%$. Although this level of uncertainty is substantially greater than expected for U-Th-Pb ion microprobe analyses of zircon or monazite, Th-Pb ages of allanite can still be used to address important geologic questions.

This method is used to date two metamorphic allanite grains from the footwall of the MCT, Nepal Himalaya, and an allanite grain from the Pacoima Canyon pegmatite, California. Allanite inclusions in garnet from Nepal yield significantly older ages than the coexisting monazite, indicating allanite formation in these rocks records a previous metamorphic cycle predating slip along the fault. The Pacoima Canyon allanite grain

yields a younger age than reported for zircon, implying Pb loss during cooling of the pegmatite.