

CHAPTER 5. *In situ* methods of analysis.

I knock at the stone's front door.

“It's only me, let me come in.”

“I don't have a door,” says the stone.

[Excerpt from “Conversations with a Stone” Szymborska (1993)]

5.1. Introduction

Th-Pb ion microprobe ages of monazite inclusions in garnet porphyroblasts and within the deformed rock matrix were obtained from samples adjacent to the Main Central Thrust (MCT) in northern India, central and eastern Nepal. These data are combined with thermobarometric estimates from their garnet-bearing metamorphic mineral assemblages.

This method to obtain the deformation history of the Himalayan orogen differs from that attempted previously in that earlier efforts required mineral separation (e.g., Hodges et al., 1992; Nazarchuk, 1993; Hodges et al., 1996; Coleman, 1998; Dèzes et al., 1999; Simpson et al., 2000). This dissertation reports *in situ* ion microprobe analyses of radiogenic element-bearing minerals in standard polished rock thin sections (e.g., Hinton, 1995). The technique is non-destructive of textural relationships, analysis of small grains (~15 μm) and zones within larger grains is feasible, and results are available within a few minutes (e.g., Harrison et al., 1995). Despite the capability of textural preservation, most

ion microprobe studies report ages of minerals separated from the sample (e.g., Wiedenbeck et al., 1996; Whitehouse et al., 1997; Seth et al., 1998; Mishra et al., 1999; Aleinikoff et al., 2000). The ages reported here are *in situ*, meaning “in thin section.”

Himalayan garnets typically contain monazite inclusions, and the combination of thermobarometric and geochronologic analyses is a powerful strategy to decipher the chronology of metamorphic events recorded in the range. Ion microprobe dating offers a rapid, *in situ* method for obtaining timing information from domains within the garnet that provide pressure-temperature (P-T) constraints. This chapter demonstrates the methods used to preserve and interpret the critical textural context of the ages to better understand the complex, multistage history of the Himalayan orogeny.

5.2. *In situ* Th-Pb ion microprobe dating of monazite

5.2.1. Review of monazite petrogenesis and chemistry

Monazite (CePO_4) is a common accessory mineral found in the metapelitic lithologies that dominate Himalayan metamorphic sequences. The mineral preferentially incorporates ThO_2 (e.g., Overstreet, 1967) and is typically zoned. For example, Figure 5.1 shows grains of monazite 554, the age standards used in this study. These grains are ~4 wt% ThO_2 (Table 5.1), considered a medium range for the mineral (see Stern and Sanborn, 1998), which has been reported to incorporate ~32 wt% ThO_2 (Overstreet, 1967). Th cations enter the monazite structure via the coupled substitution of $\text{Th} + \text{Si} \rightarrow \text{REE} + \text{P}$ (e.g., Burt, 1989). Compositional analyses of the mineral from a variety of

geologic settings clearly demonstrate the relationship (Tables 5.1 and 5.2; Fig. 5.2). Th cations can also be accompanied by Ca^{2+} , F, or $(\text{OH})^-$ (Kucha, 1980).

Monazite is an excellent candidate for geochronology. The mineral sustains little radiation damage upon annealing (e.g., Eyal and Kaufman, 1982; Montel et al., 1996; Meldrum et al., 1998), and has even been explored as a durable host phase for radioactive waste from nuclear weapons and reactors (e.g., Meldrum et al., 1996; Bakker et al., 1998). Its natural “radiation resistance” is speculated to be due to strong bonds between P and O and its mineral structure, which has a lower symmetry compared to zircon, thereby mitigating α -particle damage (Meldrum et al., 1996, 1997). Monazite is relatively impervious to Pb loss (Kingsbury et al., 1993; Smith and Gilletti, 1997; Teufel and Heinrich, 1997), and inclusions in garnet are further armored due to the low solubility and permeability of the daughter product in the host (Montel, 1995; Zhu et al., 1997; Montel, 1999).

Numerous studies attempted to date monazite using an electron microprobe (e.g., Montel et al., 1996; Bindu et al., 1998; Braun et al., 1998; Cocherie et al., 1998; Finger et al., 1998; Crowley and Ghent, 1999; Williams et al., 1999; Martelat et al., 2000). The instrument’s detection limit for Pb hinders the utility of the chemical age results (e.g., Olsen and Livi, 1998). Montel et al. (1996) suggest the technique is feasible for >100 Ma monazite, and typical precision is $\pm 30\text{-}50$ Ma for a total counting time of ~ 10 min. The precision of ion microprobe monazite analysis is limited by the reproduction of a calibration curve, and is usually $\pm 2\%$ for Th-Pb ages of ~ 20 Ma grains (Harrison et al., 1995, 1999b).

Table 5.2 lists compositions of Himalayan monazites from three rocks collected along the Marysandi River transect. These grains range in ThO₂ concentrations from 0.3-10.8 wt%, whereas the UO₂ contents are 0.4-0.7 wt%. Montel (1993) reports monazite compositions from the Greater Himalayan Crystallines and Manaslu injection complex in central Nepal of 3.4-8.6 wt% ThO₂ and 0.02-2.4 wt% UO₂. Based on 731 analyses, Overstreet (1967) reports that uranium is commonly present in monazite but rarely >0.5 wt%. Despite these observations, most workers insist on dating aliquots of Himalayan monazite using the U-Pb system, producing ages with large uncertainties (see Nazarchuk, 1993; Hodges et al., 1996; Coleman, 1996b, 1998 for examples).

Problems could originate with the U-Pb isotope dilution method of dating if the grains contain: (1) an inherited component (e.g., Copeland et al., 1988), (2) small amounts of U and Pb thereby meeting instrumental limitations, or (3) excess ²⁰⁶Pb from enrichments in ²³⁰Th during crystal growth (Schärer, 1984; Parrish, 1990). External influences can also lead to greater uncertainty including: (1) Pb loss from prolonged experience above the closure temperature, (2) Pb loss due to a dissolution-reprecipitation process, or (3) incorporation of unsupported radiogenic ²⁰⁶Pb or ²⁰⁷Pb from included minerals, such as uraninite or xenotime (e.g., Hawkins and Bowring, 1997). The spatial resolution of the ion microprobe and its capability to preserve textural relationships help to identify and overcome many of these issues, and problems with U-Pb dating can be resolved by using the Th-Pb method.

5.2.2. Sample preparation

Monazite grains were located in uncovered thin sections of rock using backscattered electron (BSE) petrography and energy dispersive X-ray spectroscopy (EDS) with a scanning electron microscope or electron microprobe. Many are zoned, irregularly shaped, and vary from 20 to 200 μm . The grains were easily spotted using this technique because this mineral was typically the brightest phase.

Monazite grains suitable for ion microprobe analysis were documented with detailed BSE images. An image was taken of the mineral at close range and mosaics recorded its location relative to easily identifiable features in the thin section, such as large garnets, tourmaline grains, or cracks. The conductive carbon coating was then stripped off using diamond polishing compound.

The monazites were re-identified and documented using an optical microscope so the portion containing the grains and minerals used for thermobarometry could be removed with a high-precision saw. The portion of the section was then mounted in epoxy with a block of ~5 grains of polished age standards (monazite 554; Harrison et al., 1999b). Figure 5.3 is an example of a 1-inch epoxy ion microprobe mount.

To aid in grain relocation using the ion microprobe, reflected light images were taken of the mount using an optical microscope fitted with a digital camera. The sample was cleaned in distilled water and high-purity ultrasonic cleanser, and carbon or gold coated. Monazite grains were analyzed using a CAMECA ims 1270 ion microprobe at UCLA.

5.2.3. Details of the *in situ* ion-microprobe monazite dating technique

The dating method takes advantage of the kinetic energy distribution of the Th and Pb ions sputtered from monazite using a primary oxygen (O) beam focused to a 15 x 20 µm spot (see Harrison et al., 1995, 1999b for details). The primary beam varied from 2-20 nA, depending on the speculated age of the unknown. Typically, a 50 eV energy window and a ~10 eV offset for Th⁺ were used. At a mass resolving power of ~4500, all Pb and Th isotopes were resolved from any significant molecular interferences.

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 $^{208}\text{Pb}^* / \text{Th}^+ = (^{208}\text{Pb}^+ / \text{Th}^+) \{ 1 - [(^{208}\text{Pb} / ^{204}\text{Pb})_s (^{204}\text{Pb}^+ / ^{208}\text{Pb}^+)] \}$, 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 (see Harrison et al., 1995). Isotopic data collected from several ion microprobe spots on the age standard define this linear relationship (e.g., Fig 5.4), and allow a correction factor to be derived by dividing the measured $^{208}\text{Pb}^+ / ^{232}\text{Th}^+$ 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 limited by the reproducibility of the calibration curve (Harrison et al., 1995, 1999b).

5.3. Thermobarometric analytical procedures

After the monazite grains were documented with BSE petrography (see section 5.2.2.), the thin section was subjected to thermobarometric analysis using an electron microprobe.

Garnets commonly show zoning that reflects growth events or diffusional modification (e.g., Spear, 1993; Spear and Kohn, 1996; Azor et al., 1997; Davidson et al., 1997; Kohn et al., 1997), thus provide information about the integrated thermal history of the sample. X-ray compositional maps in Mn, Ca, Fe, and Mg were taken of Himalayan garnets using an electron microprobe to qualitatively evaluate their zoning patterns. A current of 120-200 nA, beam size of ~2 μm , and count-times of 30-35 ms. gave in the clearest results. These maps identified regions on the garnet with the lowest Mn and Fe/(Fe+Mg), ideal areas for estimating minimum P-T conditions (e.g., Spear and Peacock, 1989).

Recent reviews of Himalayan P-T data predict a majority of samples experienced retrograde net transfer reactions (ReNTRs), which involve the production and consumption of minerals used for thermobarometry (see Kohn and Spear, 2000). Biotite and garnet become more Fe-rich, causing the estimated temperatures to be greater than the actual peak experienced. Conditions reported elsewhere for the garnet-bearing rocks of the Greater Himalayan Crystallines may be erroneous by hundreds of degrees and several hundred megapascals.

To address the potential for ReNTRs in the Himalayan assemblages analyzed in this dissertation, several analyses of minerals important for the thermobarometric calculations were taken both near and far from the garnet to explore compositional

heterogeneity. Garnet, muscovite, plagioclase, biotite, and chlorite were analyzed with the electron microprobe operating at an accelerating potential of 20 kV and a primary current of ~10 nA. Maximum count-times were 20 s, and all raw data were reduced using the ZAF matrix correction. Typically, matrix mineral compositions were taken, but for some rocks along the Everest transect (ET33, ET52), plagioclase and biotite inclusions in garnet were analyzed.

Peak pressure and temperature conditions attained by samples collected along the MCT were then estimated using thermodynamic calculations. The garnet-biotite thermometer of Ferry and Spear (1978) with the Berman (1990) garnet solution model and the garnet-plagioclase-biotite-muscovite barometer of Hoisch (1990) were used. In some rocks, plagioclase was not found, so only a maximum temperature was estimated. Different thermobarometric calibrations change the P-T conditions reported for these samples by $\pm 25^{\circ}\text{C}$ and ± 1 kbar (e.g., Hodges and Spear, 1982; Powell and Holland, 1988), but the general trends are preserved. For sample ET45, the garnet-chlorite thermometer of Dickenson and Hewitt (1986) and Laird (1988) with the Berman (1990) garnet solution model was applied. In one garnet amphibolite collected along the Darondi Khola (DH38), the garnet-hornblende geothermometer of Graham and Powell (1984) and the barometer of Kohn and Spear (1990) were employed. Evidence to support the pressures and temperatures reported for the samples analyzed here is that the estimated conditions agree with (1) the observed mineral assemblages, (2) absence of partial-melting textures, and (3) P-T conditions of other assemblages collected nearby.

P-T path calculations were obtained using the methods outlined in Spear and Selverstone (1983) and Spear (1993). Details regarding samples from the Darondi Khola transect is also reported by Kohn et al. (2000). All rocks were modeled with the observed solid assemblage garnet + biotite + chlorite + muscovite + plagioclase + quartz in the MnNCKFMASH system. A pure H₂O fluid at lithostatic pressure was also assumed. Activity models do not significantly affect the trends of retrieved P-T paths (Kohn, 1993), and all mineral solutions were assumed to be ideal, excepting garnet for which the Berman (1990) activity model was assumed. No staurolite, chloritoid, or carbonate minerals are present in these samples, either as matrix minerals or as inclusions in the garnet. Chemical zoning in the garnets analyzed is smooth and typical of garnet growth in the observed assemblage. Plagioclase grains show core-rim zoning with higher-Ca cores and lower-Ca rims. This is also the expected consequence of garnet growth and fractional crystallization in a closed chemical system, as growth of garnet depletes the remaining matrix in Ca (Spear et al., 1990). For some Darondi Khola samples, an intermediate point was used in the P-T path calculations.

5.4. Discussion: linking the P-T-time information

Combining monazite ages and thermobarometric constraints is a powerful method of obtaining the tectonic history of the Himalaya. The rock is temporally constrained at depth within the Earth, and its exhumation rate can be calculated. The garnet rim P-T data allows an evaluation of the amount of Pb diffusion possibly suffered by the monazite

grain (see Smith and Gilletti, 1997). The age of an inclusion within the garnet core can be placed at the origin of an estimated P-T path.

The monazite grains analyzed in this dissertation were found in rocks that experienced differing tectonic and thermal histories. Rocks with garnets that yield zoning patterns characterized by diffusion (e.g., Mn increases at the rims) tend to reveal a range of Th-Pb monazite ages. In these samples, monazite inclusions in garnet were older than those in the matrix. Rocks with garnets that show prograde growth patterns (e.g., bell-shaped Mn profiles) typically contain monazite grains that suggest a single age population and inclusion ages are within error of those in the matrix. In some cases, rocks contain monazite inclusions in fragmented pieces of garnet and P-T conditions appear unrecoverable. In these scenarios, information was derived from multiple analyses of monazite found in different textural situations within the rock as well as thermobarometric and geochronologic data from surrounding samples, thereby allowing an age interpretation.

The *in situ* ion microprobe monazite ages reported here are unaffected by problems plaguing studies that rely on mineral separation. The spatial resolution of the ion microprobe allowed other radiogenic-bearing minerals near or in contact with the monazite grain to be avoided, and the polymetamorphic history of samples and core-rim relationships of grains could be clarified. The history of rocks adjacent to the MCT predicted by models of the evolution of the Himalaya can be evaluated using the methods outlined in this chapter.