Monazite Th-Pb age depth profiling

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ABSTRACT
The significant capabilities of the ion microprobe for thermochronometric investigations of geologic materials remain largely unexploited. Whereas 208Pb/232Th spot analysis allows ~10-mm-scale imaging of Pb loss profiles or overgrowths in sectioned monazite grains, the spatial resolution offered by depth profiling into the surface region of natural crystals is more than two orders of magnitude higher. We document here the ability of the high-resolution ion microprobe to detect 208Pb/232Th age differences of <1 m.y. with better than 0.05 μm depth resolution in the outer micron of Tertiary monazites from the hanging wall of the Himalayan Main Central thrust. Age gradients on this scale are inaccessible to ion microprobe spot analysis or conventional thermal ionization mass spectrometry. Interpretation of the near-surface 208Pb distributions with available monazite Pb diffusion data illustrates the potential of the approach for recovering continuous, high-temperature thermal history information not previously available.

EXPERIMENTAL APPROACH
Specimen DH-68-96 was obtained from a posttectonic granite pegmatite dike in the Darondi Khola, central Nepal, that was intruded into hanging-wall gneisses of the Main Central thrust. The sampled location is 100–200 m structurally above the mapped position of the thrust (Colchen et al., 1986). Existing thermochronologic data indicate that the hanging-wall rocks were exhumed from ~20 km depths during the late Miocene and Pliocene (8–3 Ma) by renewed thrusting in the shear zone beneath the Main Central thrust (Harrison et al., 1997, 1998). Tabular monazites exhibiting morphologies consistent with preservation of primary crystal faces were hand-selected from a heavy mineral concentrate. Grain dimensions parallel to the basal plane of monazite (Zeitler et al., 1989). However, available Pb diffusion data (Smith and Giletti, 1997) indicate that significant age variations can be expected near the margins of monazite following protracted cooling or transient heating. By forward modeling age profiles from the outer several microns of monazite using appropriate solutions to the diffusion equation (Dodson, 1973), it should be possible to obtain continuous thermal histories extending from well above 600 °C to about 400 °C (Smith and Giletti, 1997). We have developed a method to determine precise 208Pb/232Th age profiles in the near-surface region of monazite crystals as young as 5 Ma with a depth resolution of better than 0.05 μm. This method was applied to a hanging wall of the Main Central thrust in the central Himalaya with the goal of recovering thermal history information related to its displacement history.

INTRODUCTION
Because the traditional goal of basement geochronology is to determine rock formation ages, dating methods based upon daughter products of radioactive decay that are not completely retained within mineral hosts under crustal conditions failed in this role. However, the recognition that the inhomogeneous distribution of daughter product produced by diffusion in comparatively unretentive phases can provide a rich record of paleotemperature variation with time has significantly expanded the focus of radiometric age dating (Dodson, 1973). Until recently, such thermal history analysis has largely been the domain of the K-Ar and fission-track dating methods, which has restricted its applicability to temperatures less than about 500 °C (McDouggall and Harrison, 1988). With the advent of U-Pb ion microprobe dating of accessory minerals (Compston et al., 1984), it has become possible to routinely resolve age variation down to the ~10-mm-scale imaging of Pb loss profiles or overgrowths in sectioned monazite grains, the spatial resolution offered by depth profiling into the surface region of natural crystals is more than two orders of magnitude higher. We document here the ability of the high-resolution ion microprobe to detect 208Pb/232Th age differences of <1 m.y. with better than 0.05 μm depth resolution in the outer micron of Tertiary monazites from the hanging wall of the Himalayan Main Central thrust. Age gradients on this scale are inaccessible to ion microprobe spot analysis or conventional thermal ionization mass spectrometry. Interpretation of the near-surface 208Pb distributions with available monazite Pb diffusion data illustrates the potential of the approach for recovering continuous, high-temperature thermal history information not previously available.

Details of analytical protocols for 208Pb/232Th dating of monazite using the CAMECA ims 1270 ion microprobe were given in Harrison et al. (1995, 1999). To summarize, a mass resolving power of 4500 adequately separates all molecular interferences in the 204–208 mass range. The Pb/Th relative sensitivity factor required to calculate a Th-Pb age from isotope data obtained from an unknown is determined by referring the ThO4/Th* determined in the analysis to a calibration curve that is constructed from measurements of ThO4/Th* vs. Pb/Pb* from 554 standard monazite. The appreciable (typically 3%–8%) Th concentrations in monazite (Montel, 1993) and ~1% ionization efficiency for Pb under O+ bombardment are sufficiently favorable that the precision of 208Pb/232Th age determinations of samples older than ca. 5 Ma is limited by the reproducibility of the calibration curve (typically ±2%; Harrison et al., 1995, 1999). Data from both polished and unpolished 554 monazite were regressed together to define the calibration line used to reduce results from DH-68-96 monazite. As shown in Figure 1, results obtained from the outer 0.1 μm of unpolished 554 monazite deviates significantly from the calibration line.

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Corrections for common 208 Pb used to calculate sis indicated that drift was generally <1%/hr.

primary beam current both before and after analy-
peak centering was 2–3 min. Measurement of the sputtering to remove the Au coat and perform profiling experiments lasted 1 hr, whereas initial analysis (Table 1 [see footnote 1]). Most depth ing for the duration of initial sputtering prior to ing for drift in primary beam current and allow-
calculated from this relationship after normaliz-

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RESULTS

Depth profiling analysis of unpolished 554 monazite revealed monotonically increasing ages from 38 to 45 Ma over the first 0.15 µm and homogeneous ages thereafter (Fig. 3A). Such relatively minor near-surface depletion of 208Pb in 554 monazite (Fig. 3A) is consistent with diffusive loss during protracted residence at ~15 km depths (Anderson et al., 1988). In contrast, 208Pb/232Th age gradients measured from the outer 0.3 µm of unpolished DH-68-96 (Fig. 3B) represent more than 50% variation in the age of the specimen (Table 2 [see footnote 1]).

We emphasize that depth profiling analysis of conventionally polished grains of either standard monazite 554 or DH-68-96 produced no resolvable near-surface age variation (Fig. 3; Table 3 [see footnote 1]). Dashed lines in Figure 3B correspond to ages calculated assuming common 208Pb/207Pb = 2.7 (lower bound) and 208Pb/207Pb = 2.3 (upper bound). As indicated, low radiogenic 208Pb (208Pb*) yields near the grain surface (between 0% and 80% radiogenic assuming common 208Pb/207Pb = 2.5) cause ages measured from this region to be sensitive to the magnitude of the correction for common Pb. Th/208Pb/232Th ages obtained in the initial 0.05 µm beneath the surface tend to be younger than 40Ar/39Ar mica ages from the Darondi Khola (Copeland et al., 1991), and in some cases are even negative. Because the predicted closure temperature of Pb in monazite for this length scale (~400 °C, Smith and Giletti, 1997) is slightly higher than that for Ar in micas (McDougall and Harrison, 1988), this indicates that we have overcorrected for common 208Pb. We emphasize that while results from the outer
0.05 µm are problematic, Pb contamination contributed by the epoxy and/or gold coat is not obviously the cause. Specifically, the 206Pb/207Pb ratio of material sputtered from Au-coated, unpolished epoxy (2.55 ± 0.07) is virtually identical to the value determined for Himalayan leucogranites that we have used to estimate common Pb in DH-68-96 (Vidal et al., 1982; Schärer et al., 1986).

To ascertain the tectonic significance of age profiles measured from the outer margin of DH-68-96 monazites, we have assumed uniform Th concentrations and adapted appropriate solutions of the diffusion equation (see equation A9 in Lovera et al., 1989) to predict radial distribution of 208Pb as a function of thermal history. A single diffusion domain model with Smith and Gillett’s (1997) values for activation energy (E = 43 kcal/mol) and frequency factor (D0 = 6.6 x 10-11 cm²/s) was applied. To facilitate the forward modeling process, we have calculated a single weighted mean profile (Fig. 4A) from the eight results (Table 2 [see footnote 1]). In doing so we have normalized measured depths (r) by an assumed effective diffusion radius (re) equal to 50 µm. This value was used because it is representative of the average radius of the DH-68-96 grains examined. We emphasize that although our choice of re is somewhat arbitrary, results are relatively insensitive to the value employed because D0 is normalized in a similar fashion (i.e., D0/re²). In addition, while choice of diffusion geometry can significantly affect results at low to intermediate re/D0 values, calculated ages become independent of geometry as re/D0 approaches unity.

The form of the profile obtained (Fig. 4A) is consistent with expectations from slow cooling theory (Dodson, 1973). Considering only the possibility of monotonic cooling leads to a highly restricted set of temperature-time histories capable of reproducing the mean age profile. The best-fit solution is shown by the solid curve in Figure 4B. The variation in thermal history defined by the dashed lines in Figure 4B produces the similarly depicted age profiles in Figure 4A. As shown, resolvable differences in depth-profiling results correspond to temperature-time paths that differ only by ±20 °C at temperatures above ~400 °C.

**Th-Pb MONAZITE THERMAL HISTORIES: A HIMALAYAN EXAMPLE**

The central Himalaya and the Darondi transect in particular have been the focus of numerous petrologic and isotopic studies (e.g., Colchen et al., 1986; Hodges et al., 1988; Copeland et al., 1991; Harrison et al., 1997) and is therefore among the best locations in the Himalaya to test our new method. Attainment of peak (garnet grade) conditions within the shear zone beneath the Main Central thrust at ca. 6–8 Ma has been clearly recorded by analysis of neo-formed monazite (Harrison et al., 1997). Subsequent exhumation of these rocks at 4–2 Ma is recorded by mica closure ages (Copeland et al., 1991). Determining the evolution of the subjacent hanging wall during this interval has been hampered by the fact that conventional thermochronometers tend to record either the earlier amphibolite facies recrystallization (Hodges et al., 1996) or later exhumation (Copeland et al., 1991). However, the high-temperature portion of the retrograde evolution of the hanging wall has been recorded by the distribution of 208Pb in the rims of older monazites such as those present in DH-68-96. The form of the mean age profile shown in Figure 4A places tight bounds on the temperatures subsequent to 12.8 Ma emplacement of the pegmatite dike. The cooling history that is indicated is reasonably consistent with published geochronologic and pressure-temperature constraints (see Harrison et al., 1998) for the timing of thrust-related exhumation and cooling. However, analysis of individual profiles can lead to somewhat different results (Harrison and Grove, 1998). Nevertheless, the timing of cooling to below 400 °C (Fig. 4B) that is consistently indicated by all profiles (5–3 Ma) is highly compatible with the 4–2 Ma 40Ar/39Ar mica ages (Copeland et al., 1991) determined on either side of the Main Central thrust (Fig. 4B).

**FINAL REMARKS**

The continuous, high-temperature thermal history information afforded by analysis of near-surface monazite Th-Pb age distributions (Fig. 4B) is, to our knowledge, not recoverable by any other means. In this study we elected to deduce the thermochronologic significance of our measurements by analyzing a mean age profile. While variation in measured profiles is anticipated to result from experimental scatter (Fig. 1), it is possible that differences between profiles may reflect additional controls. Among these is the concern that analyzed surfaces may have been damaged during mineral separation and hence may not be representative of the diffusion boundary as it existed in nature. Moreover, the possible existence of metamorphic overgrowths must always be considered. Such problems can potentially be assessed by additional sample characterization, including scanning electron microscope imaging. Regardless, experiments performed with specimen DH-68-96 demonstrate that monazite Th-Pb age depth profiling offers great potential for recovering continuous thermal history data over a temperature range not previously accessible by thermochronometry. Moreover, other applications, such as detecting nanometer-scale igneous and metamorphic overgrowths on accessory minerals (e.g., Zeitler et al., 1989), are equally promising.

**ACKNOWLEDGMENTS**

This study was supported by grants from the National Science Foundation and U.S. Department of Energy. We thank Chris Coath and Kevin McKeegan for technical assistance in carrying out these measurements and discussions regarding their possible significance. Oscar Lovera assisted us with the diffusion modeling and E. Catlos provided additional information regarding the Main Central thrust. We thank I. Fitzsimons and R. A. Jamieson for helpful reviews.

**REFERENCES CITED**

