

## **APPENDIX 1. Analytical Methods**

### **U-Pb Spheue (ID-TIMS)**

All samples were processed at the laboratories in Denver. Each sample was crushed, milled, and split into heavy- and light-mineral concentrates using conventional separation techniques (MeI and Frantz magnetic separator). Mineral splits of K-feldspar, biotite, muscovite, hornblende, apatite, and zircon (and monazite and titanite, where they existed) were collected for various forms of analysis. The analytical methods for dissolution of titanite (sphene) and extraction of U, Th, and Pb are the same as those given in Premo et al. (1990) using the multi-sample, vapor-dissolution technique of Krogh (1978), and are detailed elsewhere (Premo et al., 2014, this volume).

Prior to dissolution, titanite grains were weighed into micro PFA teflon vials and then lightly leached (cleaned) in distilled 7N HNO<sub>3</sub>. Dissolution was achieved in ultrapure concentrated HF + HNO<sub>3</sub> in a large (6.5-cm-diameter) Parr-type TFE teflon dissolution vessel placed in a high Temperature oven at 210°C for about 5 days. The fractions were then dried down, re-acidified in HNO<sub>3</sub>, spiked with a <sup>205</sup>Pb-<sup>233</sup>U-<sup>236</sup>U-<sup>230</sup>Th dilute tracer solution, and taken to high temperature again for isotopic equilibration. Uranium and Pb were extracted using anion exchange resins, Pb in an HBr medium and U in a HNO<sub>3</sub> medium. Total analytical blanks (laboratory contamination) varied between 13 and 67 pg for Pb, and 7 to 25 pg for U and 0.3 to 10 for Th; the average blank concentrations (N=25) over the time span of this study were 37 pg total Pb, 23 pg U, and 7 pg Th.

Lead was loaded onto single Re filaments using the silica gel-phosphoric acid method, and isotopic ratios were measured using either an NBS-type tandem (two-stage)

single-source, single-collector, mass spectrometer equipped with an ion pulse counter at the end of the second stage or a fully automated, single-collector, VG Isomass 54R thermal ionization mass spectrometer. Lead isotopic ratios were corrected for mass fractionation and laboratory blank Pb; and initial common Pb using values measured from whole-rock U-Th-Pb systematics (see below). Uncertainties on isotopic ratios are given in Table 2, and are reported at the  $2\sigma$  level. Ages were calculated using decay constants from Steiger and Jäger (1977). Concordia intercept ages and errors were determined using the algorithms of Ludwig (1980, 1985), which use the regression approach of York (1968); uncertainties on the ages are reported at the 95% confidence level.

#### **$^{40}\text{Ar}/^{39}\text{Ar}$ Geochronology**

Rock samples were crushed, sieved, and washed with cold tap water. Once the samples were dry the desired size ranges were selected for optimal separations. Each mineral fraction was put through a magnetic separator at various power settings and angles to obtain concentrated fractions of each mineral phase (For this study: hornblende, biotite, muscovite, white mica, and K-feldspar). After putting the fractions through a magnetic separator, hornblende and biotite were further concentrated using a mixture of MeI and Bromoform with a density of  $3.1 \text{ g/cm}^3$ . All K-feldspar and hornblende concentrates were ultrasonically cleaned between 12 and 48 hours. Pure K-feldspar concentrates were obtained using the heavy liquid Lithium Heteropolytungstate (LST). All biotite and hornblende separates were treated in a dilute bath of HCl (<10%) for 15-30 minutes to dissolve any primary and secondary calcite present. Final mineral separates

were hand picked under a binocular microscope to a purity of >99.9%, with particular attention to excluding grains with abundant inclusions, adhering material, carbonate, or alteration.

Final mineral splits were washed in acetone, alcohol, and distilled water to dissolve any organics and remove dust. The samples were wrapped in aluminum packages and sealed in silica vials along with monitor minerals prior to irradiation in the TRIGA reactor at the USGS in Denver.

A Mass Analyzer Products 215 Rare Gas mass spectrometer with a Faraday cup was used to measure argon-isotope abundances. Detection limit at the time of this experiment varied considerably from year to year from the start of this work, but generally was around  $2 \times 10^{-17}$  moles argon/volt of signal. Apparent ages and associated errors were calculated from unrounded analytical data and then rounded using associated errors. All analyses were conducted in the Argon Laboratory, at the USGS-Denver, CO. Decay constants used are those of Steiger and Jäger (1977). The irradiation monitor, hornblende MMhb-1 with percent K=1.555,  $^{40}\text{Ar}_R = 1.624 \times 10^{-9}$  mole/g, with a K-Ar age = 520.4 Ma (Samson and Alexander, 1987), was used to calculate J values for this experiment.  $^{40}\text{Ar}_R / ^{39}\text{Ar}_K$  has been corrected for all interfering isotopes, including atmospheric argon. Mass discrimination in the mass spectrometer was determined by measuring the  $^{40}\text{Ar} / ^{36}\text{Ar}$  ratio of atmospheric argon. Corrections also were made for additional interfering isotopes of argon produced from irradiation of chlorine using the method of Roddick (1983). Uncertainties in calculations for the ages of individual heating steps were calculated using modified equations of Dalrymple et al. (1981).

## Apatite Fission-Track Analysis

Apatite fission-track (AFT) ages were determined using the external detector method (Naeser and McKee, 1970; Naeser et al., 1989), as follows. Apatite grains were mounted in epoxy, polished to expose internal grain surfaces, and etched in 7% nitric acid for 40 seconds at 23°C to 24°C. After etching, the grain mounts were covered with low-uranium-content-muscovite external detectors and irradiated at the U.S. Geological Survey Reactor in Denver, Colorado. National Institutes of Standards and Technology (NIST) standard glass SRM 963 (Carpenter and Reimer, 1974) was irradiated with the apatite mounts as a neutron dosimeter. Grain mounts and external detectors were counted at 1250x magnification using a 100x oil immersion objective. Ages were calculated using the zeta calibration method (Hurford and Green, 1983), with a zeta factor of 9740 (N.D. Naeser) or 10752 (C.W. Naeser) (Table 4).

Separate apatite grain mounts prepared for track-length measurements were etched in 7% nitric acid for 60 seconds at 24°C. Track lengths were measured in transmitted light at 1875x magnification, using a 100x oil immersion objective, a digitizing tablet, and a projection tube calibrated against a stage micrometer (1 unit = 0.01 mm). Only well-etched horizontal confined tracks in grains with polished surfaces approximately parallel to the crystallographic c-axis were measured. Reported track lengths are actual measurements, not corrected for length-measurement bias (Laslett et al., 1982).

The thermal history of the rocks from the time they cooled through ~110°C and entered the apatite partial annealing zone was modeled for selected samples using the measured AFT age and track-length data and Gallagher's (1995; written communication,

1996) genetic algorithm time-temperature modeling program with Laslett et al.'s (1987) annealing model for Durango fluorapatite. An annealing model based on Durango fluorapatite is considered appropriate for the analyzed samples because the mean pit widths of tracks in the apatite grains analyzed in this study indicate an annealing susceptibility comparable to Durango fluorapatite.

#### **Reference (Not Included in Chapter) for Appendices**

McIntyre, D.B., 1963, Precision and resolution in geochronometry, *in* Albritton, C.C., Jr., ed., *The Fabric of Geology*: Reading, Massachusetts, Addison-Wesley, p. 112–134.