Appendix B: Documentation of key procedures for continuous ramped heating

Details of the main analytical approach to Continuous Ramped Heating (CRH) can be found in Idleman et al. (2018). In this document we explain important updates to our analytical procedures and some caveats relevant to sample packaging and handling, laser heating and temperature measurement, gas gettering and monitoring, and data collection and reduction.

1. Sample packaging and handling

Each apatite grain, after being picked and photographed, was packaged in a niobium (Nb) tube with both ends closed – a standard approach for single-grain apatite (U-Th)/He dating. The tube was then wrapped in a Nb foil envelope (Fig. B1A). The Nb tubes we used for these experiments had an outside diameter of 0.4 mm and length of 0.7 mm. The foil envelopes were octagonal-to-circle shaped with a diameter of ~2 mm, a size chosen to fit into the indentation in a cylindrical quartz glass sample holder (Fig. B1B) and also to completely contain the measurement spot of the optical pyrometer (~1.1 mm). The holders fit into a sample rack fitted with a linear

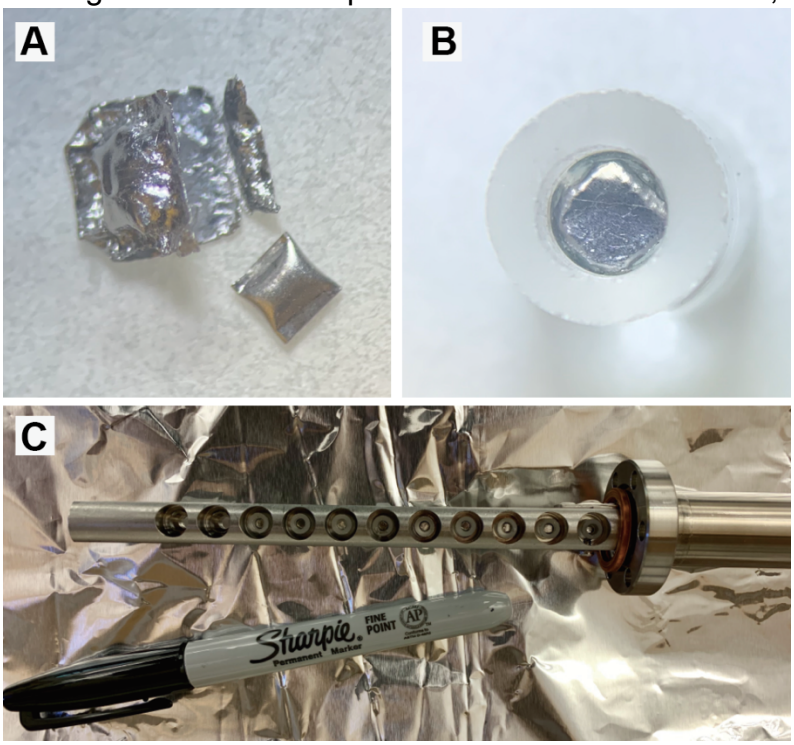

Figure. B1: Sample packaging.

actuator that allows up to 12 samples to be positioned under the laser beam (Fig. B1C). Both the Nb tubes and foil envelopes were cleaned with 7% HNO_3 and degassed for 3 hours in a vacuum furnace at 600 °C before packaging. The overall goal of our packaging strategy is to keep the sample packet as small as possible in order to allow efficient and responsive laser heating (see following section) while still providing enough packet surface area for accurate temperature measurement.

2. Laser heating and temperature measurement

The TAM samples were heated with a 30 watt 808 nm fiber-coupled diode laser, and their temperatures were monitored using a BASF Exactus optical pyrometer positioned coaxially with the laser beam path as part of a custom beam delivery system. The pyrometer was recalibrated every 8-12 sample runs against a K-type thermocouple embedded in a “dummy” sample packet in one of sample-rack positions. Temperature regulation was achieved by modulating the laser power under closed-loop PID control using a custom Labview program. For the TAM experiments we performed CRH analysis using a heating rate of 30 °C/min. This rate was chosen to balance the responsiveness of the temperature control system, the speed of ^{4}He flow and pressure equilibration within the extraction line, the efficiency of active gas cleanup, and the time needed for the ^{4}He signal to be integrated and recorded with sufficient precision.

3. Gas gettering and monitoring

CRH analysis involves continuous sample heating and measurement of released helium gas under static conditions with the sample chamber open to the mass spectrometer.

The presence of other active gas components released from both the sample and the extraction system will impact CRH analysis and therefore requires careful attention to gettering and monitoring of these active gas contaminants. We have found that hydrogen and nitrogen in particular can alter the effective ^{4}He sensitivity via pressure scattering or possibly other source effects. For the TAM experiments we used two SAES GP-50 getters operated at 20 and 200 °C in the extraction line for active gas cleanup, as described by Idleman et al. (2018). Fortunately, laser heating is particularly advantageous for CRH analysis, as the much smaller heated area relative to that required for furnace-heating experiments helps to minimize the evolution of these active gases. With our current laser heating setup, hydrogen and nitrogen co-evolved with ^{4}He have the greatest impact on the effective ^{4}He sensitivity at temperatures where the sample is almost completely degassed (i.e., > 850 °C) and can result in slight (~1-5%) underestimations of the final ^{4}He abundance. This problem can be addressed effectively by delaying the final measurement of the total ^{4}He beam intensity for ~3 minutes after the termination of laser heating, allowing the partial pressures of the active gas contaminants to fall to levels at which their suppression of the ^{4}He signal is trivial.

4. Data collection and reduction

The ^{4}He measurements were performed using a Pfeiffer Prisma Plus quadrupole mass spectrometer fitted with a channel electron multiplier. The CRH measurements were made in the static mode with the quadrupole fully open to the sample chamber.

The following sections highlight three key steps in our strategy for data collection and reduction:

Before heating. We allowed at least two minutes of measurement of the dynamic background in order to quantify the residual ^{4}He signal present before the extraction line was valved off from its pumps. Once the pump valve was closed, we performed another two to three minutes of measurement of what we found to be a linearly rising time-dependent static ^{4}He blank, allowing us to calculate the blank contribution over the course of the CRH experiment by extrapolation of these early measurements. In practice, we have found that the magnitude of this time-dependent static blank far exceeds the blank component contributed by sample heating, which in most experiments is trivial.

During heating. Temperature recording was initiated shortly before the start of laser heating. For the remainder of the experiment sample temperature and the ^{4}He beam intensity were recorded at fixed intervals of 10 s and 10.2 s, respectively. During the first 10-20 seconds of the experiment the samples were heated rapidly to ~160-170 °C under manual control to bring them within the measurement range of the pyrometer. After the sample temperature had stabilized for a few seconds control was passed to the Labview software, which then proceeded with the programmed heating schedule under closed-loop control. Heating and ^{4}He measurement continued until the sample was completely outgassed, as indicated by either a stable ^{4}He beam intensity for at

least one minutes or, more often, a slightly decreasing signal owing to the buildup of active gases.

After heating. After a sample was completely outgassed, we stopped temperature recording and allow the system to cool for three minutes, during which we commonly observed a 1-5% increase in the ^{4}He beam current until the beam current finally stabilized. This increase typically coincided with an orders-of-magnitude drop in the m/e 2 and 28 beam intensities as the sources of coevolved H_2 and N_2 cooled and these gases were gettered. We used the final ^{4}He beam intensity achieved after this cleanup step for the age calculation. Once the ^{4}He beam had been measured we introduced a calibrated aliquot of ^{4}He as a standard addition to establish the ^{4}He sensitivity of the quadrupole.

After completion of a CRH experiment, temperature and ^{4}He abundance data were synchronized by linear interpolation using the time stamps recorded with each measurement. The accumulated ^{4}He blank (static blank) was calculated using the previously determined accumulation rate and the heating duration. We then subtracted the dynamic background and the time-dependent static blank from our measured ^{4}He beam currents before calculating cumulative ^{4}He loss as a function of temperature (f), and differentiation of the cumulative loss curve to obtain fractional loss (df/dT).