$^{40}Ar/^{39}Ar$ Geochronology: Sample Preparation & Analytical Methods

Sample Preparation

Samples were crushed, sieved to 180-150 μm, and run through a Frantz magnetic separator to separate mineral phases (i.e. groundmass from plagioclase feldspar). Groundmass fractions were then leached in five separate ultrasonic baths of different aqueous solutions, each for approximately one hour. Solutions, in order, included 1M hydrochloric acid, 6M hydrochloric acid, 1M nitric acid, 3M nitric acid, and milli-Q water to remove adhering glass and clay. Samples were then rinsed three times with milli-Q water and dried overnight.

The potential for argon recoil is challenging to identify during sample preparation and experiments result in age data that is not geologically meaningful when considered alone. Samples affected by recoil do not overlap in error at their lower and higher temperature steps, preventing an age plateau from being resolved. The higher temperature steps affected by recoil often are highly radiogenic making inverse isochrons difficult to determine. This issue was addressed during sample preparation by adding a mild (5%) hydrofluoric acid (HF) bath for approximately three minutes to groundmass samples following the full suite of a standard groundmass leach. This additional step removed the altered material responsible for the argon recoil but potentially introduced atmospheric argon. Data resulting from these samples leached in hydrofluoric acid are meaningful, as their age plateaus overlapped with the non-hydrofluoric treated fraction at their intermediate temperature heating steps. And, inverse isochrons of the hydrofluoric leached samples, cut through the apex of the ellipsoids on inverse isochron plots from samples that were plagued by argon recoil. All sample ages included in the manuscript text and associated figures are the dates acquired from sample fractions what underwent this additional leaching step during sample preparation. By combining the most useful temperature steps from both sample experiments, our data is then spaced out along an inverse isochron, increasing the spreading factor. Some, but not all samples, exhibited a decrease in their K/Ca ratios from the non-hydrofluoric leached sample to the hydrofluoric leached sample.

Analytical Methods

Three new high-precision $^{40}Ar/^{39}Ar$ ages obtained by incremental heating methods using the ARGUS-VI mass spectrometer. Groundmass samples were irradiated for 6 hours (Irradiation

15-OSU-07) in the TRIGA CLICIT nuclear reactor at Oregon State University, along with the FCT sanidine (28.201 ± 0.023 Ma, 1σ) flux monitor [47].

Individual J-values for each sample were calculated by parabolic extrapolation of the measured flux gradient against irradiation height and typically give 0.2-0.3% uncertainties (1σ). The $^{40}Ar/^{39}Ar$ incremental heating age determinations were performed on a multi-collector ARGUS-VI mass spectrometer at Oregon State University that has 5 Faraday collectors (all fitted with 10^{12} Ohm resistors) and 1 ion-counting CuBe electron multiplier (located in a position next to the lowest mass Faraday collector). This allows us to measure simultaneously all argon isotopes, with mass 36 on the multiplier and masses 37 through 40 on the four adjacent Faradays. This configuration provides the advantages of running in a full multi-collector mode while measuring the lowest peak (on mass 36) on the highly sensitive electron multiplier (which has an extremely low dark-noise and a very high peak/noise ratio). Irradiated samples were loaded into Cu-planchettes in an ultra-high vacuum sample chamber and incrementally heated by scanning a defocused 25 W CO_2 laser beam in preset patterns across the sample, in order to release the argon evenly. After heating, reactive gases were cleaned up using a SAES Zr-Al ST101 getter operated at 400°C for ~10 minutes and two SAES Fe-V-Zr ST172 getters operated at 200°C and room temperature, respectively. All ages were calculated using the corrected [80] decay constant of 5.530 ± 0.097 x 10^{-10} 1/yr (2σ) as reported by [81]. For all other constants used in the age calculations we refer to Table 2 in [82]. Incremental heating plateau ages and isochron ages were calculated as weighted means with $1/\sigma^2$ as weighting factor [83] and as YORK2 least-square fits with correlated errors [84] using the ArArCALC v2.6.2 software from [85] available from the http://earthref.org/ArArCALC/ website.

Data are reduced for age calculations using the ArArCALC software provided by [85] using the currently accepted^{40}K decay constant [80]. ArArCALC software [81] was used to reduce the isotopic data and make age calculations. Further details of analytical procedures were described in[86] (see also the OSU laboratory website, http:// www.coas.oregonstate.edu/research /mgg/chronology .html).