

### *Argon Measurements*

The noble gas system used for the Ar measurements at LDEO was installed in 1997 for  $^{40}\text{Ar}/^{39}\text{Ar}$  measurements of small samples and consists of a fully custom built and automated micro-extraction system. On this system samples may be heated with either a 30-Watt CO<sub>2</sub> laser from Mercantek or a 50-Watt diode laser from PhotonMachines. Automation of the vacuum valves is achieved by using pneumatically operated valves that are activated by electro-pneumatic solenoid valves. Gasses released from the heating of samples are scrubbed of reactive gases such as H<sub>2</sub>, CO<sub>2</sub>, CO and N<sub>2</sub> by exposure to Zr-Al sintered metal alloy getters from SAES, run at 400°C. The remaining inert gasses, principally Ar, are then admitted to the mass spectrometer and the Ar-isotopic ratios are determined using automated data collection software (MassSpec).

The VG5400 mass spectrometer employs a modified Neir ion-source and a 90° sector extended-geometry. The mass spectrometer is operated in static mode and peak hopping with the magnet- typically 6 to 8 cycles are measured. M/e 36 cold procedural blanks for both the extraction system and mass spectrometer are less than  $5 \times 10^{-14}$  cc STP (most of the 36 is from the mass spectrometer and is not Ar). Desorption of  $^{40}\text{Ar}$  in the stainless-steel wall of the vacuum envelope is less than  $1 \times 10^{-12}$  cc STP/min. The detection limit of the VG5400 is approximately  $1 \times 10^{-14}$  cc STP ( $\sim 5 \times 10^{-19}$  moles), and the sensitivity is about  $1 \times 10^{-3}$  Amps/Torr at 200  $\mu\text{A}$  trap current. The mass spectrometer is equipped with a  $10^{11} \Omega$  resistor and an electron multiplier connected to a Keithley electrometer and signals are typically measured with the analogue electron multiplier (Keithley) configuration. The multiplier high voltage is set to maintain a signal gain relative to a  $10^{11} \Omega$  resistor of  $\sim 100$ .

The application of naked pellets of GL-O-1 as a monitor standard to calibrate instrument sensitivity is reported in other papers [e.g. 10,11] and briefly reviewed here. For the application as a sensitivity standard one to ten pellets are generally weighed for each sample to produce a range of weights, and for each disk run three or more pits are loaded with GL-O-1. These GL-O-1 analyses are used as a check on the instrument sensitivity. We calculate the  $^{40}\text{Ar}^*$  abundance of each GL-O-1 based on its weight and concentration information from Odin et al. [2] and use the resulting signal intensity as a calibration of the abundance of Ar in the air pipette. We use the air pipettes for both consistency of sensitivity and for correcting for drift and evaluating the quality of the isotope ratios measured. To calculate the  $^{40}\text{Ar}^*$ , we subtract  $^{36}\text{Ar}$  times the  $^{40}\text{Ar}/^{36}\text{Ar}$  measured on air pipettes from the total  $^{40}\text{Ar}$ . It is important to note that for  $^{40}\text{Ar}/^{39}\text{Ar}$  dating (the primary purpose of this instrument), the accuracy of the abundances is not as important as the relative isotope abundances. Thus, our mass spectrometer sensitivity estimate has relied on the measurements of GL-O and the assumption of  $1.109 \pm 0.011$  nmol/g Ar [2].

Leading up to this study, our method is to weigh pellets of GL-O-1 or small sediment samples with a microbalance and load them as naked pellets or clods [as in 9]. However, because our goal for the study reported here is to measure K on the same aliquots as Ar in order to mitigate against sample heterogeneity, we have explored other options that avoid direct coupling between the laser and sample including Ta foil to wrap the pellets, Ta capacitor tubes, smaller Nb tubes, and a glass rod pouch. While all these methods worked from the standpoint of degassing the pellets while retaining their integrity, the approach that has the lowest Ar backgrounds and easiest manipulation is small Nb tubes, so we follow that procedure here.

The microfurnace used here is made out of a 5-mm long Nb tube (1-mm OD and 0.1-mm wall thickness) by cutting each tube from the supplier (Edgetech Industries LLC) into half with a sharp-tipped plier, resulting in two smaller, 2.5-mm long tubes with one open end and one sealed end. Each tube is pre-degassed at 1100 °C for 5 minutes in a high vacuum chamber to remove any trapped atmospheric Ar from the tube-making and handling processes. Single GL-O-1 grains or other mineral standards are weighed on a Toledo balance (precision  $\pm 1 \mu\text{g}$ ) and loaded into the pre-degassed Nb tubes. Each sample-loaded Nb tube is placed at the center of a cone-shaped pit in a Ti planchette with its open end pointing to the side wall of the pit and with its long axis surface lying gently sloped to facilitate laser coupling during degassing. The 32-spot Ti disk with loaded samples is placed into a high vacuum chamber. While pumping down the sample chamber, we heat for one to three hours at  $\sim 60$  °C pumping with a second vacuum system (we call the service vacuum) to avoid venting the main extraction line. Following the evacuation with the service

vacuum (1 to 12+ hours, depending on working hours), we isolate the service vacuum and connect to the extraction line vacuum and calibrate the x-y sample stage. We start with multiple background analyses to monitor the trend. Once the backgrounds are low and stable or trending slowly, we begin the disk run, starting with a series of BABABGBAB (B=blank, A=air pipette, G=GL-O-1), then we measure BAB after every 3 unknowns, and at the end of the series we repeat BGBABAB. Distributed approximately equally through the set we run the samples we are using for monitoring with BABGBAB pattern. As a general rule for our “sediment disks” we use the GL-O-1 results in each disk run to test the sensitivity to a given Ar abundance [e.g. 9]. We use the air run through the disk run to detrend the signals, then plot the corrected GL-O signal against the amount of  $^{40}\text{Ar}^*$  from the weight and known concentration and use that to estimate the moles of Ar per nanoamp of signal (mol/nA). We compare the implied sensitivity in each disk between with air pipettes and GL-O-1 and use that for further quality control. Each batch of measurements in a single disk is called a disk run.

Two disk runs were conducted for this study- one using the Nb microfurnaces and the diode laser and the other with naked grains and the  $\text{CO}_2$  laser. Disk run 1428 was loaded with sixteen empty Nb tubes interspaced with sixteen Nb-tubed, visually well-evolved dark green GL-O-1 pellets. All 32 tubes were heated to  $750 \pm 5^\circ\text{C}$  for 2 minutes with the diode laser. All tubed GL-O-1 grains remained intact after degassing. In order to test the Ar concentration of single pellets of visually mature dark green GL-O, a second disk run, 1442, included a combination of naked grains of GL-O-1 [2], GA-1550 [21,22], and MMhb [22,23] standards. These mineral grains were fused at 7 watts for 3 minutes with the  $\text{CO}_2$  laser to insure a complete degassing of Ar from the standards.

#### *Potassium Measurements*

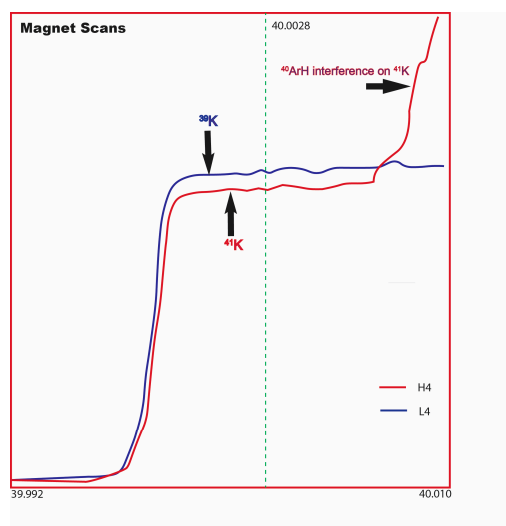
We tested the K content at the sub-pellet scale by mounting and polishing visually mature, dark green pellets, and measuring them on a CAMECA SX100 electron microprobe at the American Museum of Natural History in New York City. The probe is equipped with a fully automated WD spectrometer, operated at 15 kV accelerating voltage with a beam current of 20 nA, and calibrated against natural and synthetic oxides (Wakefield diopside for Mg and Si; K-spar for Al, K; RKFAy7 for Fe). Each element was measured using a beam size of 20  $\mu\text{m}$  with counting time of 20 seconds. Four spot measurements on the K-spar standard yielded a mean value of  $12.37 \pm 0.09\%$  for K (recommended value is 12.39%), indicating accuracy better than 2% for the K measurements.

In order to have K on the same aliquot as Ar, our preferred strategy for measuring K is to dissolve the degassed pellet, with an enriched  $^{41}\text{K}$  spike for isotope dilution analysis. The  $^{41}\text{K}$  spike solution is  $1.005 \pm 0.001\ \mu\text{mol/g}$  based on calibration against Sigma-Aldrich; Lot: BCCB7069 ICP multielement standard. A paper detailing the methods is in progress, and a brief review is provided in the following.

For measurement of the K concentrations, the degassed pellets are transferred into Teflon vials. Based on an estimate of the K abundance from the weight of the pellet, the optimum amount of  $^{41}\text{K}$ -spike, 110-562 mg of solution for the measurements reported here, is pipetted into each sample vial and weighed on a Sartorius balance, with precision of 0.05 mg. The sample-spike mix is slowly dried down on a hotplate ( $100^\circ\text{C}$ ), and then a 0.3 to 0.6 ml concentrated  $\text{HF-HNO}_3$  (3:1 ratio) acid mix is added to each vial for digestion. The vials are closed and placed on the hotplate set at  $165^\circ\text{C}$  for over 48 hours. After opening, acids are evaporated, along with  $\text{SiF}_4$ . The residue after drying is digested in 0.2 ml of 6 M HCl, heated at  $165^\circ\text{C}$  for another 24 hours to insure complete digestion and sample/spike equilibration. Then the sample-spike mix is evaporated to dryness and subsequently dissolved in 0.4 ml of 0.5 M  $\text{HNO}_3$ .

Potassium is isolated from the matrix by chromatographic separation method using Bio-RADTM Poly-Prep columns filled with 2 mL precleaned AG50-X8 cation-exchange resin (200–400 mesh) [24]. The column chemistry is done twice to insure full separation of K from the matrix (e.g., Na, Mg, and Ca). The separated K analytes of sample-spike mix are redissolved and diluted in 2%  $\text{HNO}_3$  to match the  $^{39}\text{K}$  concentration of the NIST SRM 3141a standard (2 ppm), which is used to monitor mass discrimination and signal drift. The K isotopic ratios are measured on a Nu Instruments Sapphire MC-ICPMS (SP005), using cold plasma mode (RF power = 900 W). The samples and standards are introduced with an uptake rate of  $\sim 80\ \mu\text{L/min}$  using a self-aspirating PFA nebulizer connected to a Cetac® Aridus III desolvating system, which can reduce the

HNO<sub>3</sub> solvent introduced into the plasma and enhance the K sensitivity by an order of magnitude. In addition, N<sub>2</sub> gas is added into the Aridus III and the flow rate is adjusted to minimize the signals of Ar<sup>+</sup> and ArH<sup>+</sup>. In order to achieve pseudo-high resolution for isolating the <sup>40</sup>ArH<sup>+</sup> free shoulder for <sup>41</sup>K measurements, the source slit width is reduced from 0.3 mm (lower resolution) to 0.03 mm (high-resolution). Alpha slits are also adjusted to reduce beam abbreviation. With a resolving power above 11,000 after careful tuning, the ArH<sup>+</sup> free shoulder for <sup>41</sup>K can be clearly identified and the <sup>40</sup>Ar<sup>+</sup> signal is sufficiently reduced (< 4V) for robust measurements. The <sup>40</sup>ArH<sup>+</sup> is as low as 0.5 V at peak center, so the possible interference from <sup>40</sup>ArH<sup>+</sup> tailing is negligible on <sup>41</sup>K with this procedure (Fig. 2).



**Figure S1.** Schematic plot of the peak shapes of K isotope measurements by MC-ICPMS in this study. On a Sapphire MC-ICPMS with a cold plasma setting, the Ar-interference-free shoulder can be identified under pseudo high-resolution mode. The <sup>39</sup>K and <sup>41</sup>K signals are collected by L4 and H4 cups simultaneously.

Due to mass discrimination effect on MC-ICPMS, the measured <sup>41</sup>K/<sup>39</sup>K value of NIST standard is ~ 0.075 compared with 0.072167. For the spike-sample mixes, the isotopic ratios are corrected by exponential law and reported as true ratios of the samples for concentration calculations.