Technical Notes

An Apparatus for High-Precision Helium Diffusion Measurements from Minerals

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We describe a simple and low-cost apparatus for in-vacuum helium diffusion measurements that reduces temperature gradients, set point overshoot, and ramping times compared with conventional resistance furnace techniques. The sample, suspended by a thin wire in a vacuum chamber, is heated by radiation from an Al-coated projector bulb passed through a sapphire viewport. Because the total mass of the sample package being heated is small (typically <100 mg), thermal gradients and thermal inertia are both small. In experiments with set points between 100 and 750 °C, this apparatus can achieve set point from room temperature in ~90 s, usually with <3 °C of set point overshoot persisting for just a few seconds. Helium diffusion coefficient measurements indirectly indicate that temperatures are precise and reproducible to better than ±2 °C.

A detailed and accurate knowledge of the diffusion characteristics of noble gases from minerals is important in several areas of the Earth sciences. For example, in slowly cooled rocks, ages obtained from the K/Ar and (U–Th)/He systems will reflect the competing effects of radioactive ingrowth and diffusive loss integrated over the cooling path of the rock.[1,2] The conventional approach to determining noble gas diffusivities involves extrapolation of laboratory measurements made at high temperatures and short durations (usually hours) to more-relevant lower temperatures and longer durations (usually millions of years) by assuming a thermally activated (Arrhenius) process.[1] Laboratory noble gas diffusion measurements usually employ a resistively heated vacuum furnace in which mineral grains are held isothermally for a prescribed period of time, after which the liberated noble gas is measured.[1] This technique can suffer from problems[1] including (1) thermal gradients between sample and thermocouple, (2) long ramping times, (3) temperature overshoot upon initial heating, and (4) imprecise temperature regulation. These effects are particularly problematic at the low temperatures (<800 °C) required for studying the diffusivity of radiogenic helium from

common minerals such as apatite,[3] titanite,[4] and zircon.

Because the extrapolations from high-temperature laboratory data to the lower temperature natural setting are usually very large (frequently many orders of magnitude in diffusivity), errors in experiment temperature and holding time can propagate into very large and potentially systematic errors in estimated diffusivity. Similarly, because diffusivity scales exponentially with temperature, set point overshoot can be a significant problem. Here we describe a simple and inexpensive apparatus designed for in-vacuum noble gas diffusion measurements (primarily of helium) at temperatures of <~750 °C in which each of these sources of uncertainty is substantially reduced.

EXPERIMENTAL SECTION

The problems described above arise predominantly from the need to heat relatively large masses of metal associated with the heater element and crucible of a conventional resistance furnace. For most diffusion experiments, this mass far exceeds that of the sample itself. As an alternative, we have designed a system in which the mass heated is only slightly greater than the sample mass, thereby permitting extremely rapid thermal response and minimizing temperature gradients (Figure 1).

In the new apparatus, radiant heat is delivered from a modified projector bulb to the sample through a viewport in an evacuated chamber. To minimize conductive losses to the walls of the vacuum chamber, the sample is supported by a length of fine-gauge wire. Under these conditions, heat is lost predominantly through conduction to the chamber walls via gas molecules within the chamber and by thermal radiation. In a vacuum, neither of these mechanisms is efficient until comparatively high temperatures are achieved.

The sample (up to ~100 mg) is wrapped in an envelope of 0.025-mm-thick copper foil, through which an uninsulated fine-gauge thermocouple pair is passed. The thermocouple is thus in intimate contact with the sample, and the entire sample package is less than square. The small size and high conductivity of the copper envelope ensure a minimal thermal gradient between sample and thermocouple junctions. A supporting wire is wrapped around the foil envelope and is held upright in an insulated ceramic tube attached to one of the thermocouple feedthrough

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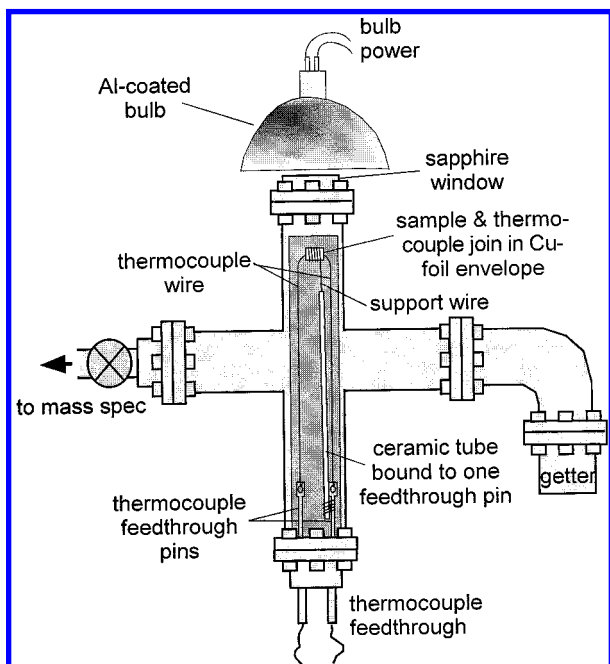
Figure 1. Design of a noble gas diffusion apparatus heated by radiation from a projector bulb. The vacuum chamber is constructed from a 1.33-in. conflat-cross. A sapphire viewport was used for its good transmission in both visible and infrared wavelengths and because it is impermeable to helium.

Figure 2. Temperature response curves for the apparatus in Figure 1 with set points between 100 and 700 °C. Solid circles indicate when the set point ± 1 °C was achieved. Numbers above each curve indicate the maximum amount of set point overshoot and, in parentheses, the duration of that overshoot.

pins for rigidity. This wire supports the envelope a few millimeters below the sapphire viewport, at the approximate focal point of the projector bulb. The thermocouple pair exits the vacuum chamber through a conflat-mounted vacuum feedthrough at the chamber bottom. We have used 0.13- or 0.26-mm-diameter K-, J-, and T-type thermocouples, depending on the range of temperatures investigated.

Power to the bulb is regulated using a proportional output temperature controller (Watlow model 945). The proportional output signal is amplified to deliver between 0 and 60 VDC to the projector bulb. We use a model ENX halogen bulb with a vapor-deposited Al coating on the reflector (provided by Guernsey Coating Laboratories, Inc). The Al coating is critical for efficient heating because it projects the abundant infrared radiation forward into the chamber rather than letting it penetrate backward through the reflector. This bulb is rated for 82 V operation, but we find sufficient power at 60 V to achieve temperatures up to ~780 °C. Bulb life is substantially enhanced at lower voltages; we have run these bulbs many hundreds of hours longer than their rated life span at full power.

To perform an experiment, the sample is loaded into the foil envelope and inserted into the vacuum chamber. The chamber is then evacuated using a turbomolecular pump to a pressure of <1 $\times 10^{-7}$ Torr, after which the chamber is valved off. The sample is then heated and held for the requisite period (minutes to days) to diffuse noble gases into the chamber for measurement. For temperatures of <~450 °C, we find that pressure remains sufficiently low to prevent excessive heat loss to the chamber walls. However, at higher temperatures outgassing of H_2 becomes very significant and, if unchecked, will restrict the maximum temperature achievable. To control this problem, we use an SAES ST 101 pill 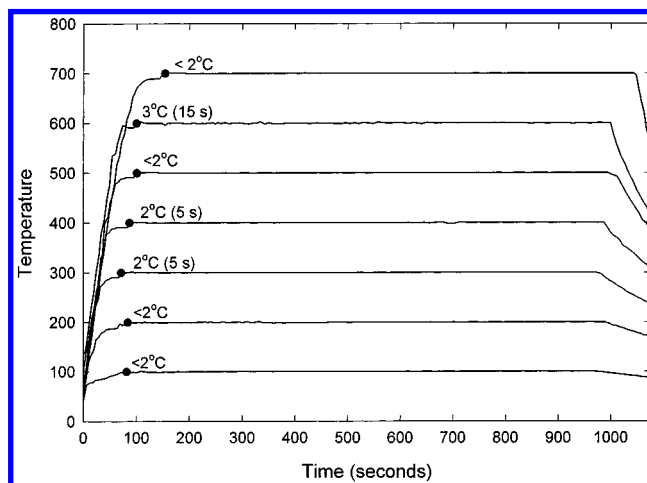getter mounted directly in the sample chamber to continuously consume H_2 and any other reactive gases. During initial pump down, this getter is outgassed and activated at 800 °C. With this getter, temperatures of at least 750 °C can be held indefinitely.

RESULTS AND DISCUSSON

To demonstrate the thermal response and stability character-istics of this device, Figure 2 shows the temperature trajectory of the illuminated sample from approximately room temperature to set points between 100 and 700 °C, followed by 15 min of dwell time, and finally cool down after the bulb is extinguished. The major features of these temperature profiles are that (1) the set point is achieved very rapidly, usually within 90 s, (2) set point overshoot does not exceed 3 °C and never persists for more than 15 s, and (3) after set point is achieved, the total range in temperature does not exceed ± 1 °C (the limit of the controller). The sample cools back to room temperature in less than 15 min.

We have used this device to study helium diffusion from various mineral phases including apatite[3] and titanite.[4] The apparatus is sufficiently robust that we can automate an entire stepped-heating schedule in which diffusivity is measured at dozens of temperatures in an experiment that lasts several weeks. Because both the heating and the helium analysis steps are under computer control (using Labview code), the entire experiment can be performed without user intervention. Calculation of diffusivities by this techniques requires knowledge of the total amount of diffusant in the sample. In general it is necessary to fuse minerals to guarantee complete extraction of noble gases, but the projector bulb apparatus cannot reach the melting point of most minerals. Instead, for the final step of a diffusion experiment, we remove the copper foil pouch from the diffusion apparatus and fuse it in a conventional resistance furnace.

The helium diffusion experiments provide a means to assess the precision of our temperature measurement. We have studied[3] the temperature dependence of helium diffusivity from a natural helium-rich mineral (Durango fluorapatite) using this apparatus. The precision of our temperature estimates can be assessed by how well our diffusivity data conform to the expected Arrhenian
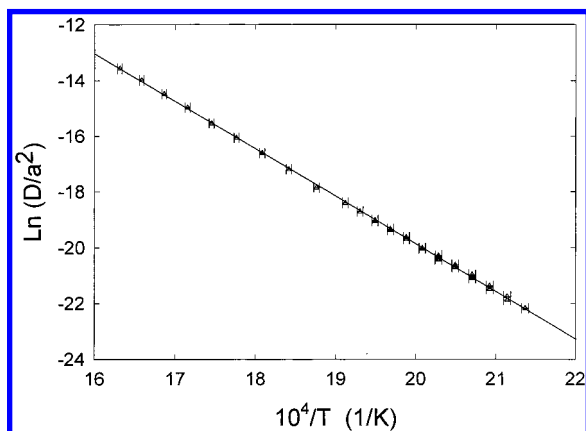
Figure 3. Measured helium diffusion coefficients from Durango fluorapatite.[3] Error bars are ±1 °C. The high degree of linearity on this plot as well as the reproducibility of diffusion coefficient determinations at a given temperature indicates that thermal gradients within the sample package must be small. Details of the diffusion coefficient measurements will be described elsewhere.

behavior and how reproducible our measurements at any given temperature are for different aliquots of the same sample. We thus are essentially using diffusivity and its change with temperature as a surrogate thermometer. Note that errors arising from temperature overshoot and holding time uncertainty will propagate into these measurements.

As shown in Figure 3, across the temperature range ~190−330 °C, the natural log of the measured He diffusion coefficient from the apatite sample is linear with reciprocal temperature (r^2 = 0.9999). This demonstrates that the diffusion process is thermally activated. More importantly for present purposes, not one of the 31 data points lies off the correlation line by more than the expected temperature uncertainty of ±1 °C. Furthermore, reproducibility of diffusion measurements at a given temperature after unloading and reloading the sample into the copper foil requires that sample temperature is reproduced to better than ±2 °C (not shown). The high degree of linearity and reproducibility in these measurements is unlikely if thermal gradients of more than ~1 °C exist between sample and thermocouple.

Helium blanks in this device are generally low, in the range 1−4 fmol. The blanks do not scale strongly with either temperature (measured up to 750 °C) or holding time. Despite the fact that during illumination the sapphire viewport itself can achieve temperatures of up to ~300 °C, it does not allow atmospheric He to penetrate into the chamber. We have not yet determined blanks for the heavier noble gases.

The greatest limitation of the present design is the inability to achieve temperatures greater than ~800 °C. For example, the procedure for diffusion coefficient determinations could be streamlined by obviating the need to perform the final step in a resistance furnace. If a simple procedure could be found, it might be possible to routinely measure helium diffusivity at the same time that He age determination is being made. In the case of apatite, total He extraction is achieved at ~900 °C in ~30 min, so the present design is close to this goal. Similarly, to be generally useful for studying diffusion of the heavier noble gases, especially argon, higher temperatures must be reached. Higher temperatures might be achieved by using a more powerful bulb and/or a bulb specifically designed for radiant heating. In this case, care must be taken to keep the sapphire viewport below its rated temperature of 300 °C. As alternatives, we are presently investigating (1) illuminating the sample from both sides using a pair of sapphire windows that sandwich the sample and (2) heating a small length of Nichrome wire in the vacuum chamber within a few millimeters of the sample to supplement the radiant heating. Regardless of these details, higher temperatures will require rapid gettering of evolved gases to maintain the efficiency of the illumination technique.