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ARGON ANALYTICAL PROCEDURES FOR POTASSIUM-ARGON DATING, 1980

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ABSTRACT

A manual for the argon analytical methods involved in potassium-argon geochronology, including:

i) operating procedures for the ultra-high vacuum argon extraction/purification equipment for the analysis of nanolitre quantities of radiogenic argon in rocks, minerals and gases;

ii) operating procedures for the AEI-MS10 gas source mass-spectrometer.

KEYWORDS

* GEOCHRONOLOGY
* ARGON ISOTOPES
ULTRA-HIGH VACUUM
MASS SPECTROMETRY

1. INTRODUCTION

1.1 Basic Theory

Most rocks contain potassium, which occurs in varying amounts in the constituent minerals. The potassium-bearing minerals most commonly used in K-Ar dating are brown and white micas, feldspar and hornblende.

Radioactive ^{40}K decays to ^{40}Ca + ^{40}Ar at a known rate*, so to find the age of a rock the ^{40}K and ^{40}Ar (radiogenic) contents must be measured and compared. All rocks contain air, which has a known content of argon. Atmospheric argon occurs as the ^{40}Ar + ^{36}Ar isotopes, in an atomic ratio of 295.3. Thus the atmospheric ^{40}Ar content must be corrected out for each sample before the age can be calculated.

We use a method of isotope dilution for measuring samples: each run is calibrated by the addition of a known quantity of an artificial isotope, ^{38}Ar, from a gas pipette. When the argon is let into the mass spectrometer, the peak heights at masses 36,38 and 40 are measured and the results are used to calculate the age

* Decay constants for ^{40}K: $\lambda_\beta = 4.962 \times 10^{-10} yr^{-1}$

$\lambda_e = 0.581 \times 10^{-10} yr^{-1}$

Isotopic abundance $^{40}K/K$ = 0.01167 atomic %
(Steiger & Jager, 1977, E.P.S.L.)

1.2 Basic Method

The samples consist of either crushed total rocks or mineral separates which have been sieved. The mesh size normally used is 211-422 μ, which is fine enough

to be easily dissolved in acid and fused in the argon line, yet coarse enough to avoid problems of argon loss which occur with fine powders.

Five samples are loaded into the furnace tube each night to be run the following day. The extraction line is baked out overnight at 200°C to remove any water and gases which may be absorbed on the inside of the glass and metal tubing. During the day the samples are run one by one, with a half-hour bakeout between each to avoid contamination.

A run consists of fusing the rock sample in an ultra-high vacuum to extract the gases, removing water and carbon dioxide on a molecular sieve and non-inert gases with a titanium getter or sublimator, then passing the inert gases into the mass spectrometer. The argon peaks at masses 36,38,40 are measured, then the results are fed into the computer.

2. SAMPLE PREPARATION

2.1 Take five beakers from the oven and place in the dessicator to cool.

Tweezers must be used for all handling as dirt and grease from fingers may contaminate samples or alter weights.

2.2 Fill in sample details on analysis sheets.

2.3 Clean the riffler before changing samples, split off an appropriate amount of each sample. Weigh the empty beaker, then re-weigh with the sample, filling in beaker number and weights on analysis sheets.

2.4 Place beakers in the lab. oven for about an hour to dry, then return to dessicator to cool for at least half an hour.

2.5 Re-weigh beakers with dry samples.

3. PREPARING FURNACE TUBE

3.1 Remove from the oven five sets of quartz liners and the long quartz tube. Do not handle with bare hands as fingerprints may contain argon or organic substances which will contaminate the runs.

3.2 Decide on the order of samples to be run and mark the analysis sheets accordingly. Make certain that the samples are in this order at all times.

3.3. Lay the long tube on the bench so that it does not roll, then load the samples. In the loaded furnace tube, the first sample will be the one at the flange end.

3.4 Loading Procedure

3.4.1 Wipe the bench clean and put on nylon gloves.

3.4.2 For each sample in turn take a molybdenum or tantalum crucible and lid and place a small amount of quartz wool in the bottom. This will prevent the sample from being in direct contact with the metal and heating up too fast.

3.4.3 Carefully pour the sample into the crucible, using the small brush to ensure that all the sample is transferred. If this is not possible (e.g. with a particularly sticky mica) then re-weigh the 'empty' beaker and use this reading for calculating sample weight. As long as the bench has been cleaned, any spillage may be brushed back into the beaker and re-transferred to the crucible.

3.4.4 Carefully put more quartz wool on top of the sample to stop it coming out when heated, then put the lid on. The beaker number may be scratched on the lid to avoid mistakes.

3.4.5 Place the crucible in the centre of a quartz liner. If using short liners and spacers place one spacer either side of the sample holder in the long tube, placing tantalum 'mirrors' between spacers. The mirrors stop the heat from fusing samples from heating up and releasing argon from neighbouring samples. Ensure that the sample closest to the flange is not within the graded glass seal.

3.4.6 When all samples are in the long tube a small quartz spacer tube should be placed in front of the first sample to prevent the liners from sliding towards the flange in the furnace tube.

3.4.7 Rinse the beakers in acetone and return them to the oven.

4. CHANGING FURNACE TUBE

4.1 Check that valves to the rotary pump, diffusion pump, ion pump, clean section and spike tank safety valve are closed.

4.2 Place asbestos stand under centre of furnace tube. Loosen all the bolts and remove, leaving the top one until last. Support the tube while removing the last bolt, and remove to bench. Remove the copper gasket and put it in the drawer for re-annealing.

4.2.1 When removing the bolts, put their nuts on them as both tend to get heat stressed and will only work one way. Leave the last one loose to make replacing easier.

4.3 Remove the long quartz tube from the furnace tube and slide the new tube in. If the furnace tube requires cleaning, see section 4.10.3. If the tube has a fixed flange remember to align the thermocouple hole correctly.

4.4. Replace the furnace tube on the line using a fresh copper gasket. Put in all the bolts and do up finger tight. Use the spanner and ring spanner to go round the flange three times, tightening the bolts evenly to ensure a good seal. Do not overtighten.

4.5 Close "rotary" valve between the rotary and diffusion pumps, then slowly open the bypass valve to remove air from the line. The valve should not be opened too fast as the samples may be sucked from their crucibles.

4.6.1 When the pressure on the Pirani gauge falls below 0.05τ, the bypass valve is closed, the "rotary" valve is opened and the diffusion pump valve opened.

4.6.2 If the pressure does not fall below 0.05τ try tightening all the bolts again.

4.6.3 Failing this, change the copper gasket.

4.7 Open the spike safety valve.

4.8 Start the bakeout (see section 5).

4.9 Remove the liners from the used quartz tube one by one, checking that the numbers were in the right order and that the samples have fused.

4.10.1 Place the liners in a polythene beaker of 'Magic' in the sink to clean them, then rinse with distilled water or acetone and dry them in the oven.

4.10.2 If the long quartz tube needs cleaning, use the same procedure.

4.10.3 If the pyrex furnace tube needs cleaning, use the squeeze bottle of 'Magic' to avoid getting acid on the metal flange. Use only a small amount and swirl it around carefully, then dilute it thoroughly with water before tipping out to avoid damaging the metal flange. Rinse with distilled water and acetone and dry in the oven. The furnace tube should not be cleaned unless absolutely necessary.

5. BAKEOUT PROCEDURES

5.1 Starting Overnight Bakeout

5.1.1 Switch off the ionisation gauge then slide the metal furnace into place over the pyrex tube. Avoid damaging the thermocouple. Plug the furnace into its socket.

5.1.2 Check that the diffusion pump "rotary" and spike safety valves are open and the ion pump and clean section valves are closed. The clean section remains isolated during bakeout. The valve between the mass spectrometer and the ion pump should be open and the variable leak valve closed. There is a trip switch in the ion pump which will turn off the filament in the mass spectrometer before it burns out, if the pressure rises too high during bakeout.

5.1.3 Turn the thermostat to 150°C, Bakeout 1 (controlling heat tubes) to 4, molecular sieve on and set to 3, plug in any extra heat tapes in use. The TSP water supply should be off, and the TSP should be on instructions see section 7).

5.1.4 Turn Bakeout 2 (band tapes on M/S) on to 3 and switch on the Pirani over-pressure relay (tripping at 0.1 τ).

5.1.5 If the timer is used to switch off bakeout, turn Timer Power switch on. Fill the cold trap on the diffusion pump with liquid nitrogen.

5.2 Starting Bakeout Between Samples

5.2.1 Follow steps 5.1.1-5.1.3. Bakeout 2 is OFF.

5.2.2 Leave on for at least half-an-hour.

5.2.3 Around midday fill the cold trap with liquid nitrogen.

5.3 Turning off the Bakeout

5.3.1 Turn off all bakeout switches and plugs. After overnight bakeout, fill the cold trap with liquid nitrogen and leave the line hot for several minutes to allow any gases, including mercury vapour, to be sucked back into the pump.

5.3.2 Remove the furnace from the pyrex tube. Use the fans to cool the line.

5.3.3 With the ion gauge on carefully open the valve to the clean section. If the pressure rises fast and continues to rise, close the valve and refer to section 11 (leak checking). If not, then outgas the getter (section 6.2), titanium sublimation pump (section 7) and ionisation gauge for 5-10 minutes to clean away any gases which may be absorbed. Turn off the RF generator, TSP and gauge outgas.

5.3.4 Turn on the water supply to the TSP to cool it.

5.3.5 When the pressure drops to about 2×10^{-7} τ open the line to the ion pump. If the pressure is higher than 7×10^{-7} τ the pump cannot work efficiently, so opening the ion pump

drop onto 10^{-8} range.

5.3.6 The pressure may be further decreased by using the the ionisation gauge as a pump, running it on 10 mA for a few minutes, then on outgas for a few minutes.

5.3.7 Finally, clean out the volume in the gas pipette as follows:

5.3.7.1 Using the torque wrench, close the lower valve (to the first click only).

5.3.7.2 Open the top valve for a few seconds.

5.3.7.3 Close the top valve.

The line is now ready for running samples.

6. THE GETTER

6.1 If the titanium sublimation pump is not in use the getter is operated during each run at approximately 1000°C for 1-5 minutes to clean up all the non-inert gases which have been extracted from the sample. To do this, the RF coil is put over the getter, switched on and turned up from 0 to full power. The cooling fan is directed at the getter. After the appropriate time the power is turned down before switching off.

6.2 Before each run the getter is outgassed to remove the gases which have embedded themselves in the metal, and to act as a pump to reduce the pressure in the line. If a particularly dirty sample has been run the getter may be outgassed through the rotary pump before system bakeout.

6.2.1 When outgassing before a run, pump through the diffusion pump.

6.2.1.1 Open the valve to the clean section.

6.2.1.2 Place the RF coil over the getter and turn on the power

6.2.1.3 Press the start button with the dial on 0, then slowly turn up to full power. The cooling fan is not used.

6.2.1.4 When the pressure falls to $2 \times 10^{-5}\tau$, turn the dial back to 0, and switch off.

6.2.2 When outgassing after a run, pump through the rotary pump.

6.2.2.1 Check that the diffusion pump is valved off, then close the "rotary" valve.

6.2.2.2 Open the bypass valve.

6.2.2.3 Follow instructions 6.2.1.1 - 6.2.1.3.

6.2.2.4 When the pressure falls below 0.05τ on the Pirani gauge return to the diffusion pump: close bypass valve, then open the "rotary" valve. Open the diffusion pump valve.

6.2.2.5 Leave the RF generator on as long as time permits, then turn the power back down to 0 and switch off.

6.2.2.6 Put on the bake out, or change the furnace tube.

7. THE TITANIUM SUBLIMATION PUMP

For full operating instructions see the manufacturers manual.

7.1 During each run the TSP is operated on 40-50 amps to remove all non-inert gases from the sample. For very clean samples e.g. old muscovites it may not be necessary to switch the TSP on. Normal cleanup time is 1-5 minutes, bringing the pressure of the sample in the clean section down to the $10^{-6}\tau$ range. The fastest cleanup is obtained at 48 amps.

7.2 Before each run the TSP is outgassed to remove any gases that have embedded themselves in the metal, and to act as a pump to reduce the pressure in the line. If a particularly dirty sample has been run the TSP should be outgassed

into the diffusion pump before putting the bakeout on.

8. ARGON EXTRACTION

8.1 Having followed procedures 5.3.1 - 5.3.7.3, take a reading of the pressure and write it on the analysis sheet (INITIAL PRESS).

8.2 Valve off the diffusion pump to avoid pumping away the sample.

8.3 Valve off the clean section and the ion pump so that the extracted gas will initially remain in the dirty section. This is a safety procedure to avoid contamination of the clean section in case of problems such as a leak developing.

8.4 Let in the spike:

8.4.1 Check that the pump and clean section valves are closed.

8.4.2 Using the torque wrench, check that the top valve is closed (one click).

8.4.3 Open the lower valve for about 10 seconds to allow the spike gas into the gas pipette, then close it again.

8.4.4 Close the lower valve, then open the top valve to let the spike into the system. The gas will take a minute or so to filter through the molecular sieve.

8.4.5 Fill in the Argon No. and Spike No. on the analysis sheet, and the Argon No. and Sample No. on the spike list.

8.4.6 Close the upper valve.

8.5 Sample Fusion

8.5.1 Place the RF coil around the furnace tube, centred on the appropriate sample. Normally the samples are run in order from the flange end to the far end. Turn on

8.5.2 Set up the cooling fan at the far end of the tube, and place the mirror beneath the sample.

8.5.3 Check that the dial on the RF generator is at 0 before switching on. Even at 0 the RF is too powerful for most samples so the heating must be started very gently. To do this, flick the start button, then the stop button quickly for several minutes. Once the crucible is glowing dull red most of the gas has evolved and the power may be left on.

8.5.4 Carefully increase the power to full scale or until the crucible is glowing brightly (~1500° when gold coloured).

8.5.5 Leave on for 6-7 minutes, or longer for a large sample, then reduce the power slowly and switch off.

8.6 Clean-up

As the gas leaves the sample it passes over a 3 Å molecular sieve to remove water. Other gases are removed by using the titanium sublimation pump and/or getter.

8.6.1 Valve off the ion pump and switch the ionisation gauge to 10 μA, 10^{-4} τ and 10 scale.

8.6.2 Move the RF coil and the cooling fan onto the getter, if it is to be used.

8.6.3 Open the valve to the clean section then close valve after a minute to avoid possible contamination from the molecular sieve.

8.6.4 Turn on the titanium sublimation pump (see section 7.1), until the sample pressure drops onto 10^{-6} τ range. If it will not come down, the getter may be used as well. Large samples (e.g. air capsules) may be run on 10^{-5} τ range.

8.6.5 If the pressure will not come on scale on the 10^{-4} range after using the sublimator and getter for 20-30 minutes the sample may require splitting:

8.6.5.1 With the central valve firmly closed, open the diffusion pump valve and pump the 'dirty' section for several minutes before closing it again.

8.6.5.2 Open the central valve to allow the gas to expand into the entire system, for a minute or two. Close the valve and turn on the sublimator as before.

8.6.5.3 If the pressure is still off-scale after splitting the sample twice, there is probably a leak somewhere and the sample must be abandoned.

8.6.6 Once a good pressure has been reached (normally $1\text{-}5\text{x}10^{-6}$ T) turn on the chart recorder and use AUTOSCAN to check masses 34-42 for peaks on amplifier range 1.

8.6.7 When young samples are being run, and routinely at least once a week the Ion Repeller and Electron Beam Control voltages on the mass spectrometer should be checked. Using the avometer (with red terminal in right hand), the IR voltage is measured across the centre pin on the white plug and the one to its right. The centre pin has a red spot. The voltage should read 1.0 on range 10. The EBC is measured across the centre pin and the one on its left, and should read 70 on range 100. Use the appropriate dial and screw to adjust if required. If in doubt, read the MS10 manual.

8.6.8 Take a reading of the pressure and write it on the analysis sheet (FINAL PRESSURE). The pressure should be on 10^{-5} T or 10^{-6} T scale. If higher, then re-getter for a few seconds to bring it down.

8.6.9 Start the mass spectrometry.

9. MASS SPECTROMETRY

9.1 Close the valve to the ion pump at the back of the mass spectrometer.

9.2 Tune the mass spectrometer to mass 40 and start letting in the gas. Open the variable leak valve to about 100, at which stage the peak should be rising, and use the fine tune to sit on top of the peak. Continue to open the variable leak valve to 250, changing amplifier ranges as required. On amplifier range 250 do a quick check of the fine tuning. If the sample weight has been judged correctly, all the gas will go into the mass spectrometer without the 40 peak going off scale on range 1000. If the peak is still rising rapidly halfway up range 1000, care must be taken to ensure that the variable leak valve is closed before the peak goes over the top of the range,

9.2.1 Close the variable leak valve.

9.2.2 If all the gas is in the mass spectrometer, start the bakeout for the next sample. If some of the sample remains in the vacuum line, start the bakeout <u>except</u> BAKEOUT 1, and see section 9.6.

9.3 Start the mass spectometry: the 36,38, 40 peaks are measured in this sequence five times as follows :

9.3.1 Turn the mass dial to 34 to get a zero for the 40 peak. Label the peak with mass and amplifier range.

9.3.2.1 Switch to the amplifier range appropriate for the 36 peak and allow the zero to settle. This is usually range 2.5, but will possibly be 10 for very young or 1 for very old

samples, or if the sample weights have been over- or under-estimated.

9.3.2.2 Tune in to the top of the 36 peak and leave for a minute or two to get at least 0.5cm of stable measurement. Label with mass and range.

9.3.2.3 Turn back to mass 34 to get a zero, and allow it to stablise.

9.3.3 Switch to the amplifier range for mass 38- usually 100. Tune into the top of the peak and make a measurement. Turn back to mass 34.

9.3.4 Switch to the amplifier range for mass 40 and measure the peak, One entire scan has now been completed.

9.4 Repeat the steps in section 8.3 four more times to make a total of five scans.

9.5 If all the sample has been let into the mass spectrometer, turn off the chart recorder and open the valve to the ion pump at the back of the mass spectrometer to pump it out. Fill in INITIAL/FINAL FRACTION on analysis sheet as 1.0,0.0.

9.6 If all the sample has not been let in, tune to mass 38 on range 100 and open the variable leak valve to 250 until all the gas has been let in. Close the variable leak valve then turn off the chart recorder and open the mass spectrometer to the ion pump. Turn on BAKEOUT 1. Calculate the FINAL FRACTION by dividing the difference between the 38 peak heights before and after re-opening the leak valve by the final 38 peak height. The INITIAL FRACTION is always 1.0 unless some gas was pumped away while letting in the sample, i.e. if the 40 peak overshot range 1000.

9.6.1 Outgas the getter and start the bakeout for the next sample.

10. CHART MEASUREMENT

Join the peak tops together along the page for the 40 and 38 peaks. For the 36 peaks the baseline has a tendency to wander, so lines are drawn through the tops of the individual peaks, following the slope. Extend the 40 line back to where the gas was let in.

10.2 Join together the baselines for 40 and 38 peaks. Draw in baselines for each individual 36 peak, paying more attention to the baseline after the peak than that before.

10.3 Draw in a line up each 36 peak at the point where the flat top finishes and drops back to zero. This is the line along which measurements are taken for each set.

10.4 Read off the peak heights: place the centimetre scale of the ruler along the measuring line, making sure that the 0 is on the baseline. Read off the 40 and 38 peak heights to 0.01 cm, and write in on the analysis sheet without the decimeal point. e.g. 10.42 cm = 1042. Read off the 36 peak height, remembering to shift the ruler to the appropriate baseline. Write the amplifier ranges used on the analysis sheet. (or KARAGE on WORKSTATION)

10.5 Calculate the sample using the AGE program on the computer.

LEAK CHECKING

11.1 The most obvious sign of a leak in the vacuum system is that the system pressure rises, or will not fall. A large leak will show as a pressure rise on the ion gauge as soon as the clean section valve is opened, even with the diffusion pump operating. Smaller leaks will be visible as a pressure rise only when the pumps are valved off, and then may be confused with the results of a bad bakeout.

11.2 If the pressure rises rapidly when the clean section is opened after bakeout, check first that the system has cooled enough (molecular sieve $100^{\circ}C$), then that the diffusion pump has been pumping the system, i.e. the bypass valve is closed, the "rotary" valve is open, and the diffusion pump valve is open. If not, remedy and re-bake for at least half an hour.

11.3 Next, check the copper gasket on the large flange where the sample tube is attached. Acetone sprayed on should provide a temporary seal and cause a visible drop in pressure on the ion gauge. If the pressure is already off-scale, a brief outgassing of the getter may bring it down enough to read.

11.3.1 If a large leak is not found in the large gasket, try spraying acetone over small joints valves, and glassware, in turn. Try tightening the bolts first but if there is no improvement change any offending gasket and refer Section 11.6.11.9 for pumping and baking.

11.4 Small leaks are harder to detect: it is possible to get a pressure reading on 10^{-8} range with a small leak. Often the first sign of a very small leak is a slight elevation of pressure in the ion pump when it is opened. To detect, valve off both ion and diffusion pumps and watch the ion gauge. If the pressure rises then stops there is probably not a leak, but if it continues try spraying acetone on the joints in turn. The leak can be isolated to

valve.

11.5 A helium leak test may be necessary if acetone has not isolated the problem, particularly if the leak is in a valve. Helium can only be used if the pressure is lower than 9×10^{-4} , as it involves opening the mass spectrometer to the system.

11.5.1 Tune the mass spectrometer onto the helium peak by first finding the H_2 peak on range 10 then switching to mass 4. Close off the valve between the mass spectrometer and ion pump, and open the variable leak valve.

11.5.2 Depending on how fast the system pressure is rising, the valves on the rest on the system should be balanced so that the pressure remains relatively stable. Very small leaks are most easily found with the ion pump and diffusion pump valved off, but it may be necessary to keep the diffusion pump working slightly. Similarly,,it may be necessary to pump the mass spectrometer.

11.5.3 Turn the helium supply at the cylinder and carefully go over every joint, valve and glass section. The leak will show up as a rise in the helium peak in the mass spectrometer, and with care can be pinpointed accurately. If the problem is not found above the bench, check all joints below, i.e. around the titanium sublimation tank, diffusion pump, spike tank, rotary pump.

11.5.4 When the leak is located, valve off all pumps and the mass spectrometer before changing the offending gasket, valve, etc.

11.6 Pump out the system and prepare the bakeout: Use the rotary pump, following normal procedures (Section 4.3), but opening up the pump much more slowly to cope with the large volume of air, Pump out the "Dirty" section first, then if the "Clean" section has been let up to air, open the central valve. If not, then bakeout as usual.

11.7 If the "Clean" section has been let up to air, once the pressure has dropped to O.S. 0.5τ (this may take some time), outgas the getter and ion gauge as normal. Outgas the titanium submlimation pump, starting on a low current and building up. Once it has been outgassed for several minutes at 48-50 amp, switch to AUTO and turn on the rest of the bakeout. The system should be baked for at least an hour with the clean section open to the diffusion pump. If the ion pump has air in it, then it must be pumped out into a reasonably clean vacuum system: cool the line after bakeout then with the ion pump switched off open the valve. Once the air has been pumped out remove the high tension lead, drop the magnet, and wrap a heat tape around the ion pump. Bake the entire system into the diffusion pump for at least an hour then cool and replace the magnet. Valve off the ion pump before switching on, then bake the system as usual.

11.8 The mass spectrometer may require baking if air has got in; switch off the filament and mains, remove the magnet and wrap a heat tape around the body. Proceed as with the ion pump, baking out into a clean

band heaters after the filament has been turned on, as gases will have been absorbed onto the cold filament.

11.9 Once the system has been baked and cooled, outgas the sublimator, getter and ion gauge and run a helium leak test to ensure there are no further problems!