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$^{40}Ar/^{39}Ar$ GEOCHRONOLOGY AT THE INSTITUTO DE GEOCIÊNCIAS, USP

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Introduction

The recent construction of the $^{40}Ar/^{39}Ar$ laboratory facility at CPGeo/USP and the establishment of a cooperation agreement between USP and the *Instituto de Pesquisas Energéticas* (IPEN), facilitating access to the IEA-R1 nuclear reactor, provides the South American geological community with a new powerful geochronological tool. We will present a full description of the new CPGeo/USP laboratory installations, equipment, analytical procedures, and results of calibration tests and analyses of standards. We will also discuss future developments for the laboratory.

Laboratory Installations and Instrumentation

The CPGeo/USP $^{40}Ar/^{39}Ar$ laboratory is a fully automated laser extraction noble gas analytical facility. The laboratory complex occupies an area of 48 m^2, divided into four interconnected rooms: a temperature and humidity controlled room housing the mass spectrometer and extraction line; a restricted access laboratory equipped with a microscope, fume hood, and a lead-lined cabinet for handling and storing radioactive samples; a sample preparation room for grain picking and loading irradiation disks; and a plant room housing UPS units and transformers. Two UPS units and a 150 KVA, 220V, three-phase diesel generator ensure clean and continuous power to the entire facility and instrumentation.

A home built fully automated noble gas extraction and purification system is composed of an optical table, where sample visualization and gas extraction by a 6-W Coherent continuous Ar-ion laser occurs, and a stainless steel ultra-high vacuum (UHV) gas purification system equipped with a Polycold Cryocooler and two C-50 Fe-Ti-Zr SAES getters.

The Mass Analyser Products (UK) MAP-215-50 mass spectrometer at USP is a 15-cm radius with extended geometry and 50mm 90° sector electrostatic analyzer equipped with a Nier-type source (Nier, 1940), which ensures high sensitivity and resolution. The mass spectrometer houses two independent collectors, a Faraday collector positioned on the high-mass side of the optic axis and a Balzers 217 electron multiplier positioned on the low-mass side. A fixed collector slit enables mass resolution of ca. 440-450 (10% valley), allowing the resolution of all argon peaks from their nearest-neighbor hydrocarbon interferences.

The mass spectrometer is linked to the extraction line through a pneumatic controlled valve and a stainless steel inlet tube. Volume ratio between extraction line and mass spectrometer ensures that 77% of the gas extracted from the sample expand into

the mass spectrometer, minimizing uncertainties due to kinetic-dependent mass discrimination of Ar isotopes. At installation, mass spectrometer sensitivity was 8.6 x 10^{-4} amps.torr^{-1}, ^{40}Ar rise rate was 3.6 x 10^{-6} A.min^{-1} (ca. 8,7 x 10^{-13} cc.min^{-1}) and resolution was 446. Periodic scans, from mass 3 to mass 60, in dynamic and static modes, provide information on the cleanness of the system. Gas extraction and mass spectrometry are fully automated through Mass Spec v. 5.11, a Macintosh software written specifically for ^{40}Ar/^{39}Ar analysis and data reduction (Deino, 1996, unpublished Mass Spec software manual). Full automation is possible because the extraction line and the mass spectrometer are equipped with remotely controlled pneumatically actuated valves.

Analytical Procedures

The main types of analyses performed at the CPGeo/USP ^{40}Ar/^{39}Ar laboratory are total fusion and incremental heating analysis of single grains, grain clusters, or rock fragments. Total fusion analysis are ideal for clean, single phase, homogeneous grains with a simple thermal history, when the distribution of radiogenic ^{40}Ar* and neutron induced ^{39}Ar is expected to be uniform throughout the grain. We have so far restricted the single fusion method to the analysis of standards, which, in general, meet the requirements above. The incremental heating method is our chosen procedure for unknown analysis. However, optically transparent Fe-poor silicates such as quartz and alkali-feldspars, particularly sanidine, do not couple well, precluding their analysis by the incremental heating method.

Grains in the 0.2-2.0 mm range are ideal for ^{40}Ar/^{39}Ar analysis using the laser-heating method. Samples larger than 2.0 mm are difficult to heat homogeneously with the laser beam, and samples smaller than 0.2 mm may be difficult to manipulate. When the desired phase is extremely fine grained, it is possible to load several individual crystals in the sample wells and heat these grains with a defocused laser beam.

During sample analysis, each grain in the sample disk is pre-programmed for gas extraction. Sample pit position, laser output power, laser beam diameter, laser rise rate and time at full intensity, and gas clean-up time are programmed for each grain. A sample/blank ratio of 10:1 is desirable for precise analysis, but smaller signals can be reliably measured. Mass spectrometric analysis is fully automated and is carried out by the peak hopping method, where mass/e positions 40, 39, 38, 37, 36, and baseline at 36.2 and 35.8 are measured. To ensure precision, the signals at mass/e 40, 39, 38 and 37 are measured 7 times and the signal at mass/e 36 is measured 25 times. Eight cycles are routinely measured for each fraction of gas extracted. These measurements are extrapolated to time zero (time of gas inlet into the mass spectrometer) and the extrapolated values are used in age calculation. An important parameter during mass spectrometry is the shape of the signal intensity for each isotope vs. time curve (isotope evolution). Linear or slightly parabolic isotope evolutions, typical at the CPGeo/USP laboratory operating conditions, permit precise and accurate extrapolation to time zero.

At the CPGeo/USP ^{40}Ar/^{39}Ar laboratory, we routinely measure full system blanks immediately before and immediately after a mineral/rock grain is analyzed; when necessary, we also program full system blanks during a mineral/rock analysis. To monitor mass spectrometer sensitivity and discrimination we introduce 0.2 cc of purified atmospheric argon (containing approximately 1.2 x 10^{-13} moles of Ar) from a gas pipette attached to the ultra-high vacuum extraction line. An air pipette is measured between each sample and the discrimination ($D = [R_t/R_m]^{1/\Delta M}$) is calculated, enabling automatic discrimination correction. Measured ratios in our system are relatively constant at ca. 289.

IPEN IEA-R1 reactor and irradiation procedures

Samples (single crystal, cluster of crystals, rock fragment, glass, etc.) are irradiated, together with appropriate neutron flux standards (we routinely use AC sanidine, FC sanidine, GA1550 biotite, and Hb3gr hornblende), at the IPEN/CNEN IEA-R1 nuclear reactor, located at USP. The IEA-R1 reactor is a swimming pool reactor with 5 mega-Watts capacity currently operating at 2 mega-Watts. Experimental measurements of fast, epithermal, and thermal neutrons, using gold foil at position 58-5 (and with the reactor operating at 5MW capacity) (Table 1) place the IEA-R1 reactor well within the neutron flux values of other reactors used in ^{40}Ar/^{39}Ar geochronology (McDougall and Harrison, 1999, p. 56).

Samples and standards are placed in the correct positions in the Al-irradiation disks and the disks are closed with appropriate lids and individually wrapped with Al-foil. Individually wrapped disks are stacked and wrapped together with Al-foil and encapsulated in a silica tube. The sealed vial is placed, through remote manipulation tongs, inside a 1.5 mm-wall Cd-

container, this container is placed in a rotatable Al-rod, and the rod is placed in the irradiation position 58-5, just outside the reactor core. After irradiation, the Cd-container is removed from the rotatable Al-rod, is remotely opened inside the reactor pool, and only the sealed Si tube is removed from the reactor pool.

Reactor calibration

The first calibration test for sample irradiation at the IPEN reactor, with the samples irradiated in a stationary position, yielded J-factors for a single disk ranging from 0.001535 to 0.001790, resulting in a mean value of 0.001635, standard deviation of 0.00013, and a coefficient of variation of 7.9%, values unacceptable for precise and accurate $^{40}Ar/^{39}Ar$ analysis. To circumvent this problem, subsequent irradiations were carried-out with the samples placed in the rotatable Al-rod driven by an external motor. The 9 m-long rod is inserted into the reactor position EIF58 and the samples are rotated during the irradiation. The rotational and precessional movements of the sample container inside the Al-rod ensures that each position in the irradiation disks receives the same neutron dosage, despite the heterogeneity intrinsic to the neutron flux. J-factors calculated from the analysis of a minimum of 10 grains of sanidine Fish Canyon standards from each well in one such irradiation ranged from 0.004792 to 0.004828, yielding a mean value of 0.00481, standard deviation of 0.0000095, and a coefficient of variation of 0.197% for the J-factor in a disk, parameters well suited for $^{40}Ar/^{39}Ar$ geochronology. Fish Canyon sanidine standards, arranged in radial geometry and irradiated in ten different sample disks stacked into a vertical column, were also analyzed. The results (0.000004 units x mm^{-1}) are comparable to similar tests carried out in the Oregon State University (USA) triga reactor (Vasconcelos, unpublished results), indicating that the vertical neutron flux does not pose problems for the sample sizes and the sample disks used in the USP laboratory.

Finally, to derive correction factors for the reactions ^{40}Ca (n,nα) ^{36}Ar, ^{40}Ca (n,α) ^{37}Ar, and ^{42}Ca (n, α) ^{39}Ar we irradiated grains of synthetic $CaSi_2$. To correct for the reaction ^{40}K (n,p) ^{40}Ar, we irradiated synthetic K_2SO_4 salt grains precipitated from a solution made with analytical grade salts. Total fusion analyses of these grains yield the correction factors listed in Table 1. These values are similar to values for these correction factors obtained from similar reactors elsewhere (McDougall and Harrison, 1999).

Standard Analysis

To test the accuracy and precision of geochronology results at the CPGeo-USP laboratory, we analyzed international standards (Table 1) using Fish Canyon sanidine as the neutron fluence monitor. The results are indistinguishable, at the 2σ level, from the accepted ages for these standards (Table 2).

Table 1 - Data on the IPEN-USP nuclear reactor used for irradiation by the CPGeo Ar Laboratory

Reactor, location, and irradiation position	Type	Cadmium Shielding	Slow N flux ($n.cm^{-2}.s^{-1}$) (x 10^{13})	Epithermal N flux ($n.cm^{-2}.s^{-1}$) (x 10^{13})	Fast N flux ($n.cm^{-2}.s^{-1}$) (x 10^{13})	J/h (x 10^{-4})	$(^{36}Ar/^{37}Ar)_{Ca}$ (x 10^{-4})	$(^{39}Ar/^{37}Ar)_{Ca}$ (x 10^{-4})	$(^{40}Ar/^{39}Ar)_{K}$ (x 10^{-4})
IPEN IEA-R1 USP, São Paulo, Brazil EIF (58-Level 5)	swimming pool	1.5 mm	4.72	2.91	1.68	1.6	2.39 ± 0.01	15.52 ± 0.05	7.7 ± 2

Table 2- Standards analyzed at USP.

Std No.	Mineral	K-Ar (Ma) ± 1σ	$^{40}Ar/^{39}Ar$ (Ma) ± 1σ (published)	(USP) $^{40}Ar/^{39}Ar$ (Ma) ± 1σ
GA 1550	biotite	97.9 ± 0.9[a]	98.8 ± 0.5[e]	**99.08 ± 0.15**
KA-86	lepidolite	97.3 ± 3.1[b]	-	**97.9 ± 0.3**
KA-83	orthoclase	95.4 ± 3.9[b]	-	**92.6 ± 0.5**
P-207	muscovite	81.0 ± 2.1[c]	-	**82.0 ± 0.5**
FC-2	sanidine	-	28.02 ± 0.16[e]	**[28.02]**
B4M	muscovite	18.6 ± 0.4[a]	-	**18.53 ± 0.17**
B4B	biotite	17.3 ± 0.2[a]	-	**17.30 ± 0.20**
AC	sanidine	1.12 ± 0.02[a]	1.194 ± 0.007[e] 1.186 ± 0.006[f]	**1.189 ± 0.005**

a. McDougall and Harrison, 1999; b. University of São Paulo (K-Ar ages- K-Ar laboratory, unpublished results); c. Dalrymple and Lamphere, 1969; d. Roddick, 1983; e. Renne et al., 1998; f. Turrin et al., 1994.
Age in [ ] is the nominal age for the neutron fluence monitor used to calculate the other $^{40}Ar/^{39}Ar$ ages in the column.

Future Developments and Conclusions

The experimental results illustrated above indicate that the Ar Laboratory at CPGeo/USP is fully operational. The instrumentation has been repeatedly tested in fully automated mode with exceptional results. The analyses of mass spectrometer blanks, extraction line blanks, and air aliquots reveal very low blanks, the steady maintenance of the ultra-high vacuum, and analytical parameters (beam stability, sensitivity, discrimination, etc.) suitable for modern $^{40}Ar/^{39}Ar$ geochronology.

Results from calibration tests for the IEA-R1 nuclear reactor are extremely encouraging, indicating that the IPEN reactor is suitable for the type of irradiation necessary for modern, precise, and accurate $^{40}Ar/^{39}Ar$ geochronology. The introduction of the rotational device for sample irradiation circumvents the problem of heterogeneous neutron flux, ensuring that J-factors calculated for a sample disk are applicable to all samples in that disk, irrespective of its position in relation to the neutron fluence monitors. The calibration tests for interfering isotope reactions at the IPEN reactor yield parameters very similar to those obtained for other reactors. Geochronological investigations requiring total fusion and incremental-heating analysis of single grains or clusters of grains (except for grains that do not couple with Ar-ion lasers such as sanidine) can be routinely carried out at the USP laboratory.

References:

Dalrymple, G. B., and Lanphere, M. A. 1969. Potassium-argon dating. Freeman, San Francisco.

McDougall, I., and Harrison, T.M. 1999. Geochronology and Thermochronology by the $^{40}Ar/^{39}Ar$ Method, 2nd ed., Oxford, Oxford University Press, 269 p.

Merrihue, C., and Turner, G. 1966. Potassium-argon dating by activation with fast neutrons. J. Geophys. Res. 71: 2852-2857.

Nier, A. O. 1940. A mass spectrometer for routine isotope abundance measurements. Rev. Sci. Inst. 11: 212-216.

Renne, P. R., Swisher, C. C., Deino, A. L., Karner, D. B., Owens, T. L., and DePaolo, D. J. 1998. Intercalibration of standards, absolute ages and uncertainties in $^{40}Ar/^{39}Ar$ dating. Chem. Geol. 145: 117-152.

Roddick, J. C. 1983. High precision intercalibration of ^{40}Ar-^{39}Ar standards. Geochim. Cosmochim. Acta 47: 887-898.

Turrin, B.D., Donnelly, N.J.M., and Hearn, B.C.Jr., 1994. $^{40}Ar/^{39}Ar$ ages from the rhyolite of Alder Creek, California; age of the Cobb Mountain normal-polarity subchron revisited: Geology 22: 251-254.

Vasconcelos et al. (2001) $^{40}Ar/^{39}Ar$ Geochronology at the Instituto de Geociências, USP: Instrumentation, Analytical Procedures, and Calibration. Submitted to Anais da Academia Brasileira de Ciências.