

Open File Report OF-AR-1



New Mexico Bureau of Geology and Mineral Resources
A division of
New Mexico Institute of Mining and Technology

$^{40}\text{Ar}/^{39}\text{Ar}$ Geochronology at the New Mexico Bureau of Geology and Mineral Resources

Prepared By:

William C. McIntosh, Matthew Heizler, Lisa Peters and Richard Esser
New Mexico Bureau of Geology, Socorro, NM 87801

NEW MEXICO BUREAU OF GEOLOGY AND MINERAL RESOURCES

Peter A. Scholle, *Director and State Geologist*

a division of

NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY

Daniel H. López, *President*

BOARD OF REGENTS

Ex Officio

Bill Richardson, *Governor of New Mexico*

Michael J. Davis, *Superintendent of Public Instruction*

Appointed

Ann Murphy Daily, *President, 1999–2004, Santa Fe*

Randall E. Horn, *Secretary/Treasurer, 1997–2003, Albuquerque*

Sidney M. Gutierrez, *2001–2007, Albuquerque*

Anthony L. Montoya, Jr., *2001–2003, Socorro*

Robert E. Taylor, *1997–2003, Silver City*

NEW MEXICO GEOCHRONOLOGY RESEARCH LABORATORY STAFF

WILLIAM MCINTOSH, *Geochronologist*
MATT HEIZLER, *Geochronologist*

LISA PETERS, *Argon Laboratory Technician*
RICHARD ESSER, *Argon Laboratory Technician*

BUREAU STAFF

BRUCE D. ALLEN, *Field Geologist*
RUBEN ARCHULETA, *Metallurgical Lab. Technician II*
SANDRA H. AZEVEDO, *Cartographer II*
ALBERT BACA, *Lead Maintenance Carpenter*
JAMES M. BARKER, *Associate Director for Operations, Senior Industrial Minerals Geologist*
PAUL W. BAUER, *Associate Director for Government Liaison, Senior Geologist, Manager of Geologic Mapping Program*
LYNN A. BRANDVOLD, *Senior Chemist*
BRIAN S. BRISTER, *Petroleum Geologist*
RON BROADHEAD, *Associate Director for Industry Liaison, Principal Senior Petroleum Geologist*
RITA CASE, *Administrative Secretary II (Alb. Office)*
STEVEN M. CATHER, *Senior Field Geologist*
RICHARD CHAMBERLIN, *Senior Field Geologist*
SEAN D. CONNELL, *Albuquerque Office Manager, Field Geologist*
RUBEN A. CRESPIN, *Manager, Fleet/General Services*
JEANNE DEARDORFF, *Assistant Editor*
NELIA W. DUNBAR, *Analytical Geochemist*
RICHARD ESSER, *Senior Lab. Associate*
ROBERT W. EVELETH, *Senior Mining Engineer*
KARL FRISCH, *GIS Technician*
PATRICIA L. FRISCH, *Assistant Curator of Mineral Museum*
LEO O. GABALDON, *Cartographer II*
NANCY S. GILSON, *Editor*
KATHRYN E. GLESENER, *Senior Cartographer/Manager, Cartography Section*
DEBBIE GOERING, *Business Office Coordinator*
TERRY GONZALES, *Information Specialist*
IBRAHIM GUNDILER, *Senior Extractive Metallurgist*
LYNN HEIZLER, *Senior Lab. Associate*
MATT HEIZLER, *Assistant Director for Laboratories, Geochronologist*
LYNNE HEMENWAY, *Geologic Information Center Coordinator*
GRETCHEN K. HOFFMAN, *Senior Coal Geologist*

GLEN JONES, *Assistant Director for Computer/Internet Services*
THOMAS J. KAUS, *Cartographer I*
PHILIP KYLE, *Professor, Geochemistry*
SUSIE KYLE, *Administrative Secretary I*
LEWIS A. LAND, *Hydrogeologist*
ANNABELLE LOPEZ, *Petroleum Information Coordinator*
THERESA LOPEZ, *Administrative Secretary I*
DAVID W. LOVE, *Principal Senior Environmental Geologist*
JANE A. CALVERT LOVE, *Managing Editor*
VIRGIL W. LUETH, *Assistant Director for Public Outreach, Mineralogist/Economic Geologist, Curator of Mineral Museum*
MARK MANSELL, *GIS Specialist*
DAVID MCCRAW, *Senior Geologic Lab. Associate*
WILLIAM MCINTOSH, *Senior Volcanologist*
CHRISTOPHER G. MCKEE, *X-ray Facility Manager*
VIRGINIA T. MCLEMORE, *Minerals Outreach Liaison, Senior Economic Geologist*
PATRICIA JACKSON PAUL, *Geologic Lab. Associate*
LISA PETERS, *Senior Lab. Associate*
L. GREER PRICE, *Senior Geologist/Chief Editor*
ADAM S. READ, *Senior Geological Lab. Associate*
BEN REBACH, *Cartographer II*
WILLIAM D. RAATZ, *Petroleum Geologist*
MARSHALL A. REITER, *Principal Senior Geophysicist*
JOHN SIGDA, *Geohydrologist*
GREGORY SANCHEZ, *Mechanic-Carpenter Helper*
TERRY THOMAS, *ICP-MS Manager*
FRANK TITUS, *Senior Outreach Hydrologist*
LORETTA TOBIN, *Executive Secretary*
AMY TRIVITT-KRACKE, *Petroleum Computer Specialist*
JUDY M. VAIZA, *Assistant Director for Finance*
MANUEL J. VASQUEZ, *Mechanic II*
SUSAN J. WELCH, *Manager, Geologic Extension Service*
MAUREEN WILKS, *Geologic Librarian, Manager of Publication Sales*

EMERITUS

GEORGE S. AUSTIN, *Emeritus Senior Industrial Minerals Geologist*
CHARLES E. CHAPIN, *Emeritus Director/State Geologist*
JOHN W. HAWLEY, *Emeritus Senior Environmental Geologist*

JACQUES R. RENAULT, *Emeritus Senior Geologist*
SAMUEL THOMPSON III, *Emeritus Senior Petroleum Geologist*
ROBERT H. WEBER, *Emeritus Senior Geologist*

Plus research associates, graduate students, and undergraduate assistants.

$^{40}\text{Ar}/^{39}\text{Ar}$ and K-Ar dating

Often, large bulk samples (either minerals or whole rocks) are required for K-Ar dating and even small amounts of xenocrystic, authigenic, or other non-ideal behavior can lead to inaccurate ages. The K-Ar technique is susceptible to sample inhomogeneity as separate aliquots are required for the potassium and argon determinations. The need to determine absolute quantities (i.e. moles of $^{40}\text{Ar}^*$ and ^{40}K) limits the precision of the K-Ar method to approximately 1% and also, the technique provides limited potential to evaluate underlying assumptions. In the $^{40}\text{Ar}/^{39}\text{Ar}$ variant of the K-Ar technique, a sample is irradiated with fast neutrons thereby converting ^{39}K to ^{39}Ar through a (n,p) reaction. Following irradiation, the sample is either fused or incrementally heated and the gas analyzed in the same manner as in the conventional K-Ar procedure, with one exception, no argon spike need be added.

Some of the advantages of the $^{40}\text{Ar}/^{39}\text{Ar}$ method over the conventional K-Ar technique are:

1. A single analysis is conducted on one aliquot of sample thereby reducing the sample size and eliminating sample inhomogeneity.
2. Analytical error incurred in determining absolute abundances is reduced by measuring only isotopic ratios. This also eliminates the need to know the exact weight of the sample.
3. The addition of an argon spike is not necessary.
4. The sample does not need to be completely fused, but rather can be incrementally heated. The $^{40}\text{Ar}/^{39}\text{Ar}$ ratio (age) can be measured for each fraction of argon released and this allows for the generation of an age spectrum.

The age of a sample as determined with the $^{40}\text{Ar}/^{39}\text{Ar}$ method requires comparison of the measured $^{40}\text{Ar}/^{39}\text{Ar}$ ratio with that of a standard of known age. Also, several isotopes of other elements (Ca, K, Cl, Ar) produce argon during the irradiation procedure and must be corrected for. Far more in-depth details of the determination of an apparent age via the $^{40}\text{Ar}/^{39}\text{Ar}$ method are given in Dalrymple et al. (1981) and McDougall and Harrison (1999).

Analytical techniques

Sample Preparation and irradiation details

Mineral separates are obtained in various fashions depending upon the mineral of interest, rock type and grain size. In almost all cases the sample is crushed in a jaw crusher and ground in a disc grinder and then sized. The size fraction used generally corresponds to the largest size possible, which will permit obtaining a pure mineral separate. Following sizing, the sample is washed and dried. For plutonic and metamorphic rocks and lavas, crystals are separated using standard heavy liquid, Franz magnetic and hand-picking techniques. For volcanic sanidine and plagioclase, the sized sample is reacted with 15% HF acid to remove glass and/or matrix and then thoroughly washed prior to heavy liquid and magnetic separation. For groundmass concentrates, rock fragments are selected which do not contain any visible phenocrysts.

The NMGRL uses either the Ford reactor at the University of Michigan (to be phased out by the summer of 2003), the McMaster Nuclear Reactor, at McMaster University, or the Nuclear Science Center reactor at Texas A&M University. At the Ford reactor, the L67 position is used (unless otherwise noted) and the D-3 position is always used at the Texas A&M reactor. All of the Michigan irradiations are carried out underwater without any shielding for thermal neutrons, whereas the Texas irradiations are in a dry location, which is shielded with Boron and Cadmium. Depending upon the reactor used, the mineral separates are loaded into holes drilled into Al discs or into 6 mm I.D. quartz tubes. Various size Al discs are used. For Michigan irradiations, six hole or twelve hole, 1 cm diameter discs are used and all holes are of equal size. Samples are placed in the 0°, 120° and 240° locations and standards in the 60°, 180° and 300° locations for the six hole disc. For the twelve hole disc, samples are located at 30°, 60°, 120°, 150°, 210°, 240°, 300°, and 330° and standards at 0, 90, 180 and 270 degrees. If samples are loaded into the quartz tubes, they are wrapped in Cu foil with standards interleaved at ~0.5 cm intervals. For Texas irradiations, 2.4 cm diameter discs contain either sixteen or six sample holes with smaller holes used to hold the standards. For the six hole disc, sample locations are 30°, 90°, 150°, 210°, 270° and 330° and standards are at 0°, 60°, 120°, 180°, 240° and 300°. Samples are located at 18, 36, 54, 72, 108, 126, 144, 162, 198, 216, 234, 252, 288, 306, 324, 342 degrees and standards at 0, 90, 180 and

270 degrees in the sixteen hole disc. Following sample loading into the discs, the discs are stacked, screwed together and sealed in vacuo in either quartz (Michigan) or Pyrex (Texas) tubes.

Extraction Line and Mass Spectrometer details

The NMGRL argon extraction line has both a double vacuum Molybdenum resistance furnace and a CO₂ laser to heat samples. The Mo furnace crucible is heated with a Tungsten heating element and the temperature is monitored with a W-Re thermocouple placed in a blind hole drilled into the bottom of the crucible. A one inch long Mo liner is placed in the bottom of the crucible to collect the melted samples. The furnace temperature is calibrated by either/or melting Cu foil or with an additional thermocouple inserted in the top of the furnace down to the liner. The CO₂ laser is a Synrad 50W laser equipped with a He-Ne pointing laser. The laser chamber is constructed from a 3-3/8" stainless steel conflat and the window material is ZnS. The extraction line is a two-stage design. The first stage is equipped with a SAES GP-50 getter, whereas the second stage houses two SAES GP-50 getters and a tungsten filament. The first stage getter is operated at 450°C as is one of the second stage getters. The other second stage getter is operated at room temperature and the tungsten filament is operated at ~2000°C. Gases evolved from samples heated in the furnace are reacted with the first stage getter during heating. Following heating, the gas is expanded into the second stage for two minutes and then isolated from the first stage. During second stage cleaning, the first stage and furnace are pumped out. After gettering in the second stage, the gas is expanded into the mass spectrometer. Gases evolved from samples heated in the laser are expanded through a cold finger operated at -140°C and directly into the second stage. Following cleanup, the gas in the second stage and laser chamber is expanded into the mass spectrometer for analysis.

The NMGRL employs a Mass Analyzer Products (MAP) model 215-50 mass spectrometer which is operated in static mode. The mass spectrometer is operated with a resolution ranging between 450 to 600 at mass 40 and isotopes are detected on a Johnston

electron multiplier operated at ~ 2.1 kV with an overall gain of about 10,000 over the Faraday collector. Final isotopic intensities are determined by linear regression to time zero of the peak height versus time following gas introduction for each mass. Each mass intensity is corrected for mass spectrometer baseline and background and the extraction system blank.

Blanks for the furnace are generally determined at the beginning of a run while the furnace is cold and then between heating steps while the furnace is cooling. Typically, a blank is run every three to six heating steps. Periodic furnace hot blank analysis reveals that the cold blank is equivalent to the hot blank for temperatures less than about 1300°C . Laser system blanks are generally determined between every four analyses. Mass discrimination is measured using atmospheric argon, which has been dried using a Ti-sublimation pump. Typically, 10 to 15 replicate air analyses are measured to determine a mean mass discrimination value. Air pipette analyses are generally conducted 2-3 times per month, but more often when samples sensitive to the mass discrimination value are analyzed. Correction factors for interfering nuclear reactions on K and Ca are determined using K-glass/ K_2SO_4 and CaF_2 , respectively. Typically, 3-5 individual pieces of the salt or glass are fused with the CO_2 laser and the correction factors are calculated from the weighted mean of the individual determinations.

Data acquisition, presentation and age calculation

Samples are either step-heated or fused in a single increment (total fusion). Bulk samples are often step-heated and the data are generally displayed on an age spectrum or isochron diagram. Single crystals are often analyzed by the total fusion method and the results are typically displayed on probability distribution diagrams or isochron diagrams.

The Age Spectrum Diagram

Age spectra plot apparent age of each incrementally heated gas fraction versus the cumulative % $^{39}\text{Ar}_K$ released, with steps increasing in temperature from left to right. Each apparent age is calculated assuming that the trapped argon (argon not produced by *in situ* decay of ^{40}K) has the modern day atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ value of 295.5. Additional parameters for each heating step are often plotted versus the cumulative % $^{39}\text{Ar}_K$ released. These auxiliary parameters can aid age spectra interpretation and may include radiogenic yield (percent of ^{40}Ar which is not atmospheric), K/Ca (determined from measured Ca-derived ^{37}Ar and K-derived ^{39}Ar) and/or K/Cl (determined from measured Cl-derived ^{38}Ar and K-derived ^{39}Ar). Incremental heating analysis is often effective at revealing complex argon systematics related to excess argon, alteration, contamination, ^{39}Ar recoil, argon loss, etc. Often low-temperature heating steps have low radiogenic yields and apparent ages with relatively high errors due mainly to loosely held, non-radiogenic argon residing on grain surfaces or along grain boundaries. An entirely or partially flat spectrum, in which apparent ages are the same within analytical error, may indicate that the sample is homogeneous with respect to K and Ar and has had a simple thermal and geological history. A drawback to the age spectrum technique is encountered when hydrous minerals such as micas and amphiboles are analyzed. These minerals are not stable in the ultra-high vacuum extraction system and thus step-heating can homogenize important details of the true ^{40}Ar distribution. In other words, a flat age spectrum may result even if a hydrous sample has a complex argon distribution.

The Isochron Diagram

Argon data can be plotted on isotope correlation diagrams to help assess the isotopic composition of Ar trapped at the time of argon closure, thereby testing the assumption that trapped argon isotopes have the composition of modern atmosphere which is implicit in age spectra. To construct an “inverse isochron” the $^{36}\text{Ar}/^{40}\text{Ar}$ ratio is plotted versus the $^{39}\text{Ar}/^{40}\text{Ar}$ ratio. A best-fit line can be calculated for the data array which yields the value for the trapped argon (Y-axis intercept) and the $^{40}\text{Ar}^*/^{39}\text{Ar}_K$ value (age) from the X-axis intercept. Isochron analysis is most useful for step-heated or total fusion data that have a significant spread in radiogenic yield. For young or low K

samples, the calculated apparent age can be very sensitive to the composition of the trapped argon and therefore isochron analyses should be performed routinely on these samples (cf. Heizler and Harrison, 1988). For very old (>Mesozoic) samples or relatively old sanidines (>mid-Cenozoic) the data are often highly radiogenic and cluster near the X-axis thereby making isochron analysis of little value.

The Probability Distribution Diagram

The probability distribution diagram, which is sometimes referred to as an ideogram, is a plot of apparent age versus the summation of the normal distribution of each individual analysis (Deino and Potts, 1992). This diagram is most effective at displaying single crystal laser fusion data to assess the distribution of the population. The K/Ca, radiogenic yield, and the moles of ^{39}Ar for each analysis are also often displayed for each sample as this allows for visual ease in identifying apparent age correlations between, for instance, plagioclase contamination, signal size and/or radiogenic concentrations. The error (1σ) for each age analysis is generally shown by the horizontal lines in the moles of ^{39}Ar section. Typically, one color or symbol style represent the analyses used for the weighted mean age calculation and the generation of the solid line on the ideogram, whereas another color or symbol style represent data omitted from the age calculation. The diagram is most effective for displaying the form of the age distribution (i.e. gaussian, skewed, etc.) and for identifying xenocrystic or other grains that fall outside of the main population.

Error Calculations

For step-heated samples, a “plateau” for the age spectrum is defined by the steps indicated. The plateau age is calculated by weighting each step on the plateau by the inverse of the variance and the error is calculated by the method of Taylor (1982). A mean sum weighted deviates (MSWD) value is determined by dividing the Chi-squared value by n-1 degrees of freedom for the plateau ages. If the MSWD value is outside the

95% confidence window, the plateau or preferred age error is multiplied by the square root of the MSWD.

For single crystal fusion data, a weighted mean is calculated using the inverse of the variance to weight each age determination (Taylor, 1982). Errors are calculated as described for the plateau ages above.

Isochron ages, $^{40}\text{Ar}/^{36}\text{Ar}_i$ values and MSWD values are calculated from the regression results obtained by the York (1969) method.

References cited

- Dalrymple, G.B., Alexander, E.C., Jr., Lanphere, M.A., and Kraker, G.P., 1981. Irradiation of samples for $^{40}\text{Ar}/^{39}\text{Ar}$ dating using the Geological Survey TRIGA reactor. U.S.G.S., Prof. Paper, 1176.
- Deino, A., and Potts, R., 1990. Single-Crystal $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the Olorgesailie Formation, Southern Kenya Rift, *J. Geophys. Res.*, 95, 8453-8470.
- Deino, A., and Potts, R., 1992. Age-probability spectra from examination of single-crystal $^{40}\text{Ar}/^{39}\text{Ar}$ dating results: Examples from Olorgesailie, Southern Kenya Rift, *Quat. International*, 13/14, 47-53.
- Fleck, R.J., Sutter, J.F., and Elliot, D.H., 1977. Interpretation of discordant $^{40}\text{Ar}/^{39}\text{Ar}$ age-spectra of Mesozoic tholeiites from Antarctica, *Geochim. Cosmochim. Acta*, 41, 15-32.
- Heizler, M. T., and Harrison, T. M., 1988. Multiple trapped argon components revealed by $^{40}\text{Ar}/^{39}\text{Ar}$ analysis, *Geochim. Cosmochim. Acta*, 52, 295-1303.
- Mahon, K.I., 1996. The New "York" regression: Application of an improved statistical method to geochemistry, *International Geology Review*, 38, 293-303.
- McDougall, I., and Harrison, T.M., 1999. *Geochronology and thermochronology by the ^{40}Ar - ^{39}Ar method*. Oxford University Press.
- Steiger, R.H., and Jäger, E., 1977. Subcommittee on geochronology: Convention on the use of decay constants in geo- and cosmochronology. *Earth and Planet. Sci. Lett.*, 36, 359-362.
- Taylor, J.R., 1982. *An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements*, Univ. Sci. Books, Mill Valley, Calif., 270 p.
- York, D., 1969. Least squares fitting of a straight line with correlated errors, *Earth and Planet. Sci. Lett.*, 5, 320-324.