

STANDARD OPERATING PROCEDURE NO. 44
⁴⁰Ar/³⁹Ar GEOCHRONOLOGICAL ANALYSES

REVISION LOG		
Revision Number	Description	Date
44.0	Original SOP	Nov. 25, 2003
44.1	Revisions by PJP	5/19/2004
44v1	Finalized by LMK for posting on Molycorp project website and to send to George Robinson for lab audit. LMK did not edit this SOP.	4/3/07
44v2	Editorial by SKA	10/24/08

1.0 PURPOSE AND SCOPE

This document outlines the procedures for sample analysis using the ⁴⁰Ar/³⁹Ar geochronological method. The ⁴⁰Ar/³⁹Ar method will be used to date minerals from alteration scars, debris flows, and rock samples.

The age results, specifically on the minerals alunite and jarosite, will allow determination of the ages of hypogene alteration (if present) and ages of supergene alteration (weathering). These ages will be used to help identify materials that have experienced the greatest degree and timing of rock weathering.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Team Leader and Characterization Team will have the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate staff to implement this SOP and for ensuring that the procedures are followed.

All New Mexico Geochronology Research Laboratory (hereafter NMGRL) personnel performing these procedures are required to have the appropriate health and safety training. In addition, all NMGRL personnel are required to have a complete

understanding of the procedures described within this SOP, and receive specific training regarding these procedures, if necessary. NMGRL personnel trained on the MAP 215-50 mass spectrometer and its ultra-high vacuum extraction line will undertake the procedures outlined in this protocol. Only NMGRL personnel trained in the use of MASS SPEC data reduction software will be allowed to reduce and interpret $^{40}\text{Ar}/^{39}\text{Ar}$ data.

All NMGRL staff is responsible for reporting deviations from this SOP to the Team Leader.

3.0 RELATED STANDARD OPERATING PROCEDURES

- SOP 1 Data management (including verification and validation)
- SOP 2 Sample management (chain of custody)
- SOP 5 Sampling outcrops, rock piles, and drill core (solid)
- SOP 25 Stable Isotope analysis
- SOP 27 X-ray diffraction analysis
- SOP 26 Electron microprobe analysis

4.0 DATA QUALITY OBJECTIVES

The $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology will be used to address objectives 2, 3, and 9 in the data quality objectives outline by Virginia McLemore for the "Geological and Hydrological Characterization at the Molycorp Questa Mine, Taos County, New Mexico".

- Determine how mineralogy, stratigraphy, and internal structure of the rock piles contribute to weathering and stability. Age constraints on the formation of secondary minerals in alteration scars and debris flows will provide long-term chronology of mineralogical changes that have occurred naturally in the various rock types in the region.
- Determine if the sequence of host rock hypogene and supergene alteration and weathering provides a basis to predict the effects weathering can have on mine rock stability. Age determinations will discriminate between hypogene alteration associated with primary mineralization and those phases formed subsequently by weathering. Age determinations will potentially calibrate degrees of weathering within various rock types.
- Determine how changes in climate over the next 100 years will affect pile weathering and stability. Ar age determinations, when coupled with stable isotope data, provide the potential to define climate changes over longer time periods. In addition, the ages may allow for inferring maximum-minimum climate conditions in the area over long time periods.

5.0 INSTRUMENTATION/EQUIPMENT LIST

- Ultra high-vacuum noble gas extraction line.
 - The NMGRL argon extraction line has both a double vacuum Molybdenum resistance furnace and a CO_2 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 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 CO₂ laser optics are equipped with a II-VI[®] Incorporated Zinc-Selenide faceted lens capable of yielding a uniform beam distribution over a 6 mm by 6 mm area. 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.

- MAP 215-50 rare gas mass spectrometer.
 - The NMGRL employs a Mass Analyzer Products (MAP) model 215-50 mass spectrometer that 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 6,000 over the Faraday collector.
- Macintosh computer and MASS SPEC data collection/reduction software.
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6.0 SAMPLE PREPARATION

- 6.1 The samples are prepared as outlined in S.O.P. 25 and 27 and provided to NMGRL by team members.
- 6.2 The ⁴⁰Ar/³⁹Ar method requires the production of ³⁹Ar from ³⁹K through a (n,p) reaction. See NMGRL Methodology at <http://geoinfo.nmt.edu/publications/openfile/argon/home.html>. Production of ³⁹Ar_K will be accomplished at the McMaster Nuclear Reactor in their 5C fast-flux position for a length of time specified by the NMGRL. Finer-grained samples will require a measure of the amount of ³⁹Ar_K lost (recoiled) from the sample during irradiation.
 - Provided samples are packaged for irradiation at the McMaster Nuclear Reactor, McMaster University.
 - Coarser-grained samples are loaded into 1.5 centimeter machined aluminum disks, containing either six or twelve equal-sized hole patterns. Samples are placed in the 0°, 120° and 240° locations and

flux monitor standards (Fish Canyon Tuff sanidine) 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° with flux monitor standards at 0°, 90°, 180° and 270°. The loaded aluminum discs are stacked and secured with an aluminum threaded rod and nuts.

- Finer-grained sample separates (<5 µm) will be encapsulated *in vacuo* prior to irradiation in quartz glass vials. Up to 8 encapsulation tubes can be irradiated in the 5C position, with non-encapsulated flux monitor standards interspersed at regular intervals.

7.0 SAMPLE ANALYSIS

The coarse-grained samples will be step-heated using the CO₂ laser.

- Weight appropriate for suspected age of sample will be loaded into a copper planchet for laser analyses.
- The copper planchet is loaded into the ultra-highvacuum extraction line. The sample chamber is baked at 75°C for 4 to 6 hours to attain analytical vacuum (~1e-9 Torr).
- Each sample is incrementally heated using a schedule consisting of 6 to 10 steps with increasing wattage. Gases evolved from an individual heating steps are expanded through a cold finger operated at -140°C and directly into the second stage where it is gettered for up to 30 minutes. After gettering, the gas is expanded into the mass spectrometer.
- Following equilibration, the measurement of the five necessary argon isotopes (⁴⁰Ar, ³⁹Ar, ³⁸Ar, ³⁷Ar, ³⁶Ar) begins. The five isotopes are sequentially focused on the collector in the mass spectrometer for 5 to 15 repetitions (cycles). Interspersed throughout the 5 to 15 cycles are baseline measurements – a measure of the noise of the collector. Final isotopic intensities are determined by regression to time zero of the peak height versus time following gas introduction for each mass. Prior to data regression, each mass intensity is corrected for mass spectrometer baseline.
- Interspersed throughout each sample heating schedule are 2 to 4 extraction line blank + mass spectrometer background measurements. The duration of each blank measurement is equivalent to the getting time (up to 30 minutes). Each mass intensity is corrected for extraction system blank and mass spectrometer background.

8.0 DATA REDUCTION

- 8.1 **J-Factor standard.** The amount of $^{39}\text{Ar}_k$ produced in any given irradiation will be dependant on the ^{39}K concentration, the length of the irradiation, the neutron flux the neutron capture cross section for ^{39}K , and the neutron energy distribution. However, because each of these parameters is difficult to determine independently, a mineral standard, or fluence monitor, of known age is irradiated with the samples of unknown age. By irradiating standards and unknowns in a known geometry, the neutron flux (J-factor) can be determined for each unknown following irradiation of the standards..
 - Four to six crystals of Fish Canyon Tuff sanidine (assigned age = 27.84 Ma) per monitor standard location in the irradiation disc are analyzed using the CO_2 laser total fusion method. The resulting $^{40}\text{Ar}/^{39}\text{Ar}$ ratio and assigned age (27.84 Ma) are used to calculate the J-factor for samples from the study.
- 8.2 **Nuclear interference correction factors.** During neutron irradiation, several argon isotopes are produced in addition to the target isotope ^{39}Ar . These reactor-produced isotopes of argon must be corrected for in order to determine an accurate age. The monitoring of the interfering reactions is performed through the use of laboratory salts and glasses. To determine the amount of reactor produced ^{40}Ar from ^{40}K , potassium-rich glass is irradiated with the samples. The $(^{40}\text{Ar}/^{39}\text{Ar})_k$ of the glass is then measured in the mass spectrometer to determine the correction factor that must be applied to the rest of the samples in that irradiation. CaF_2 is also routinely irradiated and measured to determine the $(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ and $(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ correction factors.
- 8.3 **Mass spectrometer discrimination.** In general, electron multipliers detect the lighter isotopes with greater efficiency. To account for this aliquots of atmospheric argon with a known $^{40}\text{Ar}/^{36}\text{Ar}$ ratio (295.5) are measured periodically and a discrimination correction is determined. This correction is applied to each analysis.
- 8.4 **Age determination.** After the argon isotopic analyses are complete and the backgrounds, J-factor, interference correction factors and mass discrimination are applied to the data using the MASS SPEC data reduction software, the NMGR staff interpret the results and assign an apparent age.
- 8.5 **Data presentation.** The resulting $^{40}\text{Ar}/^{39}\text{Ar}$ data will be presented in a publishable table format, and also plotted on an age spectrum and isotope correlation diagrams (McDougall and Harrison, 1999).

9.0 DATA STORAGE

- All $^{40}\text{Ar}/^{39}\text{Ar}$ data collected at the NMGRL is stored in multiple secure locations on several Macintosh computers to maximize data security.

10.0 REFERENCES

McDougall, I., and Harrison, T.M., 1999, Geochronology and Thermochronology by the $^{40}\text{Ar}/^{39}\text{Ar}$ Method: New York, Oxford University Press, xii, 269 p.