**Detailed Methods for Tephrochronology and Geochronology**

**at the New Mexico Institute of Mining and Technology**

**Tephrochronology**

**Sample preparation for electron microprobe analysis**

Lake Mead samples were prepared for quantitative geochemical analysis by electron microprobe analysis first by air drying, and then assessing individual samples for the best preparation method. Samples that were easily disaggregated were prepared as grain mounts in leucite sample molds (Dunbar et al., 2003), and those that were more lithified with prepared as individual rock pieces mounted in plugs. Many of the lithified samples contained significant pore space, and so were placed in a vacuum impregnator during sample preparation so that the epoxy (Spurr low-viscosity 4-part mix) was able to penetrate the pore spaces as completely as possible. Samples were then ground to a completely flat sample surface using diamond-impregnated metal disks, followed polishing using 15, 6 and 1 micron pure diamond grit suspended in distilled water.

Samples were then carbon coated to a thickness of 200 angstrom thickness prior to analysis.

**Electron Microprobe analysis**

The purpose of geochemical analyses of Lake Mead tephra samples was to provide correlations between different units, as well as to assess samples for suitability for 40Ar/39Ar analysis. Towards this end, all samples were investigated using a Cameca SX-100 electron microprobe located at New Mexico Institute of Mining and Technology. Samples were first examined in backscattered electron imaging (BSE) in order to assess the presence or absence of glass shards, as well as to qualitatively assess the phenocryst abundance, size and composition. For fined grained samples, or ones with complex mineralogy, maps of the K concentration of a representative area of sample were collected, in order to be sure to not miss any population of K-rich feldspar. Wherever present, the composition of glass fragments were analyzed, typically 20-30 individual points per sample. If feldspar and fresh biotite were also present in a glass-bearing sample, a representative number of points were collected on these phases. If no glass was present in a sample, a greater number of points were collected on feldspar and biotite, typically 30 points on feldspar and 10-20 on biotite. If two feldspar compositions were present, both were analyzed, and if any zoning appeared to be present, cores and rims of feldspar were analyzed separately. Elements analyzed on glass points include Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, and Fe. An accelerating voltage of 15 kV was used, and a probe current of 10 nA. Beam size of 20 µm was used for all glass points in order to avoid Na loss (Nielsen and Sigurdsson, 1981). For feldspar analyses, determinations for Na, Al, Si, K, Ca, Fe, Sr, and Ba were made, using a 15 kV accelerating voltage, 20 nA beam and 10 µm beam size. Biotite analyses included F, Na, Mg, Al, Si, Cl, K, Ca, Ti, Mn, and Fe, and analyses were made using a 15 kV accelerating voltage, 20 nA beam and 10 µm beam size. Details of all analytical procedures, including count times, crystals used, lines analyzed, background positions, and calibration standards can be found in supplementary documents.

Analytical precision, which is an important factor when making correlations between tephra layers, is determined based on replicate analyses of certified reference materials, which were run several times in each analytical run for all runs over the several year duration of the project. These standard reference materials, including feldspars, amphiboles, and glasses were run as unknowns in each analytical session to monitor calibration accuracy, and inter-run reproducibility. These values are listed as footnotes in the tables of analytical data, and are typically very similar to precision determined based on counting statistics.

**Correlations:**

The ideal material for making geochemical correlations between tephra layers is volcanic glass, which is typically, although not always, unique for a given eruptive event (Perkins et al., 1995). Correlation between glass compositions for different tephra layers can be done quantitatively using statistical difference correlation techniques (Perkins et al., 1995). This method involves calculation of the Euclidean distance function, D, (in standard deviation units) between chemical analyses. The distance function takes into account the analytical error on the analyses, and therefore more heavily weights elements with higher analytical precision. In the case of the analyses presented in this study, the elements that are typically weighted the most highly are Fe, Ca, Ti, Mg and K. The precision on determinations of Si, Al, P, Mn, Na and F tends to be lower, either due to analytical constraints, low abundances, or, as in the case of Na, volatility under the beam, particularly at smaller beam sizes. If two analyses were perfectly identical, the D value would be 0. However, because of normal statistical error of techniques used for shard analysis, the mean composition of two, coarse-grained, chemically identical tephra samples will typically have a D value of around 4 (Perkins et al., 1995). Any value below 10 suggests a high degree of similarity between samples.

If the glass component of a tephra layer has been altered through progressive hydration in which the absorption of water cause mobility of alkali elements (Cerling et al., 1985; Friedman and Long, 1976; Shane, 2000) and eventual breakdown of the glass structure into clay and zeolitic minerals. The glass in many of the tephra layers in the Lake Mead area has been altered to the point of not being able to yield useful chemical compositions, and in these cases, correlations must be done based on phenocrysts content and composition, rather than glass. This method is less quantitative than the glass correlations, but can still yield useful results. The main correlation tool for non-glass-bearing Lake Mead tephra layers has been feldspar composition. Many of the Lake Mead tephra layers contain feldspar. Many contain two feldspar compositions, typically a single sanidine feldspar composition, and a compositional range of plagioclase. Some contain only sanidine or only plagioclase. Some contain anorthoclase. The distribution of feldspar composition can be used as a first indication of correlation or lack of correlation between tephra layers. Adding to this assessment, the exact composition of sanidine, along with the range of Ba concentrations exhibited, provides more detail on correlations between tephra layers. The abundance and composition of biotite are also used as secondary indicators of correlation, but much of the biotite in Lake Mead tephra layers has undergone some level of chemical alteration.

**40Ar/39Ar Geochronology**

Mineral separates, including K-feldspar, anorthoclase, and biotite, were separated from tephra samples and dated using 40Ar/39Ar techniques at the New Mexico Geochronology Research Laboratory. Methods are briefly summarized below.

Tephra layers at Lake Mead consist of variable mixtures of glass, altered glass and crystals. The majority of the crystals are feldspar (including K-bearing anorthoclase or sanidine feldspar) and biotite. Feldspar crystals in the coarsest tephra layers are as large as several mm, although some samples contain very fine (~100 µm) feldspar grains. Some crystals are enclosed within pumice or glass fragments; others occur are free crystals, some with thin glass selvedges.

Sanidine was separated by crushing, sieving and washing the samples followed by a 5-minute treatment in dilute HF acid. The sized material was separated for sanidine using standard magnetic and heavy liquid methods. Sample 19-WB-01 did not use heavy liquids but rather the sized material was placed in a dish and immersed in wintergreen oil where sanidine could be easily handpicked while being viewed under a polarizing binocular microscope. Following handpicking, the crystals were thoroughly cleaned in an ultrasonic bath while immersed in acetone to remove the wintergreen oil. Several of the samples contained a significant plagioclase component that was identified by the measured 37Ar/39Ar ratio and these plagioclase analyses are not reported.

The samples were irradiated in 4 separate irradiations at either the USGS TRIGA reactor in Denver, Colorado or the Oregon State Reactor. The irradiation discs are 1” diameter aluminum trays with either 20 or 24 holes drilled around the perimeter. The crystals were placed around the holes along with interlaboratory standard Fish Canyon sanidine (FC-2) that occupied 8 or 10 of the holes in the disc. Six flux monitor grains from each monitor hole were analyzed and the J-values of the unknown locations were determined with a planar fit to the flux monitor locations. FC-2 is assigned an age of 28.201 Ma (Kuiper et al., 2008) and all ages are calculated with a 40K decay constant of 5.463e-10 /a (Min et al., 2000) while isotope abundances are after Steiger and Jäger (1977).

After irradiation, monitors and unknowns were loaded into either stainless steel or copper trays, evacuated and baked at temperatures of between 100 and 140°C for 4 hours. A CO2 laser was used to fuse the crystals. For 5 of the 6 samples, the extracted gas was analyzed using a Thermo-Fisher Scientific ARGUS VI multi-collector mass spectrometer equipped with five Faraday cups, and one electron multiplier (CDD) operated in ion-counting mode. The configuration has 40Ar, 39Ar, 38Ar, 37Ar and 36Ar on the H1, Axial, L1, L2, and CDD detectors, respectively. The resistor configurations varied between the samples. For sample 19-WB-01 they were 1013 Ohms for 40Ar and 39Ar, 1014 Ohms for 38Ar and 37Ar. For samples 19-WB-42, LMLL-263, LMLL-241 and LMLL-258 all Faradays used 1012 Ohm resistors. For all ARGUS VI analyses, 36Ar was measured on the CDD that has a dead time of 14 ns. Sample 19-WB-243 utilized an MAP-215-50 mass spectrometer. All isotopes were measured using a Balzers SEV-217 electron multiplier for this sample. For the ARGUS VI analyses, the extracted gas was cleaned with two NP 10 getters one operated at 1.6 A and one at room temperature. Gas cleanup occurred during a 45 fusion followed by 15 seconds of additional gettering. For the MAP-215-50 analyses, the extracted gas was cleaned with two GP-50 getters, one operated at 2.0 A and one at room temperature. Gas cleanup occurred during a 30 fusion followed by 60 seconds of additional gettering.

For the ARGUS VI analyses, calibration gases of air and a gas mixture enriched in radiogenic 40Ar along with 39Ar were analyzed interspersed with the analysis to monitor instrument drift and determine detector intercalibration factors. For the MAP-215-50 analyses, air argon was used to determine mass spectrometer discrimination and a power law based on 40Ar/36Ar measurements determined the mass discrimination for all isotopes. ARGUS VI data collection was conducted with the in-house Pychron software where s the MAP-215-50 analyses utilized the program MassSpec developed at the Berkeley Geochronology Center. All data reduction utilized MassSpec version 7.875. Extraction line blanks that include mass spectrometer background are given in the raw intensity worksheet for each analysis. K-glass and CaF2 were included in the irradiations to determine interfering reaction correction factors and these values are also included in the raw intensity worksheet as well as the footnotes to the ratio data worksheet.

The preferred eruption age is calculated based on a weighted mean with a weighting factor being the inverse variance (e.g., Taylor, 1982) and the error is the square root of the sum of 1/σ 2 values. The error is also multiplied by the square root of the MSWD for MSWD greater than 1 and errors are reported at 2σ. J-error and irradiation correction factor uncertainties are included in the weighted mean age error. The analytical data are organized to comply with FAIR data reporting norms (see for instance Schaen et al., 2020).



**References**

Cerling, T. E., Brown, F. H., and Bowman, J. R., 1985, Low temperature alteration of volcanic glass: Hydration, Na, K, 18O, and Ar mobility: Chemical Geology, v. 52, p. 281-293.

Dunbar, N., Zielinski, G., and Voisins, D., 2003, Tephra layers in the Siple Dome and Taylor Dome ice cores, Antarctica: Sources and correlations: Journal of Geophysical Research, v. 108, no. B8, p. 2374-2385.

Friedman, I., and Long, W., 1976, Hydration rate of obsidian: Science, v. 191, p. 347-352.

Kuiper, K.F., Deino, A., Hilgen, F.J., Krijgsman, W., Renne, P.R. and Wijbrans, J.R.,

2008, Synchronizing rock clocks of earth history: Science, v. 320, p. 500-504.

Min, K., Mundil, R., Renne, P. R. and Ludwig, K. R., 2000, A test for systematic errors in 40Ar/39Ar geochronology through comparison with U–Pb analysis of a 1.1 Ga rhyolite. Geochim. Cosmochim. Acta 64, 73–98.

Nielsen, C. H., and Sigurdsson, H., 1981, Qualitative methods for electron microprobe analysis of sodium in natural and synthetic glasses: American Mineralogist, v. 66, p. 547-552.

Perkins, M.E., Nash, W. P., Brown, F. H., Fleck, R. J., 1995, Fallout tuffs of Trapper Creek, Idaho; a record of Miocene explosive volcanism in the Snake River plain volcanic province: [**Geological Society of America Bulletin**](https://www.proquest.com/georef/pubidlinkhandler/sng/pubtitle/Geological+Society+of+America+Bulletin/$N?accountid=14756)[V. 107, pp.](https://www.proquest.com/georef/indexingvolumeissuelinkhandler/23472/Geological+Society+of+America+Bulletin/01995Y12Y01$23Dec+1995$3b++Vol.+107+$2812$29/107/12?accountid=14756) 1484-1506.

Schaen, A.J., Jicha, B.R., Hodges, K.V., Vermeesch, P., Stelten, M.E., Mercer, C.M., Phillips, D., Rivera, T.A., Jourdan, F., Matchan, E.L., Hemming, S.R., Morgan L.E., Kelley, S.P., Cassata, W.S., Heizler, M.T., Vasconcelos, P.M., Koppers, A.A.P., Mark, D.F., Niespolo, E.M., Sprain, C.J., Benowitz, J.A., Hames, W.E., Kuiper, K.F., Turrin, B.D., Renne, P.R., Ross, J., Nomade, S., Guillou, H., Laura E. Webb, L.E., Cohen, B.A., Calvert, A.T., Joyce, N., Morgan Ganderød, M., Wijbrans, J., Ishizuka, O., He, H., Ramirez, A., Pfänder, J.A., Lopez-Martínez, M., Huaning Qiu, H., Brad S. Singer, B.S., 2020, On the reporting and interpretation of 40Ar/39Ar geochronologic data, Geol. Soc. Am. Bull., 133 (3-4), DOI:[10.1130/B35560.1](http://dx.doi.org/10.1130/B35560.1)

Shane, P., 2000, Tephrochronology:  a New Zealand case study: Earth Science Reviews, v. 49, no. 1-4, p. 223-259.

 Steiger, R.H., and Jäger, E., 1977. Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronology. Earth and Planet. Sci. Lett., v. 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.