APPENDIX 1: ANALYTICAL METHODS

SAMPLE PREPARATION

All rock samples were prepared for analysis through the following methods. Fist-sized hand samples were reduced using a hydraulic rock splitter and a representative sample of each was saved for reference. Smaller, split fragments were cut for thin sections and standard (27 x 46 mm), standard microprobe-polished, or large format (51 x 75 mm) thin sections were obtained commercially. Weathering rinds were then trimmed from the remaining sample and post-magmatic mineralization in void space within the sample was removed by the saw. A silicon carbide belt grinder was used to remove metal shavings from trimmed fragments prior to crushing through a jaw crusher. Prior to being passed through a Braun Chipmunk brand jaw crusher (steel crushing plates), rock fragments were washed in deionized water and kept at room temperature until dry. Once through a primary crush, samples were handpicked when necessary to remove any other post-magmatic mineralization and passed through again. The entire jaw-crushed sample was then passed through the alumina ceramic crushing plates of a Braun brand pulverizer ("disk-mill"). The entire sample was then divided by repeated "cone and quartering" to obtain a homogenous, 30 ml aliquot. This 30 ml aliquot was then run through a Spex brand alumina ceramic shatterbox for 10 minutes to ensure a fine grained powder for major and trace element flux fusions. Final powders were placed in borosilicate glass vials, dried uncapped at 100º C for 12-14 hours, and then stored in a desiccator (capped).

Laboratory Procedures for Silicic Glass Purification

Tephra were processed initially closely following magnetic separation techniques detailed in Irvin (2002) and Katoh and others (1999). In all cases, the dominant more felsic glass population was isolated through these methods. In special cases where two populations were observed petrographically, the magnetic properties of the samples seemed to substantiate their dual population component. For these samples, the more felsic population was chosen. Further purification methods listed below:

Purification of Silicic Glass Using Lithium Hetero-polytungstates (LST) Density Liquid

- Purified 80-100 mesh glass was crushed using a Boron Carbide mortar and pestle to <325 mesh (<45µ)
- LST – quartz distilled H_2O mixture prepared between 2.38 g/cm^3 and 2.45 g/cm^3 or 2.45 g/cm^3 and 2.50 g/cm^3.
- Sample was centrifuged in LST to separate light fraction of glass at the top from the heavy fraction of microlitic impurities.
- Light fraction (glass) was decanted, washed with quartz distilled H_2O and dried at 60ºC.

The specific laboratory preparation procedures used on each sample are outlined below:

MB02-58A

- Crush and sieve, recording mass of separate size fractions.
- DIAA wash and acid wash 80-100 mesh (180-150 µm) with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for about 3 minutes, rinse with deionized water and dry.
- Frantz 5 grams of 80-100 mesh (180-150 µm) at 0.25 A to remove magnetic materials and lithic fragments. Run non-magnetic at 0.25 A at 1.0 A to remove feldspars. Run ~2.0 grams of 0.25-1.0 A at 0.5 A. Run 0.5-1.0 A at 0.55 A (3X), then 0.55-1.0 A at 0.95 A. Working split is 0.55-0.95 A.
- Density liquid separation yielding 0.55-0.95 LST (L) @ 2.38–2.45 g/cm$_3$.
- Major and trace element run on DCP.

MB02-58C

- Crush and sieve, recording mass of separate size fractions.
- DIAA wash.
- Acid wash both 60 to 80 (250-180 µm) and 80-100 (180-150 µm) mesh with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for approximately 3 minutes, rinse with deionized water and dry.
- Removal of ferromagnetic minerals with hand magnet.
- Frantz 60-80 size at 0.5 A; equal separation, so 80-100 size used.
- Run 80-100 size at 0.25 A (2X). Removed magnetic minerals and lithic fragments. Run at 0.75 A. Removed feldspars. Run at 0.27 A to remove lithic fragments and glass with inclusions of magnetic minerals. Stock saved

as 0.27-0.65 A. Extract ~2 grams and run at 0.37 A (5X) and run again at 0.65 A (2X).
- Handpick 0.37-0.65 A working fraction to remove altered glass and other contaminant material.

MB02-58B
- Crush and sieve, recording mass of separate size fractions.
- DIAA wash and acid wash 80-100 mesh (180-150 µm) fraction with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for approximately 3 minutes, rinse with deionized water and dry.
- Removal of ferromagnetic minerals with hand magnet.
- Frantz 80-100 size (5 grams) at 0.25 A to remove magnetic minerals and lithic fragments. Run at 1.0 A and save 0.25-1.0 A as stock. Try run at 0.5 A; equal separations. Try run at 0.35A; sample appears to be mostly non-magnetic. Run non-magnetic material at 0.8 A. Working split 0.35-0.8 A.
- Handpick ~1.0 grams of working split to remove altered glass and other contaminant material
- Major and trace element run on DCP.

MB02-57A
- Crush and sieve, recording mass of separate size fractions.
- DIAA wash and acid wash 80-100 mesh (180-150 µm) fraction with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for approximately 3 minutes, rinse with deionized water and dry.
- Removal of ferromagnetic minerals with hand magnet.
- Frantz 80-100 size (5 grams) at 0.25 A to remove magnetic minerals and lithic fragments. Run at 1.0 A to remove feldspars. Save 0.25-1.0 A as stock. Run ~ 2 grams of stock at 0.35 A. Run at 0.9 A. A small amount of feldspars and other contaminants removed. Try run at 0.75 A. Not a good split. Run at 0.8 A. Sample not as clean as possible. Run at 0.38 A. Working split is 0.38-0.8 A.
- Crude handpicking of entire working split. Lots of crystals so proceed to LST procedure
- Density liquid separation yielding (1) 0.38-0.8 LST (L) @ 2.38–2.45 g/cm^3; heavy materials from (1) separated to yield (2) 0.38-0.8 LST (L) @ 2.45–2.50 g/cm^3.
- Major and trace element run on DCP

MB00-21B
- Crush and sieve, recording mass of separate size fractions.
- DIAA wash and acid wash 80-100 mesh (180-150 µm) fraction with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for approximately 3 minutes, rinse with deionized water and dry.
- Frantz 80-100 size (5 grams) at 0.25 A to remove magnetic minerals and lithic fragments. Run at 1.0 A to remove feldspars. Save 0.25-1.0 A as stock. Run ~ 2 grams of stock at 0.35 A. Run at 0.9 A. Run magnetic at 0.9 A at 0.33 A. Working split 0.33-0.9 A.
- Handpick ~1 gram of working split to remove obvious contaminants.
- Density liquid separation yielding 0.33-0.9 LST (L) @ 2.45–2.50 g/cm^3.
- Major and trace element run on DCP.

MB02-57B
- Crush and sieve, recording mass of separate size fractions
- DIAA wash and acid wash 80-100 mesh (180-150 µm) fraction with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for approximately 3 minutes, rinse with deionized water and dry.
- Frantz 80-100 size (5 grams) at 0.1 A (minor magnetics); run at 0.25 A (minor magnetics). Extract ~2 grams of non-magnetic at 0.25 A for working split. Run working split at 0.55 A (3X). Run non-magnetic at 0.55 A at 0.55 A (3X). Working fraction is 0.55-0.95 A.
- Density liquid separation yielding 0.55-0.95 A LST (L) @ 2.45–2.50 g/cm^3.
- Major and trace element run on DCP.

MB02-17A
- Crush and sieve, recording mass of separate size fractions.
- DIAA wash and acid wash 80-100 mesh (180-150 µm) fraction with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for approximately 3 minutes, rinse with deionized water and dry.
- Removal of ferromagnetic minerals with hand magnet.
- Frantz 80-100 size (~3.7 grams) at 0.25 A to remove magnetic minerals and lithic fragments. Run at magnetic at 0.25 A at 1.0 A to remove feldspars. Run at magnetic at 1.0 A at 0.35 A. Run at 0.8 A. Sample appears to have two

populations or a complex mixture. Run magnetic at 0.35 A. Run 0.35-0.8 A at 0.58 A. Final split is 0.58-0.8 A.
- Major and trace element run on DCP.

MB02-69
- Crush and sieve, recording mass of separate size fractions.
- DIAA wash and acid wash 80-100 mesh (180-150 µm) fraction with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for approximately 3 minutes, rinse with deionized water and dry.
- Frantz 80-100 size (5 grams) at 0.25 A to remove magnetic minerals and lithic fragments. Run at 1.0 A to remove feldspars. 3 grams of 0.25-1.0 A run at 0.35 A. Run at 0.9 A and 0.8 A. Sample appears to have two populations. Try magnetic at 0.8 A at 0.55 A; majority of the glass is magnetic. Working split now 0.35-0.55 A.
- Major and trace element run on DCP.

MB00-38D
- Crush and sieve, recording mass of separate size fractions.
- DIAA wash and acid wash 80-100 mesh (180-150 µm) fraction with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for approximately 3 minutes, rinse with deionized water and dry.
- Frantz 80-100 size (5 grams) at 0.25 A to remove magnetic minerals and lithic fragments. Run at 1.0 A to remove feldspars. 3 grams of 0.25-1.0 A run at 0.35 A. Run at 0.9 A and 0.8 A. Sample appears to have two populations. Try magnetic at 0.8 A at 0.55 A (2X). Working split now 0.35-0.55 A.
- Major and trace element run on DCP.

MB01-55
- Crush and sieve, recording mass of separate size fractions.
- DIAA wash and acid wash 80-100 mesh (180-150 µm) fraction with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for approximately 3 minutes, rinse with deionized water and dry.
- Frantz 80-100 size (5 grams) at 0.25 A to remove magnetic minerals and lithic fragments. Run at 1.0 A to remove feldspars. 3 grams of 0.25-1.0 A run at 0.9 A. Magnetic material from 0.9 A run at 0.3 A (2X). Run non-magnetic at 0.3 A at 0.5 A, then 0.6 A. Working split now 0.6-0.9 A
- Handpick 600 milligrams of sample to remove obvious contaminants.
- Major and trace element run on DCP.

MB01-54A
- Crush and sieve, recording mass of separate size fractions.
- DIAA wash and acid wash 80-100 mesh (180-150 µm) fraction with 10% HCl for at least 5 minutes in ultrasonic bath, etch with 7% HF for approximately 3 minutes, rinse with deionized water and dry.
- Frantz 80-100 size (5 grams) at 0.25 A to remove magnetic minerals and lithic fragments. Run at 1.0 A to remove feldspars. 3 grams of 0.25-1.0 A run at 0.9 A. Magnetic material from 0.9 A run at 0.3 A (2X). Run 0.3-0.9 @ 0.6 A to yield a working split of 0.6-0.9 A.
- Handpick 600 milligrams of sample to remove obvious contaminants.
- Major and trace element run on DCP.

LOSS ON IGNITION (LOI)

LOIs were determined for each rock sample analyzed for major and trace element chemistry. ~1 gram of sample was weighed into a ceramic crucible and the weight was recorded. The powder and crucible was heated to 950º C for one hour, cooled at room temperature, and then weighed. The LOI was calculated by the equation: LOI = $((\text{weight}_{\text{initial}} - \text{weight}_{\text{final}})/\text{weight}_{\text{initial}})*100$ which solves for the total loss on ignition (weight percent).

MAJOR AND TRACE ELEMENT ANALYSIS

New whole-rock major and trace element analyses were performed using direct current argon plasma atomic emission spectroscopy (DCP-AES) at Miami University and X-ray fluorescence (XRF) at Franklin and Marshall College. REE and a suite of trace elements were also analyzed on a subset of samples by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) at Washington State University.

Whole Rock

Samples analyzed by DCP-AES analysis were prepared by manually mixing 200 mg of sample with 600 mg of purified $LiBO_2$ flux (Spectroflux 100A, manufactured by Johnson Mathey Materials Technology). This mixture was then fused in a graphite crucible at 950º C for 20 minutes. The molten bead generated during the fusion process was dropped into

50 ml of a 6% HNO_3 solution spiked with 3000 ppm Li, 10 ppm Ge, and 20 ppm Cd and shaken vigorously until dissolved. This solution stood at room temperature for at least 12 hours and was then ready for analysis (the trace element stock solution; TESS). A 1 ml aliquot of the TESS was added to 25 ml of a 6% HNO_3 solution spiked with 3000 ppm Li and 30 ppm Ge. Li was present as a plasma enhancer and matrix suppressant, while the Cd (major) and Ge (trace) spikes are used as internal references that within-run background corrected element intensities are normalized to for reduction of in-run machine/plasma drift. In every major element run, one procedural blank ($LiBO_2$ only) and the same 10 international rock standards (JG-2, RGM-1, GSP-1, MA-N, SDC-1, W-2, BE-N, SY-2, DNC-1, and JGb-1) were prepared and analyzed with the batch of unknown samples. Throughout the procedure, precise masses of all measured solids and solutions were recorded so that dilution factors and final concentrations could be determined accurately. During each analytical run, each sample solution was analyzed three times and the standard solutions and blank were analyzed four times. A multi-element cassette was used to allow simultaneous determination of major elements. Data collection and reduction were performed by specific software written for the DCP-AES at Miami University. Major element concentrations were determined by comparison of the intensity ratio if an unknown to calibration curves generated by the rock standards run with a given set of samples.

XRF trace element analyses (Rb, Sr, Y, Zr, Nb, Ni, Ga, Cu, Zn, U, Th, Co, Pb, Sc, Cr and V. La, Ce, and Ba) were performed on all samples in this study except purified glass separates (those discussed earlier) by Dr. Stan Mertzman at Franklin and Marshall College, following the methods described in Mertzman (2000). These are outlined and described at <http://server1.fandm.edu/departments/earthandenvironment/facilities/xrf/index.html>.

ICP-MS trace element analyses (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ba, Th, Nb, Y, Hf, Ta, U, Pb, Rb, Cs, Sr, Sc, Zr) were performed on a suite of samples at the GeoAnalytical laboratory at Washington State University following the methods of Crock and Lichte (1982), Lichte and others (1987), and Doherty (1989). These are outlined and described at <www.wsu.edu:8080/~geology/geolab/note/icpms.html>.

In Appendix 3, all reported trace element data are XRF values with the following exceptions: 1) For those samples with Hf, Ta, and Cs data, the reported Hf, Ta, Cs, Rb, Pb, U, Th, La, and Ce values are inductively coupled plasma mass spectrometry (ICP-MS) data run at Washington State University; 2) the trace element data reported for MB01-54B and all Tp2 samples are DCP-AES values run at Miami University; 3) Rb and Sr concentrations in bold are isotope dilution results.

Purified Glass Separates

Tephra were analyzed via a slightly different method than whole rock samples. 0.200 ± 0.001 g of purified and dried <325 mesh (<45 μ) glass was combined with 0.600 ± 0.005 $LiBO_2$ in a graphite crucible. This mixture was then fused at 950º C for 15 minutes. Trace element analyses on purified glass separates were performed by DCP-AES at Miami University via a standard addition technique. Further details are found in Katoh and others 1999

ISOTOPE ANALYSIS

A subset of samples was chosen for whole rock Sr, Nd, and Pb isotopic analyses. All isotopic compositions were measured by a Thermo-Finnigan Triton multi-collector thermal ionization mass spectrometer (TIMS) at Miami University. Approximately 0.1 - 0.2 g of whole rock powder was dissolved in HF-HNO_3, prior to chemical separation. Except for Sm - Nd separation, these procedures follow Walker and others (1989) and are summarized in Snyder (2005). Because of the high Rb/Sr ratio of some SC silicic units, Isotope Dilution was utilized for a subset of SC samples. For this subset, Rb concentrations were determined by ICP-MS in the Department of Chemistry at Miami University (see note at end of previous section). Sm - Nd separations were performed by methods similar to Pin and Zalduegui (1997), using EiChrom Ln-Spec resin (also summarized in Snyder, 2005). Strontium isotopic ratios were fractionation corrected using $^{86}Sr/^{88}Sr$ = 0.1194. Sixty-eight measurements of the NBS 987 strontium standard gave an average of $^{87}Sr/^{86}Sr$ = 0.710236 ± 0.000014 (2 SD). Neodymium isotopic ratios were fractionation corrected using $^{143}Nd/^{146}Nd$ = 0.7219. Sixty-one measurements of the La Jolla neodymium standard gave an average of $^{143}Nd/^{144}Nd$ = 0.511846 ± 0.000007 (2 SD). $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ were fractionation corrected by 0.1% per amu based on measured ratios in NBS 981 from values in Todt and others (1996). Errors on measured values of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ (2 SD) based on 58 measurements of NBS 981 were ± 0.01, ± 0.02, and ± 0.06 respectively.

For a detailed description of the $^{40}Ar/^{39}Ar$ method geochronology employed in this study, see Appendix 4.