

FINAL REPORT

SAMPLING, TESTING AND ANALYSIS OF THE
ANTHROPOGENICALLY ALTERED PORTIONS OF THE TSHIREGE
MEMBER OF THE BANDELIER TUFF, BANDELIER NATIONAL
MONUMENT

November 2011
Nancy J. McMillan, Frank Ramos, Annie Riggins, and April Smith
New Mexico State University
nmcmilla@nmsu.edu, 575-646-5000

TABLE OF CONTENTS

Purpose of Investigation.....	3
Research Team.....	3
Field Work	3
Literature Review.....	4
Volcanology of the Bandelier Tuff.....	4
Physical and Chemical Properties of the Bandelier Tuff	4
Weathering of Volcanic Tuff.....	5
Conservation Strategies	8
Statistics of Point-Counting	8
Bandelier National Monument.....	8
Types of Tuff Investigated	9
Fresh Tuff and Vapor-Phase Crystallization (VPC) Zones.....	10
Lichen.....	13
Sooted Ceilings.....	13
Clay-Coated Surfaces	13
Sample Collection.....	15
Summary of Results.....	17
Tuff Texture and Mineralogical Composition	18

Methods	18
Results	19
Texture of Fresh Tuff.....	19
Pumice Texture.....	20
Effect of Lichen.....	25
Effect of Soot	25
Mineralogy of Vapor-Phase Crystallization Zones.....	27
Methods	27
Results	27
Chemical Gradients	32
Methods	32
Results	33
Chemical Effects of Water-Tuff Interaction	44
Methods	44
Results	44
Resistance to Abrasion and Compression	45
Methods	45
Results	46
Resistance to Freeze-Thaw.....	46
Methods	46
Results	47
Tuff Deterioration and Strengthening	47
Future Work	49
Appendix: Reports Written by Undergraduate Researchers.....	50
Abrasion Test.....	50
Compressive Strength Test.....	52
Fresh Tuff Freeze-Thaw Test.....	55
The Porosity of the Bandelier Tuff.....	57

PURPOSE OF INVESTIGATION

This project was designed to characterize the physical and chemical properties of fresh, altered, and weathered examples of the Tshirege Member of the Bandelier tuff with the intent of understanding the phenomena that cause cavate disintegration. Some of the processes examined are natural (vapor-phase crystallization, lichen growth, clay coatings); others are anthropogenic (sooted ceilings). The data will be used to design conservation treatments for the cavates.

Three research goals were stated in the proposal:

1. To determine whether anthropogenic alteration of the tuff has changed its chemical and physical nature (anthropogenic alteration includes carving, sooting and use over time). This will be done by comparing altered samples to unaltered samples taken from the same general area.
2. To understand the weathering phenomena that causes tuff deterioration. This will be achieved through a comparison of the chemical and physical properties of cavate tuff at different stages in weathering.
3. To investigate the role of lichen in protecting or accelerating the deterioration of the tuff. This will be achieved by mineralogic and chemical analysis of tuff with and without lichen overgrowths.

This report summarizes field and laboratory work performed between January 2009 and September 2010.

RESEARCH TEAM

The NMSU research team on this project was led by Dr. Nancy J. McMillan and Dr. Frank Ramos, both in the Department of Geological Sciences at New Mexico State University. The bulk of the analytical work was performed by two geology undergraduates, Annie Riggins and April Smith. The team met weekly at NMSU to discuss findings and plan activities. The project provided invaluable research experience for the undergraduates, in addition to student employment. They enhanced their professional skills by presenting their findings at the 2009 Geological Society of America conference in a session on geoarcheology.

FIELD WORK

The NMSU team visited Bandelier National Monument twice to collect samples and interact with Shannon Dennison, Steve Merkel, and Lauren Meyer. During the first trip, 20-22 May 2009, 47 samples of tuff were collected from material that had already fallen off the cavates. No intact tuffs were collected. Specific project goals were outlined at this time. During the second trip on 22 June 2010, 10 samples were collected to complete the sample set. Samples were collected at the A-group and M-group cavates.

LITERATURE REVIEW

VOLCANOLOGY OF THE BANDELIER TUFF

- Broxton, D. E., and Eller, P.G., eds., 1995, Earth Science Investigations for Environmental Restoration—Los Alamos National Laboratory Technical Area 21: La-12934-MS, 116p.
- Broxton, D.E., and Reneau, S.L., 1995, Stratigraphic Nomenclature of the Bandelier Tuff for the Environmental Restoration Project at Los Alamos National Laboratory: Los Alamos National Laboratory LA-8461-MS, 20 p.
- Broxton, D.E., Vaniman, D., Byers, F.M., Jr., Chipera, S.J., Kluk, E.C., and Warren, R.G., 1996, Stratigraphy, mineralogy and chemistry of bedrock tuffs at Pajarito Mesa, in Reneau, S.L. and Raymond, R., Jr., eds, Geological site characterization for the proposed mixed waste disposal facility, Los Alamos National Laboratory: LA-13089-MS, 100p.
- Crowe, B.M., Linn, G.W., Heiken, G., and Bevier, M.L., 1978, Stratigraphy of the Bandelier Tuff in the Pajarito Plateau, Applications to Waste Management: Los Alamos Scientific Laboratory Informal Report LA-7225-MS, 57p.
- Izett, G.A. and Obradovich, J.D., 1994, $^{40}\text{Ar}/^{39}\text{Ar}$ age constraints for the Jaramillo normal subchron and the Matuyama-Brunhes geomagnetic boundary: Journal of Geophysical Research, v. 99, p. 2925-2934.
- Reneau, S.L., 2000, Stream incision and terrace development in Frijoles Canyon, Bandelier National Monument, New Mexico, and the influence of lithology and climate: Geomorphology, v. 32, p. 171-193.
- Smith, R.L., 1960, Zones and zonal variations in welded ash flows, 1960, U.S. Geological Survey Professional Paper P 0354-F, p. 149-159.
- Spell, T. L., Kyle, P. R., and Baker, J., 1996, Geochronology and geochemistry of the Cerro Toledo rhyolite: New Mexico Geological Society Guidebook, 47th Field Conference, Jemez Mountains Region, p. 263-268.
- Vierra, B.J., and Schmidt, K.M., 2008, The land conveyance and transfer data recovery project: 7000 years of land use on the Pajarito Plateau, Volume 1: Baseline studies: Los Alamos National Laboratory LA-UR-07-6205.

PHYSICAL AND CHEMICAL PROPERTIES OF THE BANDELIER TUFF

- Abeebe, W.V., 1979, Determination of relative hydraulic conductivity from moisture retention data obtained in the Bandelier Tuff: Los Alamos National Laboratory Informal Report LA-7625-MS, 4 p.

- Dethier, D.P., Kampf, S.K., Sawyer, D.A., and Budahn, J. R., 2007, Chemical zonation in the Upper Bandelier Tuff: Evidence from the chemistry of distal outcrops, Puye Quadrangle: New Mexico Geological Society Guidebook, 58th Field Conference, p. 333-343.
- Quane, S. L., and Russell, J.K., 2003, Rock strength as a metric of welding intensity in pyroclastic deposits: *European Journal of Mineralogy*, v. 15, p. 855-864.
- Slate, J.L., Sarna-Wojcicki, A.M., Wan, E., Dethier, D.P., Wahl, D.B., and Lavine, A., 2007, A chronostratigraphic reference set of tephra layers from the Jemez Mountains Volcanic Source, New Mexico: New Mexico Geological Society Guidebook, 58th Field Conference, p. 239-247.
- Torok, A., Forgo, L.Z., Vogt, R., Lobens, S., Siegesmund, S., and Weiss, T., 2007, The influence of lithology and pore-size distribution on the durability of acid volcanic tuffs, Hungary: *Geological Society of London Special Publications*, v. 271, p. 251-260.
- Warren, R.G., Goff, F., Kluk, E.C., and Budahn, J.R., 2007, Petrography, chemistry, and mineral compositions for subunits of the Tshirege Member, Bandelier Tuff within the Valles Caldera and Pajarito Plateau in New Mexico Geological Society Guidebook, 58th Field Conference, *Geology of the Jemez Mountains Region II*, p. 316-332.
- Warshaw, C.M., and Smith, R.L., 1988, Pyroxenes and fayalites in the Bandelier Tuff, new Mexico: Temperatures and comparison with other rhyolites: *American Mineralogist*: v. 73, p. 1025-1037.

WEATHERING OF VOLCANIC TUFF

GENERAL WEATHERING

- Ayday, C., and Goktan, R.M., 1990, A preliminary engineering geology study directed to the conservation of Midas monument: *Proc. International Earth Sciences Colloquium on the Aegean Region (IESCA)*, D.E. University, Izmir, p. 102-108.
- Benavente, D., Garci del Cure, M. A., Ernabeu, A., and Ordonez, S., 2001, Quantification of salt weathering in porous stones using an experimental continuous partial immersion method: *Engineering Geology*, v. 59, p. 313-325.
- Bundy, W.M., 1958, Wall-rock alteration in the Cochiti mining district, New Mexico: *New Mexico Bur. Mines and Mineral Res. Bull.* v. 59, 71 p.
- Esaki, T., and Jiang, K., 1999, Comprehensive study of the weathered condition of welded tuff from a historic stone bridge in Kagoshima, Japan: *Engineering Geology*, v. 55, p. 121-130.
- Guan, P., Ng, C.W.W., Sun, M., Tang, W., 2001, Weathering indices for rhyolitic tuff and granite in Hong Kong: *Engineering Geology* v. 59, p. 147-159.

- Harnois, L., 1988, The CIW index: A new chemical index of weathering: *Sedimentary Geology*, v. 55, p. 319-322.
- Irfan, T.Y., 1996, Mineralogy, fabric properties and classification of weathered granites in Hong Kong: *Quarterly Journal of Engineering Geology*, v. 29, p. 5-35.
- Irfan, T.Y., 1999, Characterization of weathered volcanic rocks in Hong Kong: *Quarterly Journal of Engineering Geology*, v. 32, p. 317-348.
- Knill, J.L., 1993, Material weathering: The Engineering Geology of Weak of Rock: *Engineering Geology Special Publication*, No. 8. Balkema, Rotterdam, p. 155-158.
- Martin, R.P., 1986, Use of index tests for engineering assessment of weathered rocks: 5th International IAEG Congress, Buenos Aires, p. 433-449.
- Rossi-Manaresi, R., 1976, Causes of decay and conservation treatments of the tuff of Castel Dell'ovo in Naples: *Proc. 2nd. Int. Symp. On the Deterioration of Building Stones*, Athens, p. 233-248.
- Ruxton, B., 1968, Measures of the degree of chemical weathering of rocks: *The Journal of Geology*, v. 76, p. 518-527.
- Toll, H.W., 1995, An Analysis of Variability and Condition of Cavate Structures in Bandelier National Monument: Intermountain Cultural Resources Center, Santa Fe, NM. Professional Paper No. 53.
- Topal, T., DeWitte, E., and Dupas, M., 1998, Pore-size distribution characteristics and durability of the Cappadocian tuff: 8th international IAEG Congress, p. 2931-2938.
- Topal, T., and Sozman, B., 2003, Deterioration mechanisms of tuffs in Midas monument: *Engineering Geology*, v. 68, p. 201-223.
- Torok, A., Forgo, L.Z., Vogt, T., Lobens, S., Siegesmund, S., and Weiss, T., 2007, The influence of lithology and pore-size distribution on the durability of acid volcanic tuffs, Hungary, *in*, Prikryl, R., and Smith, B.J. (eds.), *Building Stone Decay: From Diagnosis to Conservation*: Geological Society of London, Special Publications, v. 271, p. 251-260.

LICHEN

- Adamo, P., and Violante, P., 1991, Weathering of volcanic rocks from Mt. Vesuvius associated with the lichen *Stereocaulon vesuvianum*: *Pedobiologia*, v. 35, p. 209-217.
- Arino, X., Ortega-Calvo, J.J., Gomez-Bolea, A., and Saiz-Jimenez, C., 1995, Lichen colonization of the Roman pavement at Baelo Claudia (Cadiz, Spain): Biodeterioration vs. bioprotection: *Sci. Total Environ.*, v. 167, p. 353-363.
- Ascaso, C., and Galvan, J., 1976, Studies on the pedogenetic action of lichen acids: *Pedobiologia*, v. 16, p. 321-331.

- Bjellend, T., and Ekman, S., 2005, Fungal diversity in rock beneath a crustose lichen as revealed by molecular markers: *Microbial Ecology*, v. 49, p. 598-603.
- Chen, J., Blume, H.P., and Beyer, L., 2000, Weathering of rocks induced by lichen colonization - a review: *Catena*, v. 39, p. 121-146.
- Eckhardt, F.E.W., 1985, Solubilization, transport, and deposition of mineral cations by microorganisms – efficient rock weathering agents. In: Drever, J. I. (Ed.), *The Chemistry of Weathering*. Riedel, New York, p. 161 – 173.
- Jones, D., and Wilson, M.J., 1985, Chemical activity of lichens on mineral surfaces – a review: *Int. Biodeterior.*, v. 21, p. 99-104.
- Jones, D., Wilson, M.J., and McHardy, W.J., 1981. Lichen weathering of rock-forming minerals: applications of scanning electron microscopy and microprobe analyses: *J. Microsc.*, v. 124, p. 95-104.
- Kerr, S., and Zavada, M.S., 1989, The effect of the lichen *Acarospora sinopica* on the elemental composition of three sedimentary rock substrates in South Africa: *The Bryologist*, v. 9, p. 407-410.
- McKenchie, C., Grab, S., and Drennan, G., 2007, Documenting lichen-induced mechanical weathering of quartzitic sandstone at Kaapsehoop, Mpumalanga: *South African Journal of Science*, v. 103, p. 117-120.
- Varadachari, C., Barman, A.K., and Ghosh, K., 1994, Weathering of silicate minerals by organic acids II: Nature of residual products: *Geoderma*, v. 61, p. 251-268.
- Williams, M.E., and Rudolph, E.D., 1974, The role of lichens and associated fungi in the chemical weathering of rock: *Mycologi*, v. 66, p. 648-660.
- Wilson, M.J., 1995, Interaction between lichens and rocks: *Cryptogam. Bot.*, v. 5, p. 299-305.

FIRE

- Allison, R.J., and Goudie, A.S., 1994, The effect of fire on rock weathering: An experimental study. In: Robinson, D.A., Williams, R.B.G. (eds) *Rock Weathering and Landform*. Wiley, Chichester, p. 41-56.
- Chakrabati, B., Yates, T., and Lewry, A., 1996, Effect of fire damage on natural stonework in buildings: *Construction and building materials*, v. 10, 539-544.
- Fredrich, J.T., and Wong, T., 1986, Micromechanics of thermally induced cracking in three crustal rocks: *Journal of Geophysical Research*, v. 91, p. 743-746.
- Sippel, J., Siegesmund, S., Weiss, T., Nitsch, K.H., and Korzen, M., 2007, Decay of natural stones caused by fire damage in Building stone decay; from diagnosis to conservation, Geological Society of London, Special Publications, v. 271, p. 139-151.

CONSERVATION STRATEGIES

Matero, F., 1998. Trail preservation study, Tsankawi Mesa, Bandelier National Monument: The Architectural Conservation Laboratory, University of Pennsylvania.

Matero, F.G., 2003, Exploring conservation for ancestral puebloan sites: Conservation and Management of Archaeological Sites, v. 6, p. 1-17.

Toll, H. W., 1995, An analysis of variability and condition of cavate structure in Bandelier National Monument: Intermountain Cultural Resources Center Professional Paper No. 53, 300 p.

STATISTICS OF POINT-COUNTING

Van Der Plas, L., and Tobi, A.C., 1965, Reliability of point count results, reply: American Journal of Science, v. 263, p. 722-724.

BANDELIER NATIONAL MONUMENT

Toll, H.W., 1995, An analysis of variability and condition of cavate structures in Bandelier National Monument: Intermountain Cultural Resources Center, Professional Paper no. 53, 300 p.

TYPES OF TUFF INVESTIGATED

Highly explosive volcanic eruptions of the silica-rich lava rhyolite punctuated the most recent two million years in the development of the Jemez Volcanic Field in northern New Mexico. Two of these eruptions produced large-scale ash-flow tuffs at 1.61 Ma (Mega-annum or million years) and 1.22 Ma (Izett and Obradovich, 1994). These two tuffs comprise the Bandelier Tuff that blankets the Earth's surface surrounding Bandelier National Monument. Both were generated by collapse of the Valles Caldera. The earlier eruption, at 1.61 Ma, produced the Otowi member of the Bandelier Tuff; the 1.22 Ma eruption produced the Tshirege member (units Qbt 1g, Qbt 1vc, Qbt 1vu, Qbt 2, and Qbt 3 in Fig. 1). A third eruption was produced by the collapse of the Cerro Toledo Caldera, a smaller feature nested within the Valles Caldera. The Cerro Toledo Caldera erupted several times between 1.62 and 1.22 Ma (Spell et al., 1996), resulting in both ash-flow tuffs and volcanic domes and was especially active between 1.38 and 1.34 Ma. Volcanic rocks from the Cerro Toledo caldera are found between the Otowi and Tshirege members of the Bandelier Tuff in some areas (Fig. 1), but not in all areas because of the episodic nature of Cerro Toledo volcanism.

Frijoles Canyon, in Bandelier National Monument, was incised into the Bandelier Tuff after the eruption of the Tshirege member at 1.22 Ma. Cavates were excavated in the lower, non-welded section of the Tshirege member (unit Qbt 1g in Fig. 1). The top of the Otowi member is exposed under the A-group cavates; volcanic rocks associated with the Cerro Toledo tuff were not observed in Frijoles Canyon. All samples in this study were taken from unit Qbt 1g.

Six types of tuff were examined in this project to assess the physical and chemical changes caused by different types of weathering and alteration. The six types, all in unit Qbt 1g of the Tshirege Member, are:

1. Fresh tuff;
2. Vapor-phase crystallization zones without lichen;
3. Vapor-phase crystallization zones with lichen;
4. Fresh tuff with lichen;
5. Sooted cavate ceiling;
6. Tuff coated with clay on vertical cliff faces.



FIGURE 1. VOLCANIC STRATIGRAPHY OF THE BANDELIER TUFF IN THE JEMEZ MOUNTAINS, FROM VIERRA AND SCHMIDT (2008). THE OTOWI MEMBER, LARGELY COVERED WITH TALUS IN THIS PHOTO, WAS ERUPTED DURING THE FIRST COLLAPSE OF THE VALLES CALDERA. TUFFS IN THE CERRO TOLEDO INTERVAL ERUPTED FROM INTERMITTENT ACTIVITY OF THE CERRO TOLEDO CALDERA. MOST OF THE EXPOSED TUFF IN THE PHOTO COMPRISES THE TSHIREGE MEMBER OF THE BANDELIER TUFF, ERUPTED FROM THE SECOND COLLAPSE OF THE VALLES CALDERA.

FRESH TUFF AND VAPOR-PHASE CRYSTALLIZATION (VPC) ZONES

Fresh Tshirege tuff is extremely friable and thus very easily eroded. Two natural processes, both of which occur during cooling, can strengthen tuff: welding and vapor-phase crystallization. Welding occurs as the weight of the tuff compresses the warm, ductile glass shards and pumice fragments. This process can be recognized by a significant flattening of the pumices. The tuff in Frijoles Canyon is poorly welded.

Vapor-phase crystallization, the second process, occurs along fractures and other zones of fluid flow as magmatic gases precipitate cristobalite (a high-temperature polymorph of quartz) as the tuff cools (Reneau, 2000; Crowe et al., 1978; Broxton et al., 1995). The cristobalite coats pumice, ash, and crystal faces and cements them together. Broxton et al. (1995) report that the upper part of the Tshirege has been devitrified by vapor-phase crystallization, resulting in a very durable rock that is resistant to erosion. Devitrification (crystallization of the glass in the tuff) has not occurred in Bandelier National Monument to any noticeable extent. In Frijoles Canyon, the vapor phase crystallization occurred along cooling fractures rather than throughout the unit (Figs. 2-4). Only the outer few centimeters of the tuff have been cemented together (Fig. 3), forming the “case-hardened” surface defined by Broxton et al. (1995).

If the Tshirege Member had not been strengthened by vapor-phase crystallization, Frijoles Canyon would not have vertical cliff faces (Fig. 5). Instead, the tuff would have eroded away rapidly, leaving a broad valley in contrast to the steep canyon that exists. The vertical cliff faces

that characterize Frijoles Canyon represent surfaces that were made more resistant to erosion by vapor-phase crystallization along cooling fractures (Reneau, 2000; Crowe et al., 1978).



FIGURE 2. VAPOR PHASE CRYSTALLIZATION SURFACE AT LONG HOUSE.



FIGURE 3. CLOSE UP OF CROSS-SECTION OF VAPOR-PHASE CRYSTALLIZATION ZONE. LEATHERMAN IS 6.5 CM LONG.



FIGURE 4. VAPOR-PHASE CRYSTALLIZATION ALONG CONICAL GAS-ESCAPE FRACTURES.



FIGURE 5. VERTICAL CLIFF FACES AT GROUP M.

LICHEN

Lichen is ubiquitous on the tuff surfaces in Frijoles Canyon. Samples of fresh tuff, VPC tuff without lichen, and clay-coated tuff used in this project are not actually lichen-free, but are the samples with the least lichen colonization.

SOOTED CEILINGS

One of the features of interest in this work was the collapsing ceilings that had been coated with a layer of soot (Fig. 6). We collected several samples that had fallen completely off the cavates.



FIGURE 6. SAGGING OF SOOTED CEILING AT A-GROUP.

CLAY-COATED SURFACES

Run-off from the mesa top over the cliff surface deposits a vertical layer of clay on the tuff. When the clay hardens in the sun, it forms a resistant coat that strengthens the surface (Fig. 7). These clay coats are not as wide-spread as the VPC surfaces, but may play an important role in preserving the cliff face.



FIGURE 7. CLAY-COATED SURFACE AT GROUP M.

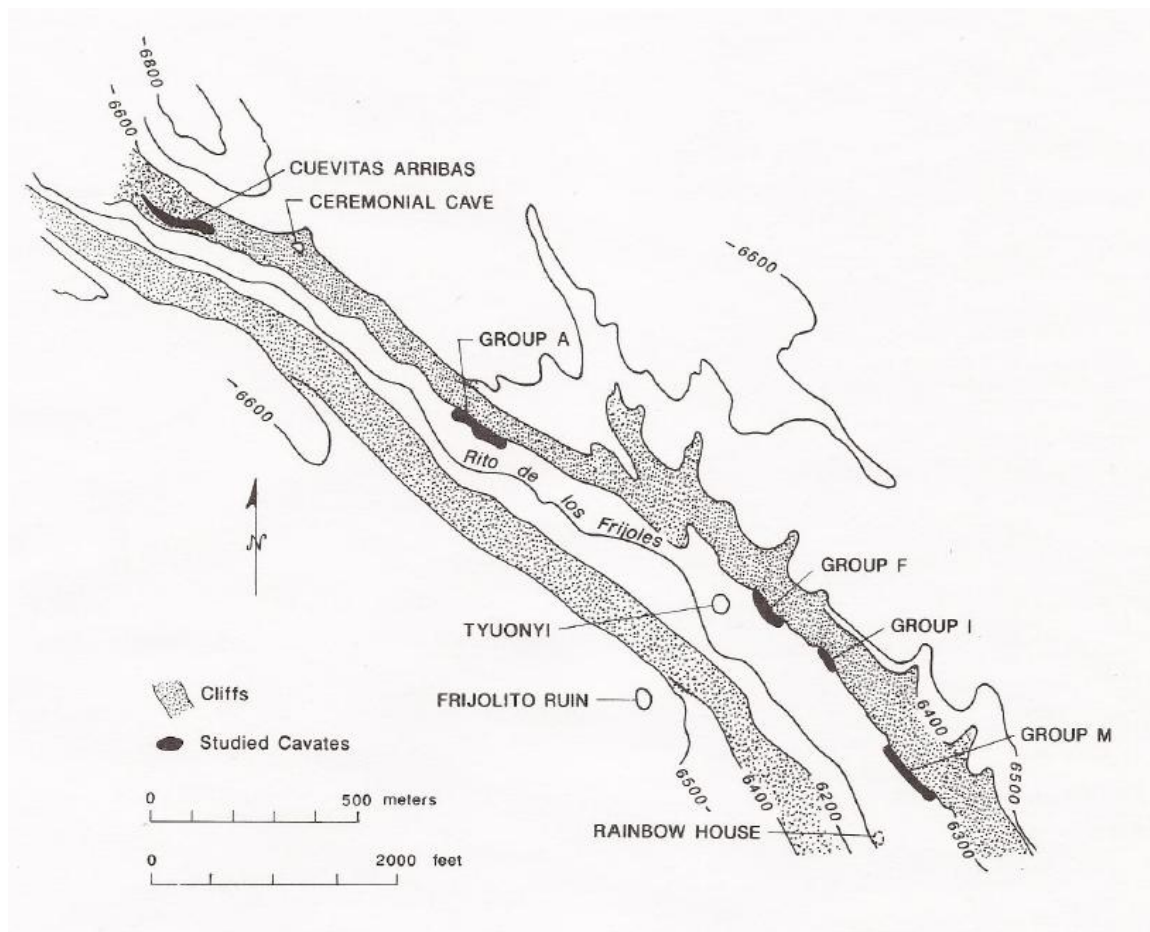


FIGURE 8. MAP OF FRIJOLAS CANYON SHOWING THE LOCATION OF GROUPS OF CAVATES. FROM TOLL (1995).

SAMPLE COLLECTION

Cavates are clustered in groups in Frijoles Canyon, as shown in Figure 8 (Toll, 1995). Samples of the various types of tuff were collected from pieces that had fallen off the cavates in groups A, D, and M.

The samples collected in this study are listed in Table 1.

Sample numbers reflect the cavate at which the sample was collected. For instance, sample M136-32B was collected in or near cavate 136 in M-group. It was the 32nd sample collected in the project, and was separated into at least two pieces for analysis in the lab (A and B). Some samples did not have any connection to a specific cavate; these sample numbers consist of the cavate group followed by the sample number. For instance, sample M-049 is a lichen-covered sample from a block of tuff that had fallen from M-group cavates, but it is not clear to which cavate the block was originally connected.

TABLE 1. SAMPLES COLLECTED FOR THIS STUDY. VPC = VAPOR-PHASE CRYSTALLIZATION.

Sample	Cavate	Tuff Type		Sample	Cavate	Tuff Type		Sample	Cavate	Tuff Type
D-001	D-group	clay vein		M82-019	M82	ceiling		M136-038	M136	fresh tuff
D-002	D-group	clay vein		M82-020	M82	ceiling		M100-039	M100	clay on surface
A112-003	A112	ceiling		M82-021	M82	ceiling		M56-044	M56	bird droppings
A112-004	A112	ceiling		M82-022	M82	ceiling		M-045	M-group	VPC with lichen
A112-005	A112	ceiling		M82-023	M82	ceiling		M-046	M-group	VPC with lichen
A114-006	Below A112	ceiling		M108-024	M108	fresh tuff		M-047	M-group	VPC with lichen
A114-007	Below A113	ceiling		M108-025	M108	fresh tuff		M-048	M-group	fresh tuff with lichen
A114-008	Below A114	ceiling		M108-026	M108	fresh tuff		M-049	M-group	VPC
A114-009	Below A115	ceiling		M136-027	M136	fresh tuff		M-050	M-group	VPC
A114-010	Below A116	fresh tuff		M136-028	M136	fresh tuff		M-051	M-group	fresh tuff with lichen
A114-011	Below A117	fresh tuff		M136-029	M136	fresh tuff		M-052	M-group	VPC
A-010	A-group	fresh with lichen		M136-030	M136	fresh tuff		M164-001	M164	clay on wall east of M164
A-011	A-group	VPC with lichen		M136-031	M136	fresh tuff		M164-02	M164	clay "ball"
A-012	A-group	fresh		M136-032	M136	fresh tuff		A148-001	A148	VPC with lichen
A-013	A-group	fresh		M136-033	M136	fresh tuff		A148-002	A148	clay on fresh tuff
M82-014	M82	ceiling		M136-034	M136	fresh tuff		A148-003	A148	VPC with lichen
M82-015	M82	ceiling		M136-035	M136	fresh tuff		A148-010	A148	fresh tuff with lichen
M82-016	M82	ceiling		M136-036	M136	fresh tuff		A148-011	A148	tuff with clay coat
M82-017	M82	ceiling		M136-037	M136	fresh tuff		TOP-001	mesa top	soil sample from mesa top at scenic turn out
M82-018	M82	ceiling								

SUMMARY OF RESULTS

The tests performed on fresh and altered tuffs from Bandelier National Monument fall into two categories: 1) observation of physical and chemical features and 2) measurement of physical properties (Table 2).

TABLE 2. ANALYTICAL METHODS EMPLOYED DURING THIS PROJECT.

Observation of Physical and Chemical Features		
Feature Observed	Analytical Method	Summary of Results
Mineralogical content and texture of rock	Point count, Polarizing Microscopy	Range in total porosity: 30-40% Range in total glass content: 44-55% Range in total mineral content: 13-19%
Texture of surfaces	Microscopy, Scanning Electron Microscopy (SEM)	Soot has little effect on texture. VPC textural differences are submicroscopic. Lichen compacts and erodes glass around crystals.
Mineralogy of Vapor Phase Crystallization (VPC) zones	Scanning Electron Microscopy with Energy Dispersive Spectroscopy (EDS)	In VPC zones, pumice fragments are cemented by a layer of cristobalite $\pm$ calcite, halite, and alkali-feldspar.
Chemical gradients away from surfaces	X-ray Fluorescence (XRF) analysis, Loss on Ignition (LOI)-a measure of the total volatile content	VPC causes the most compositional change, with variations in all major elements. Lichen causes minor compositional changes, with higher LOI at the surface (the lichen). Soot on the ceiling causes little compositional change except for an increase in LOI (the soot). Clay coats cause no measureable compositional change.
Change of composition during rock-water interaction	Powdered tuff stirred in distilled deionized water, followed by XRF analysis of control sample and solid residue.	All elements except Al and P were dissolved from the tuff; approximately 1.5% of the total tuff was dissolved.
Measurement of Physical Properties		
Property Measured	Method	Summary of Results
Resistance to abrasion	Surfaces scratched with minerals on Moh's Hardness Scale	Fresh tuff has a hardness of 0 on Moh's Scale; lichen increases hardness to 1. Sooted ceiling samples have hardness of 2. VPC increases the hardness to 3.
Resistance to compression	Samples pressed in hydraulic press until failure	Fresh tuff is too friable to test for compression. Lichen, clay coats, and soot increase the strength of the tuff somewhat. VPC increases the strength significantly.
Resistance to freeze-thaw	Samples moistened, frozen, and thawed repeatedly until failure	Fresh tuff maintains disintegrated after 1-6 freeze-thaw cycles.

TUFF TEXTURE AND MINERALOGICAL COMPOSITION

METHODS

Point counting. Point counting is a microscopy method to used measure the abundance of the various materials in a sample. It is performed by categorizing and counting the material under the cross-hairs in a grid pattern. The size of the grid is determined prior to point-counting to ensure a representative count.

At least 600 points on a regular grid were counted on each thin section; this results in errors of $\pm 2 - 4$ % absolute (Van Der Plas, I., and Tobi, A.C., 1965). For example, if the abundance of a constituent measures at 20%, and the error is ± 2 % absolute, the abundance is in the range 18 - 22%. These constituents of the tuffs were counted:

- Matrix, defined as shards of volcanic glass and other materials too small to identify
- Whole pieces of pumice
- Intergranular pores, defined as pore space outside of pumice
- Vesicles, defined as pores within pumice
- Sanidine phenocrysts (alkali-feldspar)
- Clinopyroxene (augite) phenocrysts
- Lithic, or rock, fragments entrained during or before eruption

From these data, total glass percentages were calculated as the sum of matrix and pumice. Total pore space was calculated as the sum of intergranular pores and vesicles. Three thin sections of each type of tuff were point counted. For surface tuff types (vapor-phase crystallization, lichen, and sooted ceilings), only the part of the thin section within a centimeter of the surface was counted.

Microscopy. The textural effect of alteration in the various types of tuffs was investigated by examining cross-sections from the surface to the interior in thin section with a polarizing microscope. Thin sections are slices of rock 30 μm thick on a glass slide. Thin sections allowed observations 20-30 mm below the surface.

Scanning Electron Microscopy (SEM). Samples were imaged using SEM to examine textural changes from the surface to the interior in detail. SEM images extend only 5-8 mm below the surface.

Samples Used and Sample Preparation. Samples were impregnated with blue epoxy prior to thin section preparation. This helps the tuff hold together during the process and also highlights porosity in the photomicrographs. Samples for SEM were cut to expose a flat surface; loose particles were removed using compressed air. The samples used are listed in Table 3.

TABLE 3. SAMPLES USED FOR POINT COUNTING AND SEM ANALYSIS.

Tuff Type	Microscopy and Point Counting	SEM
Fresh tuff	A114-011	---
VPC without lichen	A148-001, A-011 (areas with as little lichen as possible)	A011-01
VPC with lichen	A148-001, A-011	A011-01
Lichen	A114-010, A010	A010-01
Sooted Ceiling	A112-003, M82-020	A114-006
Clay Coat	A18-003	---

RESULTS

Photomicrographs of the various types of tuff are presented in Figures 9-11. Pumice has very low permeability because the vesicles (gas bubbles) may not be interconnected. This prevents the epoxy from filling some pore space, resulting in white pore space (i.e., the lower left image of Fig. 9C and the upper left of Fig. 10A).

The photomicrographs in Figures 9-11, the data in Table 4 and Figure 12, and the composite SEM images in the back pocket of this report demonstrate that the Bandelier Tuff is texturally complex. Pore space is distributed unevenly through the rock, and permeability is even more heterogeneous because some pumices are impermeable.

Three thin sections of each type of tuff were point counted (Table 4) to obtain statistics on the variation of the percentages of tuff constituents. In Figure 12, the percentages of various materials are plotted with bars that indicate the 1σ variation of the point count data. While it is tempting to make broad interpretations from these data, e.g., fresh tuff has the highest porosity or clay-coated tuff and vapor-phase crystallization tuff with lichen have the lowest amount of pumice, the 1σ error bars overlap for almost all constituents for all types of tuff. Thus, these data should be taken as a whole to illustrate the textural variability in the Bandelier Tuff.

Two sets of SEM images are provided in the pocket in the back of this report. One set includes traverses from the edge to the interior of sooted ceiling, VPC, VPC with lichen, and fresh tuff with lichen. The second set includes the images from the heating experiments described below. All individual SEM images are included on a CD.

TEXTURE OF FRESH TUFF

Figure 9 includes photomicrographs of the interiors (away from weathered or altered surfaces) of various types of tuff. All have high porosity, as evidenced by the blue epoxy. Variations in phenocryst and pumice content vary among these photographs; these differences reflect the variability of the tuff rather than differences between the types of tuff. The majority of the material consists of glass fragments with angular intergranular pore spaces. Sanidine phenocrysts are broken along cleavage planes (Fig. 9 B, C) as a result of the shock of volcanic eruption. Phenocrysts,

glass shards, and pieces of pumice are very loosely connected; there is no cement or other intergranular material that holds the tuff together.

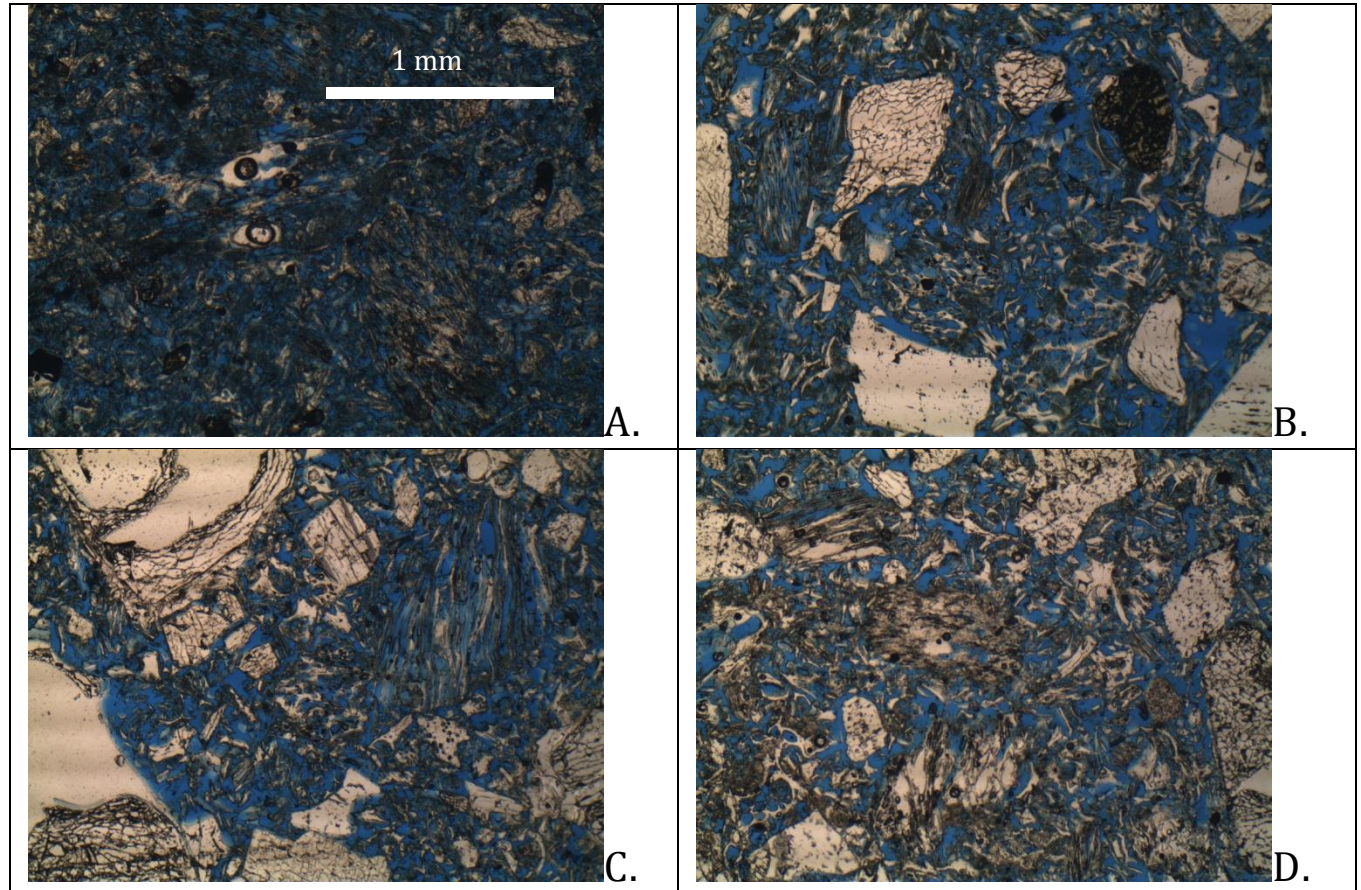


FIGURE 9. PHOTOMICROGRAPHS OF BANDELIER TUFF FROM THE INTERIOR OF VARIOUS SAMPLES. PORE SPACE APPEARS BLUE IF FILLED WITH EPOXY; EPOXY-FREE PORE SPACE IS FEATURELESS WHITE (LOWER LEFT CORNER OF FIG. 9C). GLASS SHARDS AND PUMICE ARE BROWN. QUARTZ AND SANIDINE PHENOCRYSTS ARE WHITE. A. FRESH TUFF. B. SOOTED CEILING. C. VAPOR-PHASE CRYSTALLIZATION. D. VAPOR-PHASE CRYSTALLIZATION WITH LICHEN.

PUMICE TEXTURE

Photomicrographs of pumice pieces are shown in Figure 10. The delicate bubble walls separating vesicles are easily seen, as are the impermeable nature of some vesicles that did not receive the blue epoxy. As in the samples of the interior of the tuffs, differences in these photos of pumice reflect the variation in pumice textures, not variations specific to the different types of tuff.

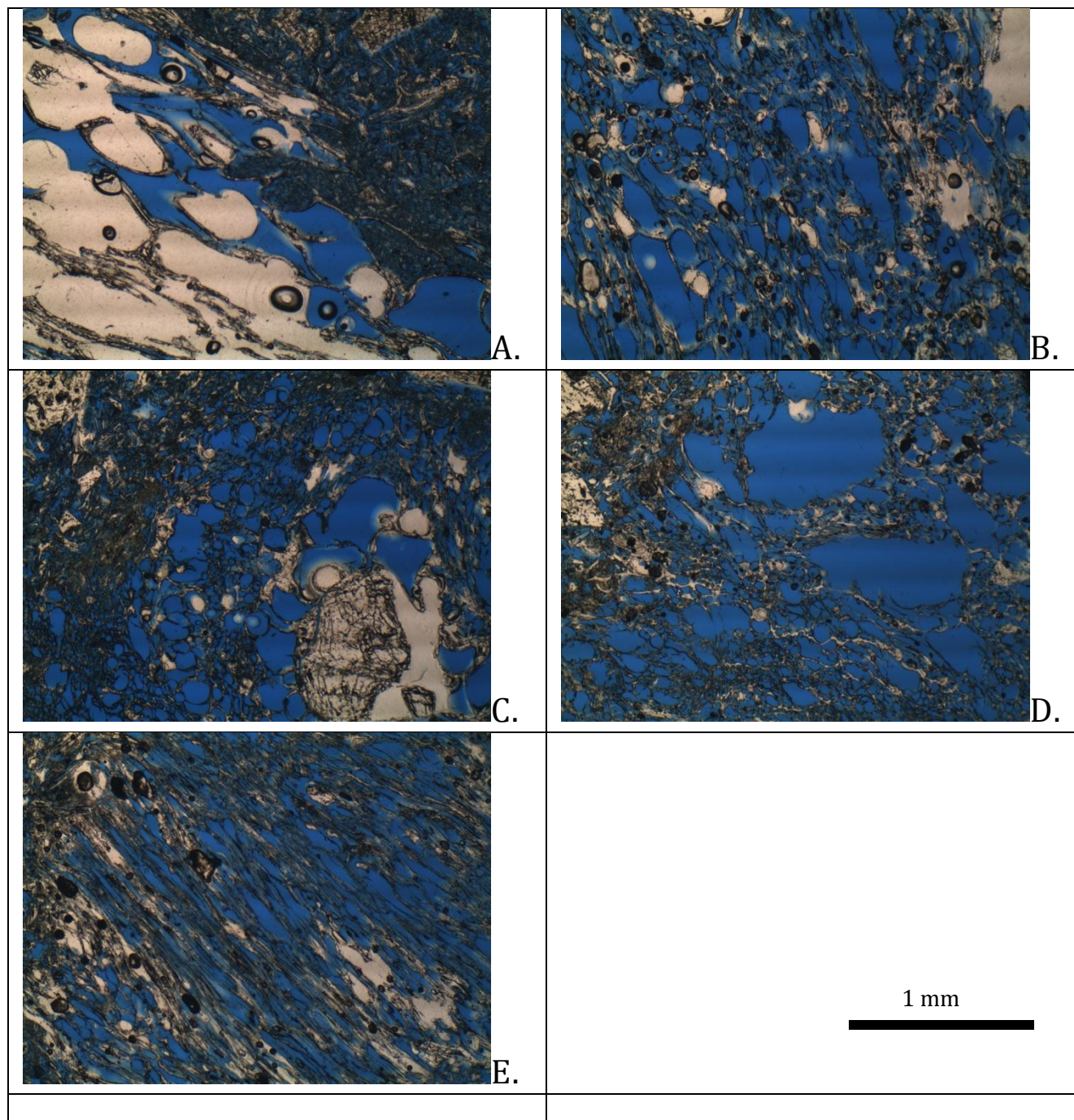


FIGURE 10. PHOTOMICROGRAPHS OF PUMICE PIECES IN VARIOUS TYPES OF BANDELIER TUFF. BLACK CIRCLES ARE AIR BUBBLES TRAPPED IN THE EPOXY DURING SAMPLE PREPARATION. A. FRESH TUFF. B. SOOTED CEILING. C. VAPOR-PHASE CRYSTALLIZATION. D. VAPOR-PHASE CRYSTALLIZATION WITH LICHEN. E. FRESH TUFF WITH LICHEN.

TABLE 4. Mineralogy, glass content, and porosity of Bandelier Tuff samples, expressed as percent.															
Tuff Type	Fresh Tuff					Ceiling					Clay Coat				
Sample Number	A114-011C-01	A114-011C-02	M136-034	Average	1σ	A112-003B	M82-020	A114-008	Average	1σ	A18-003B-01	A18-003B-02	A18-003B-03	Average	1σ
n	600	600	600			600	600	603			600	600	600		
Matrix	34.5	31.3	21.3	29.1	6.9	30.5	31.3	27.7	29.8	1.9	47.3	46.8	42.7	45.6	2.6
Pumice	13.5	18.5	15.7	15.9	2.5	32.0	15.8	15.1	21.0	9.6	11.8	10.8	4.7	9.1	3.9
IG Pores	23.7	32.7	33.0	29.8	5.3	17.0	28.3	23.9	23.1	5.7	20.0	26.7	35.3	27.3	7.7
Vesicles	9.5	2.0	16.8	9.4	7.4	5.5	6.7	13.4	8.5	4.3	3.7	1.8	1.8	2.4	1.1
Quartz	8.0	7.0	5.0	6.7	1.5	6.8	11.2	11.9	10.0	2.8	3.7	5.8	4.0	4.5	1.2
K-spar	8.3	7.2	4.8	6.8	1.8	7.0	5.0	7.3	6.4	1.2	11.8	7.7	9.3	9.6	2.1
CPX	0.0	0.3	0.2	0.2	0.2	1.0	0.0	0.0	0.3	0.6	0.5	0.3	0.0	0.3	0.3
Lithics	2.5	1.0	3.2	2.2	1.1	0.2	1.7	0.7	0.8	0.8	1.2	0.0	2.2	1.1	1.1
Total	100.0	100.0	100.0	100.0		100.0	100.0	100.0	100.0		100.0	100.0	100.0	100.0	
Total Glass	48.0	49.8	37.0	44.9	6.9	62.5	47.2	42.8	50.8	10.4	59.2	57.7	47.3	54.7	6.4
Total Por.	33.2	34.7	49.8	39.2	9.2	22.5	35.0	37.3	31.6	8.0	23.7	28.5	37.2	29.8	6.8
Tuff Type	VPC without Lichen					VPC with Lichen					Fresh with Lichen				
Sample Number	A148-001F-01	A148-001A-01	A-011M	Average	1σ	A148-001C-01	A148-001F-02	A-011L	Average	1σ	A114-010A	A-010B-07	A-010A	Average	1σ
n	659.0	601.0	603.0			600.0	603.0	601.0			600.0	600.0	600.0		
Matrix	38.2	25.3	27.9	30.7	6.9	36.2	29.9	33.4	33.1	3.2	35.0	23.3	29.0	29.1	5.8
Pumice	12.9	29.6	17.6	19.8	8.6	4.3	15.3	14.1	11.3	6.0	15.5	29.3	17.7	20.8	7.4
IG Pores	32.9	15.5	18.9	22.8	9.2	30.0	21.4	20.3	23.9	5.3	22.8	21.7	30.5	25.0	4.8
Vesicles	5.2	19.6	17.6	13.8	7.8	6.2	9.6	15.5	10.4	4.7	7.8	7.2	9.2	8.1	1.0
Quartz	5.2	1.8	15.9	7.6	7.4	7.7	13.9	11.1	10.9	3.1	6.0	13.5	4.8	8.1	4.7
K-spar	5.0	7.5	1.8	4.8	2.8	13.3	8.0	2.8	8.0	5.3	11.8	4.8	8.5	8.4	3.5
CPX	0.0	0.3	0.2	0.2	0.2	0.2	0.5	0.2	0.3	0.2	0.2	0.0	0.0	0.1	0.1
Lithics	0.6	0.3	0.2	0.4	0.2	2.2	1.5	2.5	2.1	0.5	0.8	0.2	0.3	0.4	0.3
Total	100.0	100.0	100.0	100.0		100.0	100.0	100.0	100.0		100.0	100.0	100.0	100.0	
Total Glass	51.1	54.9	45.4	50.5	4.8	40.5	45.1	47.6	44.4	3.6	50.5	52.7	46.7	49.9	3.0
Total Por.	38.1	35.1	36.5	36.6	1.5	36.2	31.0	35.8	34.3	2.9	30.7	28.8	39.7	33.1	5.8
Explanation: Matrix = shards of glass (pumice) and other material too small to identify; Pumice = whole pumices; IG Pores = intergranular pores;															
Vesicles = voids within whole pumices; K-spar = potassium feldspar crystals (sanidine); CPX = clinopyroxene crystals; Lithics = rock fragments;															
Total Glass = matrix and pumice; Total Porosity (Total Por.) = IG pores and vesicles															

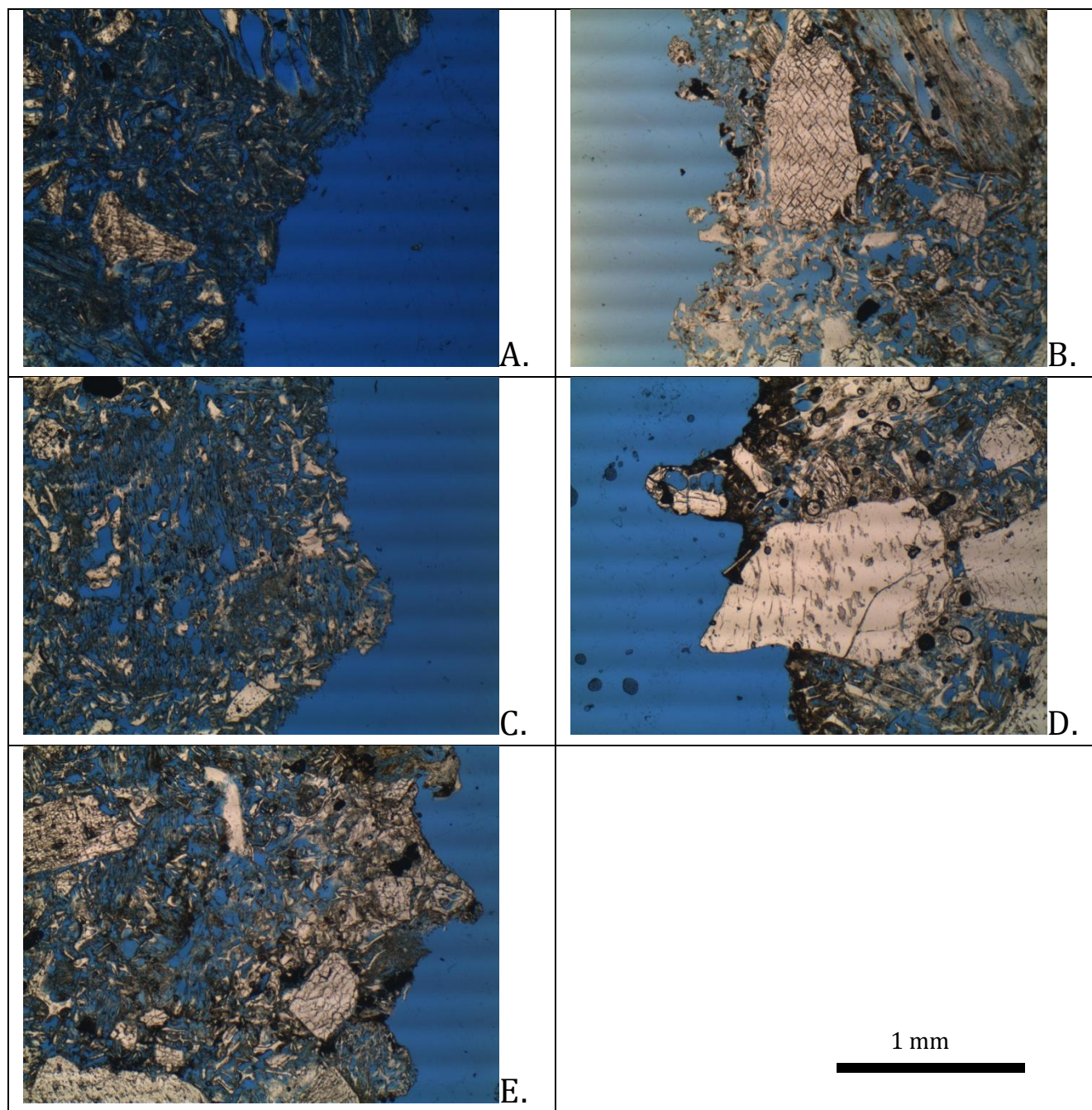


FIGURE 11. PHOTOMICROGRAPHS OF THE SURFACES OF VARIOUS TYPES OF BANDELIER TUFF. A. FRESH TUFF. B. SOOTED CEILING. C. VAPOR-PHASE CRYSTALLIZATION. D. VAPOR-PHASE CRYSTALLIZATION WITH LICHEN. E. FRESH TUFF WITH LICHEN.

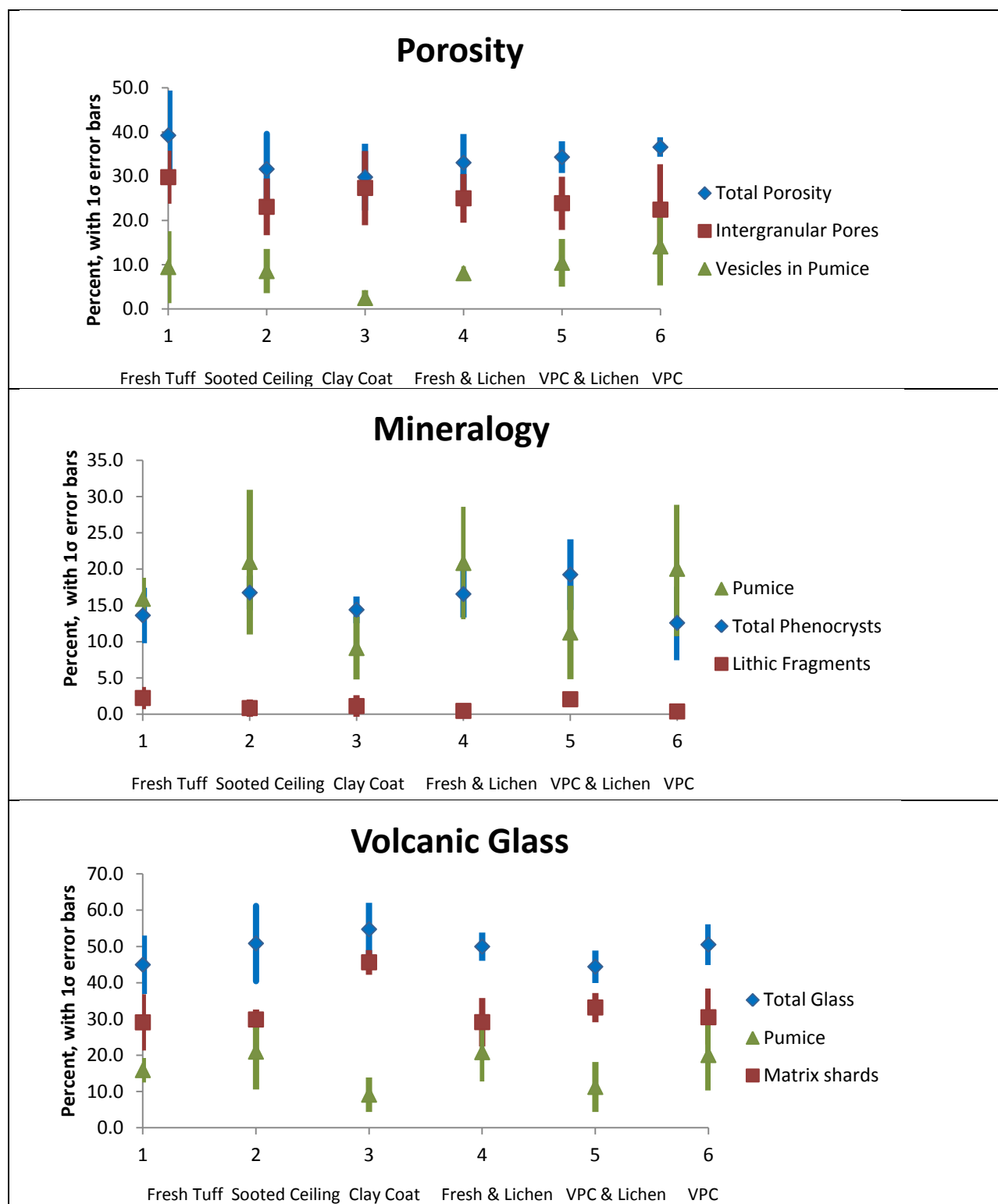


FIGURE 12. PERCENTAGES OF COMPONENTS OF VARIOUS TYPES OF BANDELIER TUFF. AVERAGES OF POINT COUNTS OF THREE THIN SECTIONS ARE PLOTTED AS POINTS; BARS GIVE THE 1σ STANDARD DEVIATION OF THE MEASUREMENTS.

EFFECT OF LICHEN

Tuff surfaces covered with lichen show the largest textural change compared to fresh tuff surfaces (Fig. 11). Lichen-encrusted surfaces (Fig. 11 D, E) are significantly more jagged than lichen-free surfaces. This is due to matrix glass being compacted and/or eroded around the phenocrysts, consistent with observations by McKenchie et al. (2007). The dark material along the surface may be the lichen hyphae, but also may be iron oxides (Fe₂O₃ = 1.40 wt % at the surface compared to 1.24-1.27 wt % in the interior; see section on Chemical Traverses). The dark material is concentrated at the surface but penetrates about a millimeter into the tuff. The interconnected coating of lichen, increased concentration of glass, reduction of pore space, concentration of crystals just beneath the lichen, and increased concentration of iron oxides all strengthen the lichen-coated surfaces.

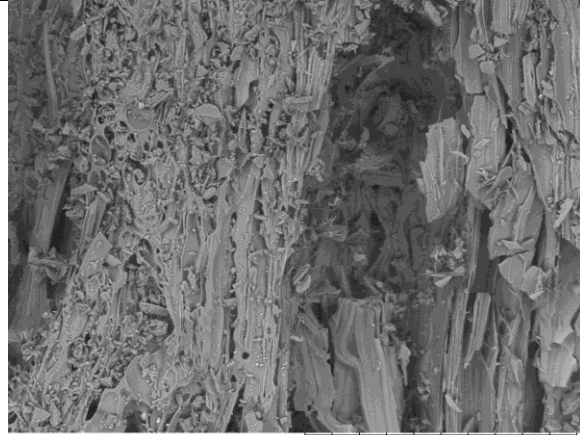
EFFECT OF SOOT

The thin layer of soot on cavate ceilings is seen as the dark matrix material in Figure 11B. The fragile texture of glass shards is preserved, and the soot appears to cement the glass and phenocrysts together. Other than this, the texture is very similar to fresh tuff.

One possibility is that tuff particles are bound together by the soot, holding the ceiling in place for some time. As tuff particles above the soot-bound layer detach from each other, the ceiling starts to sag. Gravity pulls on the sag, causing more tuff particles to detach, and eventually a section of the ceiling collapses.

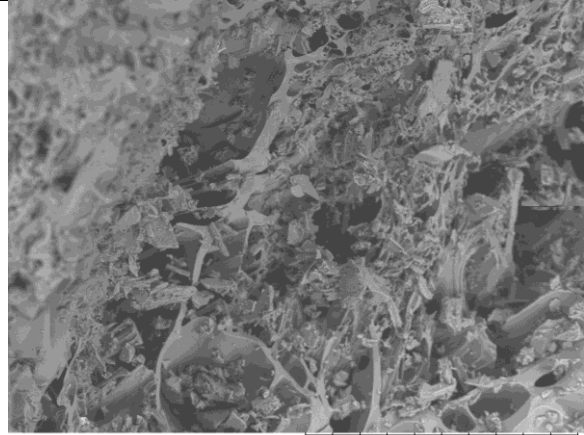
If gravity pulling on the soot-bound tuff particles were the only process, the sagging sections of ceiling would only be one or two tuff particles thick, because the soot penetrates only a few mm into the tuff (Fig. 11B). However, the sagging sections are several cm thick—thicker than the zone penetrated with soot. This observation led to a pilot study of heating the tuffs to test the hypothesis that the heat associated with the sooting process caused mineralogical changes that cemented the tuff together. Fresh tuff sample M136-033 was heated progressively to 300°, 400°, 500°, and 600° C, imaging with SEM after each heating episode (Fig. 13). At 300° C, small particles of broken glass are visible, but otherwise the glass surfaces are clean. At 500° and 600° C, however, numerous small particles are visible on glass surfaces. We hypothesize that these are minerals that grow as glass breaks down and that they serve as cement to bind the tuff particles together. These results are similar to a study of fire damage on rocks by Sippel et al. (2007). Significant mineral reactions occur at temperatures greater than 500° C.

If this interpretation is valid, cavate ceilings are held together by both soot and the small crystals formed at high temperature.



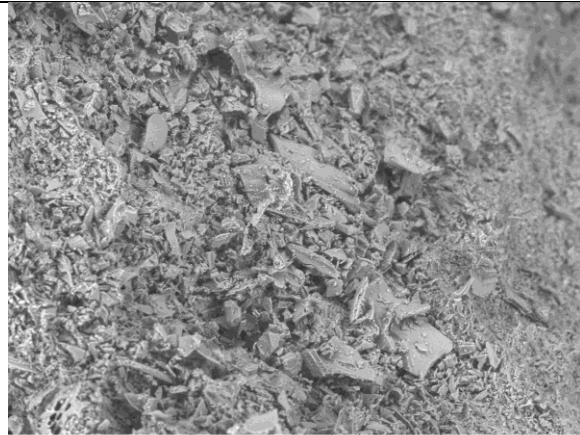
NMSU-EML 2009/10/13 13:12 L x300 300 um
3463, Df

A. HEATED TO 300° C



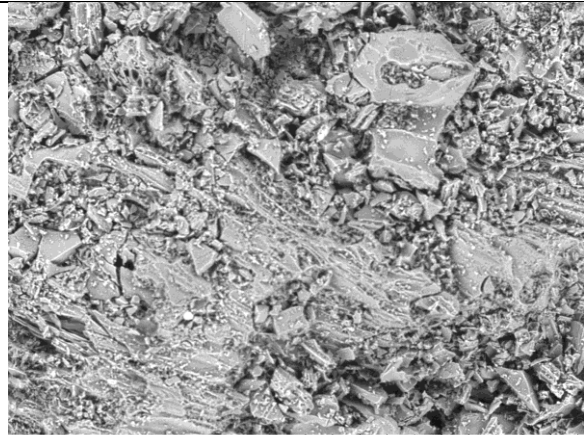
NMSU-EML 2009/10/14 15:16 L x300 300 um
w1118Xmd0.5G4>Rapv12

B. Heated to 400° C



NMSU-EML 2009/08/20 13:40 L x300 300 um
M136-033E

C. Heated to 500° C



NMSU-EML 2009/08/12 10:39 L x300 300 um
M136-033G

D. Heated to 600° C

FIGURE 13. SEM IMAGES OF FRESH TUFF SAMPLE M136 THAT WAS PROGRESSIVELY HEATED. A. 300° C; B. 400° C; C. 500° C; D. 600° C.

MINERALOGY OF VAPOR-PHASE CRYSTALLIZATION ZONES

METHODS

Vapor-phase crystallization is a major process in hardening the tuff and forming the cliff faces in Frijoles Canyon. Scanning Electron Microscopy (SEM) was used to image VPC tuff; specific spots were analyzed with Energy Dispersive Spectrometry (EDS) on the SEM. VPC sample A011D-01 was chosen for analysis.

RESULTS

Although vapor-phase crystallization has a dramatic effect on tuff strength and hardness, the mineralogical changes to the tuff are sub-microscopic in scale. Figure 11 compares photomicrographs of tuff surfaces affected by soot, vapor-phase crystallization, vapor-crystallization with lichen, and lichen alone. Although there are significant effects of lichen, the surfaces affected by vapor-phase crystallization are very similar in texture to fresh tuff and fresh tuff with lichen. Because of this, vapor-phase crystallization samples were examined by SEM.

The vapor-phase crystallization zone is only a few cm thick in Frijoles Canyon (Fig. 3). The following figures are SEM images with corresponding energy-dispersive spectra of specific areas. They demonstrate that: 1) the effect of VPC is to deposit a thin layer of cristobalite on glass surfaces, and 2) crystals of cristobalite and possibly calcite, halite, and alkali-feldspar are deposited on the cristobalite layer. It is probably the layer of cristobalite that increases the strength and hardness of VPC surfaces.

Figure 14A presents an SEM image of glass in sample A-011D-01, tuff affected by vapor-phase crystallization and lichen. Three SEM energy-dispersive X-ray spectra of representative glass in this sample are in Figures 14B, C, and D. Peaks for Si, O, Al, K, and Na are significant. Minor peaks for Cl are also discernable. These spectra of rhyolite glass in the tuff provide a foundation for comparison to analyses of areas that have been mineralized.

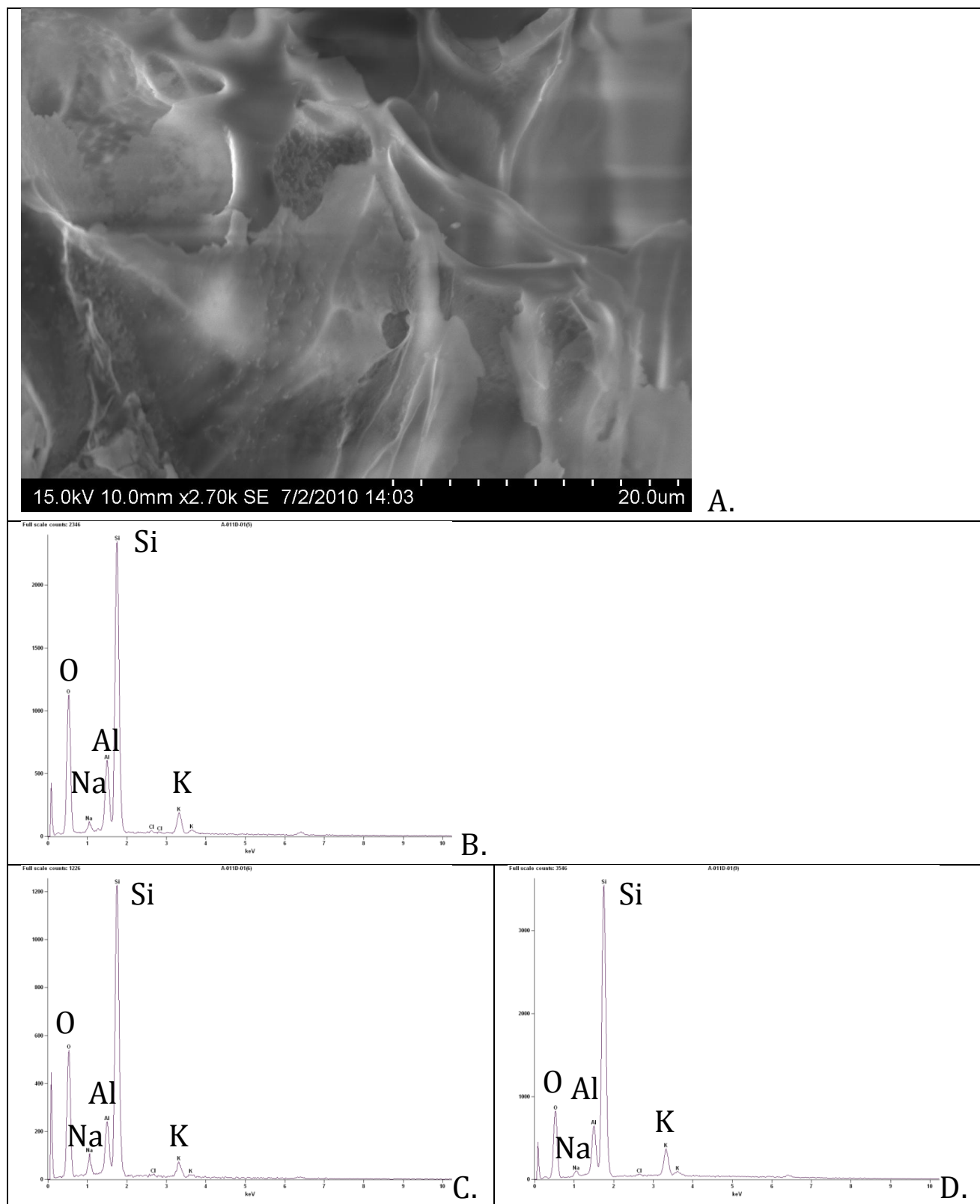


FIGURE 14. A. SEM IMAGE OF GLASS IN BANDELIER TUFF. SCALE BAR FOR IMAGE IS 20 MICROMETERS LONG. B, C, & D. EDS SPECTRA FOR THREE SPOTS ON THE GLASS. PEAKS FOR O, NA, AL, SI, AND K ARE EXPECTED FOR RHYOLITE TUFF.

For comparison, examples of glass encrusted with tiny crystals are shown in Figures 15-17. The wall of pumice in the center of Figure 15A was analyzed in two small spots, B and C. Spot B is the surface of the glass; the spectrum is shown in Figure 15B. Surprisingly, the Al peak expected in the glass is almost absent, and only peaks for Si and O are significant. This suggests that the surface is covered with a fine coating of silica, probably the high-temperature polymorph cristobalite, which has been reported as a mineral found in vapor-phase crystallized zones (Broxton et al. (1995)). Spot C is a small cluster of crystals on the cristobalite surface; the spectrum in Figure 15C is dominated by Si and O peaks, with very small peaks at Al, Na, and K. These are cristobalite crystals on the cristobalite surface. The small Al, Na, and K peaks probably represent intergrown alkali-feldspar.

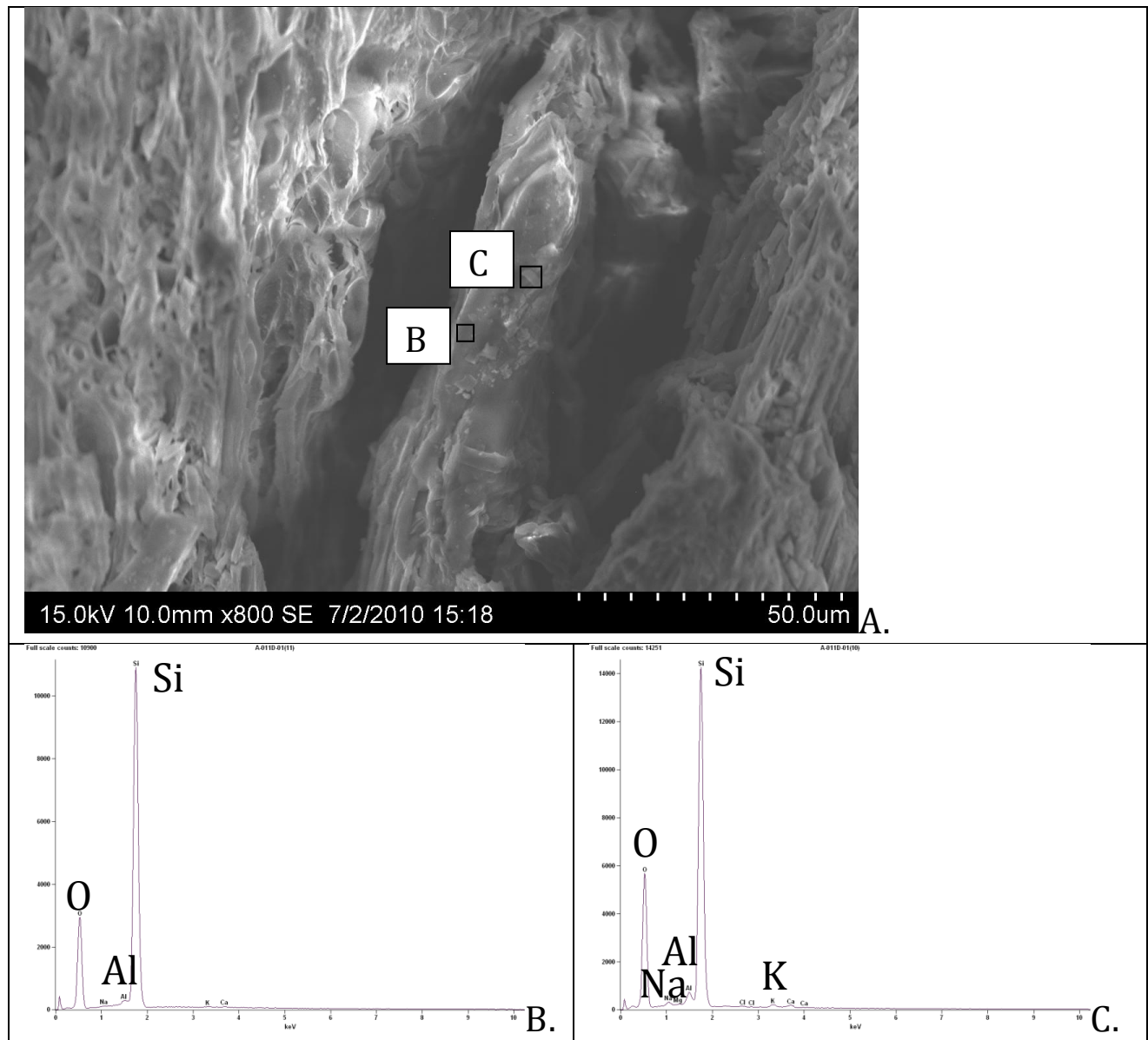


FIGURE 15. A. SEM IMAGE OF GLASS IN BANDELIER TUFF AFFECTED BY VAPOR-PHASE CRYSTALLIZATION. B. EDS SPECTRUM OF A SMALL AREA OF THE GLASS SURFACE (MARKED B IN THE PHOTO). C. EDS SPECTRUM OF A SMALL CRYSTAL ON THE GLASS SURFACE (MARKED C IN THE PHOTO).

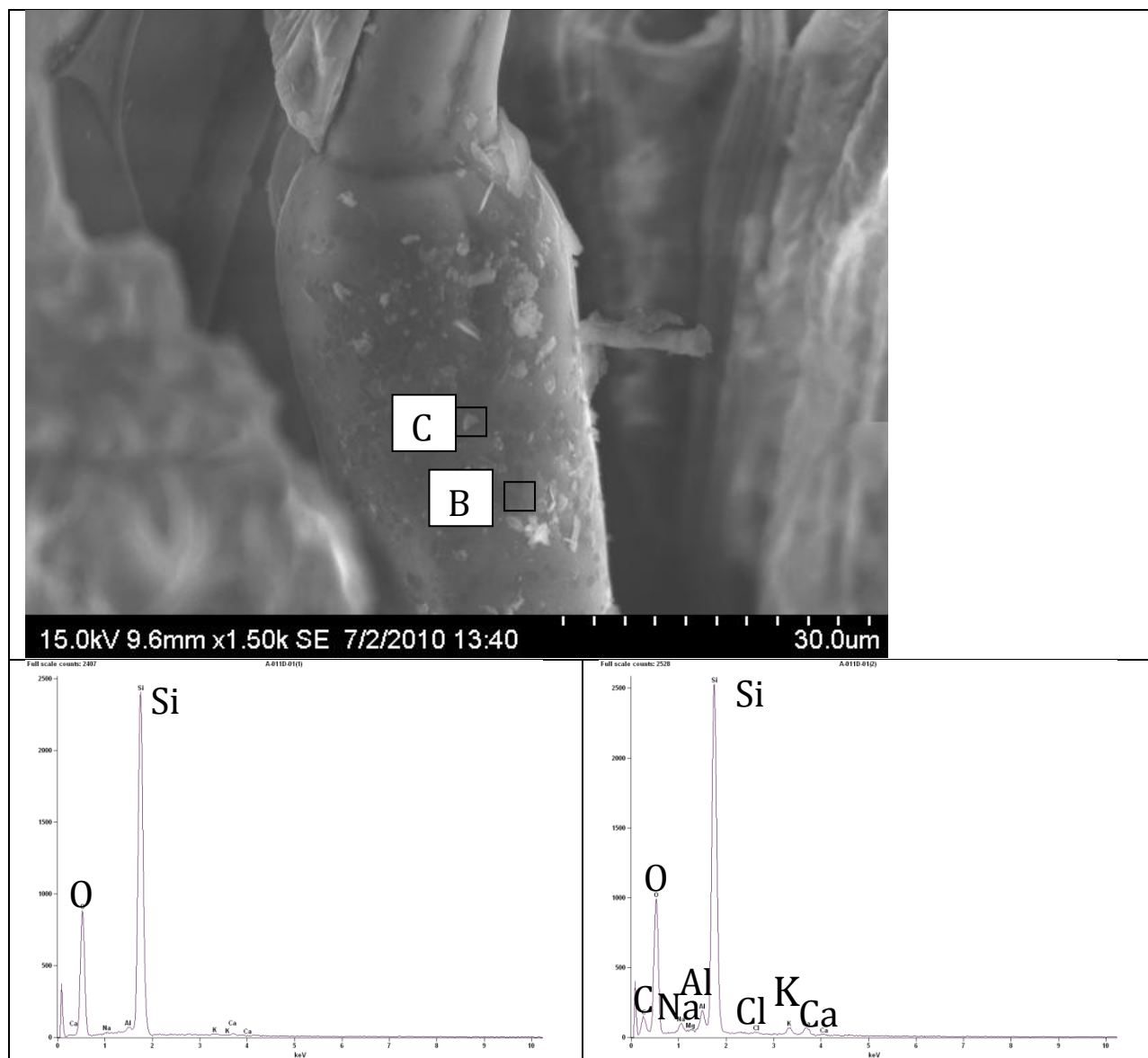


FIGURE 16. A. SEM IMAGE OF GLASS IN BANDELIER TUFF AFFECTED BY VAPOR-PHASE CRYSTALLIZATION. B. EDS SPECTRUM OF A SMALL AREA OF THE GLASS SURFACE (MARKED B IN THE PHOTO). C. EDS SPECTRUM OF A SMALL CRYSTAL ON THE GLASS SURFACE (MARKED C IN THE PHOTO).

In Figure 16, a similar phenomenon is observed. The spectrum from the glass surface is given on Figure 16B; only Si and O peaks are seen, suggesting that the surface is coated with a layer of cristobalite. Figure 16C gives the spectrum for a small crystal cluster on top of the cristobalite coating. Peaks of Si and O suggest cristobalite; C and Ca suggest calcite, and Na and Cl suggest halite. Alkali-feldspar may also be present, as indicated by Al and K peaks.

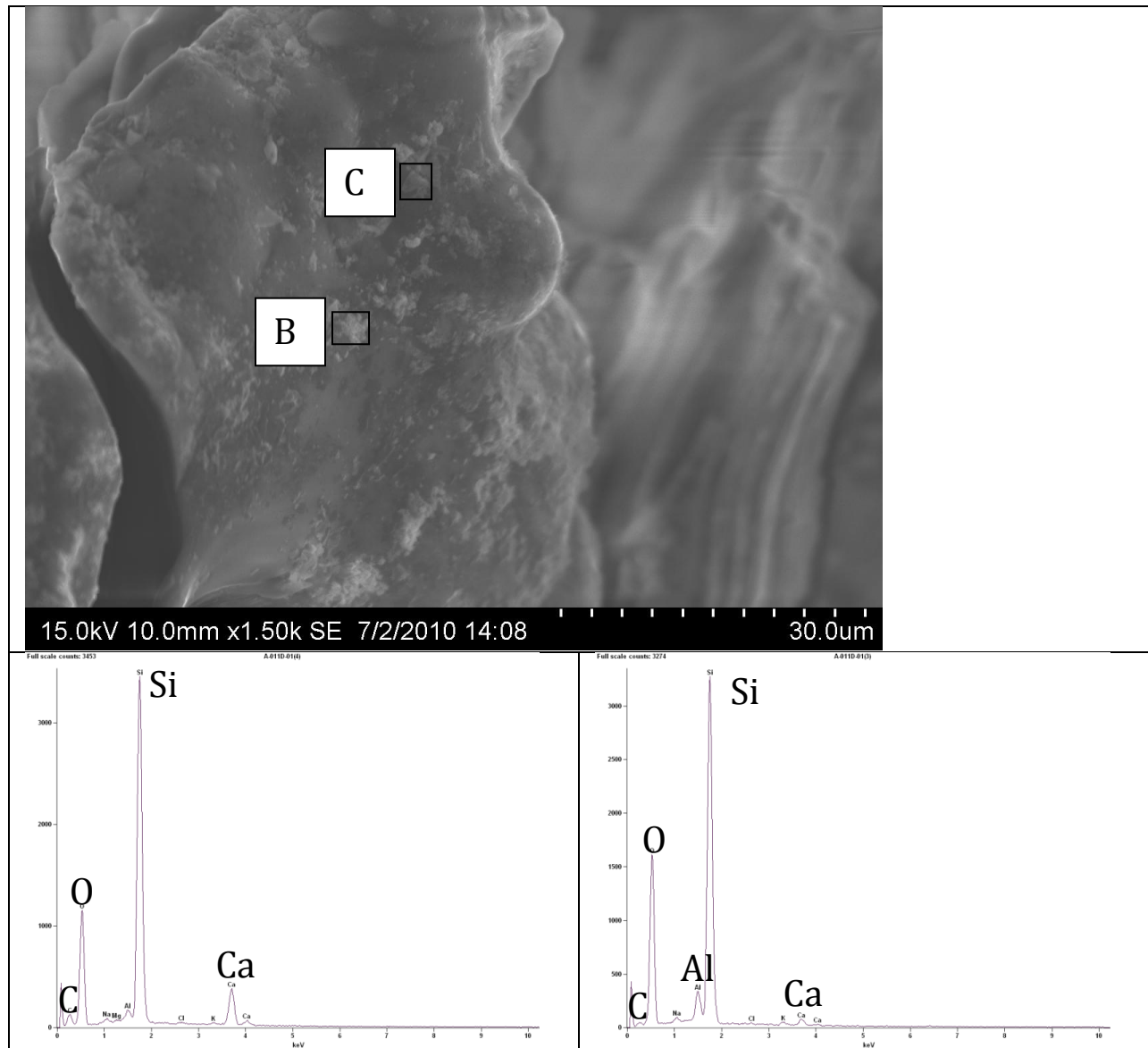


FIGURE 17. A. SEM IMAGE OF GLASS IN BANDELIER TUFF AFFECTED BY VAPOR-PHASE CRYSTALLIZATION. B. EDS SPECTRUM OF A SMALL GROUP OF CRYSTALS (MARKED B IN THE PHOTO). C. EDS SPECTRUM OF A SMALL GROUP OF CRYSTALS ON THE GLASS SURFACE (MARKED C IN THE PHOTO).

The image in Figure 17A exhibits similar mineralogy in the vapor-phase crystallization zone. The cristobalite coating was not analyzed in this case. Figures 17B and C give spectra from small crystal groups on the surface that contain the minerals cristobalite and calcite, with the addition of alkali-feldspar in Figure 17C.

Taken together, these images and spectra illustrate the processes of vapor-phase crystallization. As water-rich gases exsolve from the cooling tuff and move through fractures, the minerals cristobalite, calcite, halite, and alkali-feldspar crystallize. Cristobalite forms a fine coating on glass surfaces, and the other minerals form crystal groups on the cristobalite substrate. This mineralogic cement binds individual glass particles together, making the tuff more resistant to erosion and forming the cliff face into which the cavates were carved.

CHEMICAL GRADIENTS

METHODS

In order to assess the chemical changes associated with each type of alteration, chemical traverses were analyzed. Grooves were abraded into the tuff parallel to the altered surface using a steel file, as shown in Figure 18. The powder generated from each groove was collected and analyzed by X-ray Fluorescence for the major elements (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , and P_2O_5), the trace element Ba, and Loss On Ignition (LOI). LOI is a measure of the total volatile content of the sample, which includes water bound in mineral structures, water attached to particle surfaces, carbonate, and organic compounds. In this project, LOI also includes any lichen in the sample and the soot on the ceiling samples.

Tuff powders were ground in a porcelain ball mill, melted with a 50% Li tetraborate-50% Li metaborate flux, and quenched to glass disks in graphite crucibles. Reference rock materials (USGS) were used for calibration during XRF analysis. Samples used are listed in Table 6. Results are presented in Tables 7-12.

TABLE 6. SAMPLES USED FOR CHEMICAL TRAVERSES.

Tuff Type	Samples Used for Chemical Traverses
Fresh tuff	M136-32, M136-28, A-013
VPC without lichen	A-011, A-001, A148-001
VPC with lichen	A-001, A148-001
Lichen	A-010
Sooted ceiling	A112-003, A112-005, A112-004
Clay coating	A148-002, A148-003

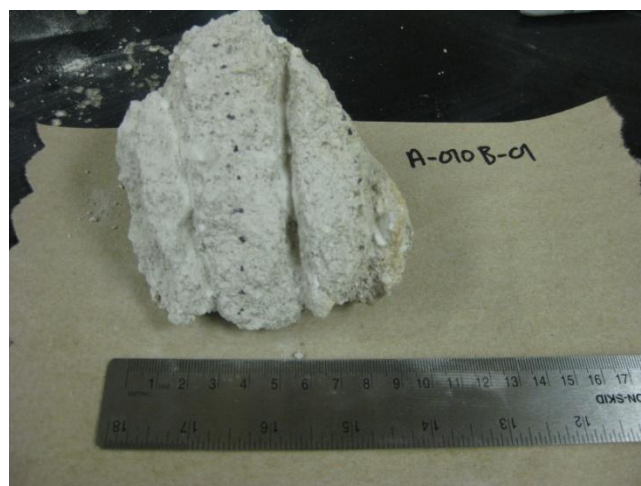
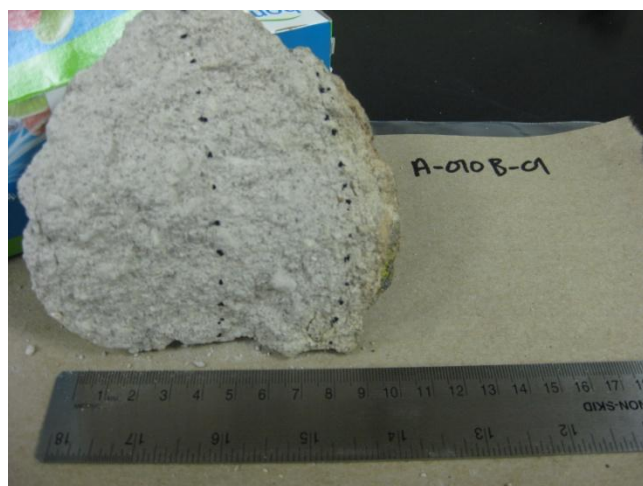


FIGURE 18. SAMPLE A010B-01 BEFORE AND AFTER ONE GROOVE WAS ABRADED, PRODUCING POWDERS FOR XRF ANALYSIS.

RESULTS

Whole-rock analyses of five samples of fresh tuff from Bandelier National Monument are presented in Table 7. These results are similar to those reported by Crowe et al. (1978), Broxton et al. (1996), Dethier et al. (2007) and Slate et al., (2007), although important and regional variations exist. For example, samples of the Tshirege Member have variable $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios. In the present study, $\text{Na}_2\text{O} < \text{K}_2\text{O}$, as reported by Broxton et al. (1996) and Dethier et al., (2007). However, Crowe et al. (1978) report $\text{K}_2\text{O} < \text{Na}_2\text{O}$ and Slate et al. (2007) report $\text{Na}_2\text{O} \cong \text{K}_2\text{O}$. These variations probably reflect sorting of glass from alkali-feldspar during pyroclastic flow (Dethier et al., 2007). Another distinct chemical characteristic of the samples in this study is the LOI content (2.88-5.14 wt%, average 3.60%, Table 7), compared to less than 2 wt% for the other studies. This can be attributed to collecting samples that have been exposed to precipitation after falling from canyon cliff faces rather than collecting a more interior, pristine sample, as is typically done in igneous petrology.

TABLE 7. XRF WHOLE-ROCK ANALYSES OF FRESH TUFF.

Sample #	M136-32B	M136-028	A-013A	A-013A	A-013A	Average	1 σ
SiO ₂	73.58	74.51	75.96	76.06	75.88	75.20	0.98
TiO ₂	0.08	0.08	0.07	0.07	0.07	0.08	0.00
Al ₂ O ₃	11.93	11.63	11.43	11.42	11.41	11.56	0.20
Fe ₂ O ₃ *	1.41	1.40	1.29	1.28	1.29	1.33	0.06
MnO	0.07	0.07	0.06	0.06	0.06	0.07	0.00
MgO	0.04	0.05	0.05	0.06	0.05	0.05	0.01
CaO	0.35	0.35	0.37	0.37	0.37	0.36	0.01
Na ₂ O	3.91	3.85	3.39	3.40	3.35	3.58	0.25
K ₂ O	4.21	4.09	4.15	4.15	4.13	4.15	0.04
P ₂ O ₅	0.01	0.01	0.03	0.03	0.03	0.02	0.01
LOI**	4.23	5.14	2.88	2.88	2.88	3.60	0.93
Total	99.82	101.18	99.69	99.79	99.53	100.00	
Ba (ppm)	bd	bd	bd	bd	bd		

* Total iron as Fe₂O₃ (Fe³⁺).

** LOI = loss on ignition, a measure of total volatile content.

Oxide data in weight %; Ba in ppm.

bd = below detection (100 ppm Ba)

TABLE 8. ANALYSES OF VAPOR-PHASE CRYSTALLIZATION TRAVERSES.

Sample #	A-011C				
mm from surface	0	5	10	25	35
SiO ₂	70.04	70.40	69.71	56.91	55.25
TiO ₂	0.07	0.07	0.06	0.06	0.05
Al ₂ O ₃	18.09	15.46	17.23	29.97	33.82
Fe ₂ O ₃ *	1.41	1.81	1.25	0.95	0.87
MnO	0.07	0.07	0.06	0.05	0.05
MgO	0.22	0.22	0.32	0.16	0.15
CaO	1.12	0.62	0.87	0.45	0.42
Na ₂ O	3.11	3.09	3.09	2.60	2.63
K ₂ O	3.58	3.73	3.74	3.12	3.11
P ₂ O ₅	0.07	0.10	0.08	0.06	0.04
LOI**	4.25	3.89	5.26	6.15	5.05
Total	102.03	99.46	101.66	100.47	101.43
Ba (ppm)	bd	bd	bd	bd	bd
Sample #	A-001B				
mm from surface	0	10	25	40	
SiO ₂	70.88	70.99	73.71	74.53	
TiO ₂	0.07	0.07	0.06	0.07	
Al ₂ O ₃	13.52	14.04	12.65	10.90	
Fe ₂ O ₃ *	1.44	1.52	1.21	1.27	
MnO	0.08	0.07	0.06	0.06	
MgO	0.15	0.37	0.15	0.08	
CaO	1.02	1.01	0.89	0.59	
Na ₂ O	3.33	3.38	3.57	3.65	
K ₂ O	3.86	3.82	4.04	4.04	
P ₂ O ₅	0.18	0.13	0.07	0.04	
LOI**	4.18	3.47	3.21	3.06	
Total	98.70	98.86	99.62	98.28	
Ba (ppm)	141	bd	bd	bd	
Sample #	A148-001B				
mm from surface	0	10	30	45	
SiO ₂	74.06	74.35	65.74	73.71	
TiO ₂	0.08	0.07	0.06	0.07	
Al ₂ O ₃	11.86	12.42	22.15	12.61	
Fe ₂ O ₃ *	1.85	1.35	1.14	1.39	
MnO	0.07	0.06		0.06	
MgO	0.07	0.02	0.05	0.02	
CaO	0.43	0.30	0.25	0.30	
Na ₂ O	3.43	3.61	3.17	3.59	
K ₂ O	3.83	4.07	3.57	4.08	
P ₂ O ₅	0.06	0.05	0.05	0.05	
LOI**	3.78	3.26	2.95	3.30	
Total	99.52	99.55	99.13	99.18	
Ba (ppm)	bd	bd	bd	bd	

* Total iron as Fe₂O₃ (Fe³⁺).

** LOI = loss on ignition, a measure of total volatile content.

Oxide data in weight %; Ba in ppm. bd = below detection (100 ppm Ba).

TABLE 9. ANALYSES OF VAPOR-PHASE CRYSTALLIZATION WITH LICHEN TRAVERSES.

Sample #	A-011C-02			
mm from surface	0	5	15	30
SiO ₂	68.19	68.35	71.23	69.44
TiO ₂	0.08	0.06	0.06	0.06
Al ₂ O ₃	12.44	17.96	14.21	15.98
Fe ₂ O ₃ *	2.01	1.57	1.34	1.19
MnO	0.10	0.06	0.06	0.06
MgO	0.45	0.25	0.25	0.25
CaO	2.61	0.76	1.30	1.72
Na ₂ O	3.58	3.17	3.25	3.33
K ₂ O	3.69	3.73	3.98	3.86
P ₂ O ₅	0.34	0.18	0.13	0.04
LOI**	5.26	3.26	3.17	3.45
Total	98.75	99.36	99.00	99.38
Ba (ppm)	258	bd	bd	bd
Sample #	A148-001D			
mm from surface	0	10	25	40
SiO ₂	70.50	73.03	63.18	70.38
TiO ₂	0.09	0.07	0.06	0.07
Al ₂ O ₃	14.80	15.30	24.22	15.88
Fe ₂ O ₃ *	1.55	1.33	1.19	1.28
MnO	0.07	0.06	0.06	0.06
MgO	0.09	0.03	0.05	0.05
CaO	0.30	0.28	0.26	0.28
Na ₂ O	3.37	3.55	3.18	3.53
K ₂ O	3.90	4.04	3.61	4.09
P ₂ O ₅	0.06	0.05	0.05	0.05
LOI**	5.21	3.10	3.31	3.06
Total	99.94	100.82	99.18	98.71
Ba (ppm)	bd	bd	bd	bd
Sample #	A148-001E			
mm from surface	0	12	27	45
SiO ₂	75.15	73.97	71.57	69.71
TiO ₂	0.20	0.14	0.08	0.08
Al ₂ O ₃	14.79	12.90	15.61	16.23
Fe ₂ O ₃ *	1.76	1.46	1.37	1.44
MnO	0.08	0.07	0.07	0.06
MgO	0.16	0.07	0.06	0.08
CaO	0.36	0.32	0.32	0.34
Na ₂ O	3.31	3.66	3.49	3.42
K ₂ O	3.96	4.20	4.10	4.04
P ₂ O ₅	0.08	0.05	0.05	0.05
LOI**	6.38	3.29	3.34	3.72
Total	99.83	100.12	100.06	99.19
Ba (ppm)	bd	bd	bd	bd

* Total iron as Fe₂O₃ (Fe³⁺).

** LOI = loss on ignition, a measure of total volatile content.

Oxide data in weight %; Ba in ppm. bd = below detection (100 ppm Ba).

TABLE 10. ANALYSES OF FRESH TUFF WITH LICHEN TRAVERSES.

Sample #	A010B-01			
mm from surface	0	10	40	60
SiO ₂	71.18	73.58	73.41	73.47
TiO ₂	0.09	0.07	0.07	0.07
Al ₂ O ₃	12.31	13.98	13.91	12.78
Fe ₂ O ₃ *	1.40	1.27	1.28	1.24
MnO	0.08	0.07	0.07	0.06
MgO	0.14	0.12	0.11	0.10
CaO	0.48	0.37	0.37	0.46
Na ₂ O	3.10	3.30	3.27	3.42
K ₂ O	3.83	3.92	3.90	4.12
P ₂ O ₅	0.05	0.03	0.03	0.07
LOI**	6.96	3.32	3.32	3.37
Total	99.62	100.02	99.73	99.16
Ba (ppm)	bd	bd	bd	bd
Sample #	A010B-08			
mm from surface	0	25	35	50
SiO ₂	73.92	73.97	74.22	74.48
TiO ₂	0.08	0.07	0.07	0.07
Al ₂ O ₃	11.57	12.60	12.63	11.87
Fe ₂ O ₃ *	1.33	1.25	1.31	1.36
MnO	0.07	0.07	0.07	0.07
MgO	0.10	0.06	0.09	0.07
CaO	0.35	0.44	0.45	0.55
Na ₂ O	3.09	3.42	3.53	3.47
K ₂ O	3.83	4.20	4.27	4.31
P ₂ O ₅	0.08	0.13	0.11	0.11
LOI**	5.10	2.91	2.76	2.98
Total	99.53	99.11	99.51	99.34
Ba (ppm)	bd	bd	bd	bd
Sample #	A010B-09			
mm from surface	0	13	30	46
SiO ₂	75.22	72.81	72.09	64.50
TiO ₂	0.08	0.08	0.07	0.07
Al ₂ O ₃	11.98	15.01	16.40	23.30
Fe ₂ O ₃ *	1.37	1.40	1.20	1.16
MnO	0.07	0.08	0.06	0.06
MgO	0.12	0.11	0.12	0.08
CaO	0.42	0.45	0.39	0.34
Na ₂ O	3.21	3.49	3.57	3.25
K ₂ O	3.92	4.19	4.17	3.91
P ₂ O ₅	0.09	0.11	0.11	0.09
LOI**	4.28	2.91	2.81	3.02
Total	100.77	100.63	100.99	99.78
Ba (ppm)	bd	bd	bd	bd

* Total iron as Fe₂O₃ (Fe³⁺).

** LOI = loss on ignition, a measure of total volatile content.

Oxide data in weight %; Ba in ppm. bd = below detection (100 ppm Ba).

TABLE 11. ANALYSES OF SOOTED CEILING TRAVERSE.

Sample # mm from surface	A112-003A			
	0	5	20	35
SiO ₂	69.83	71.47	71.47	68.31
TiO ₂	0.06	0.07	0.07	0.07
Al ₂ O ₃	11.82	14.23	14.34	18.87
Fe ₂ O ₃ *	1.21	1.33	1.29	1.19
MnO	0.06	0.06	0.07	0.06
MgO	0.05	0.05	0.06	0.08
CaO	0.39	0.30	0.31	0.29
Na ₂ O	3.54	3.82	3.65	3.50
K ₂ O	3.92	4.14	4.01	3.90
P ₂ O ₅	0.02	0.02	0.02	0.02
LOI**	7.65	3.11	2.83	2.51
Total	98.56	98.60	98.11	98.80
Ba (ppm)	bd	bd	bd	bd
Sample # mm from surface	A112-005A			
	0	19	29	
SiO ₂	70.27	65.96	65.53	
TiO ₂	0.06	0.06	0.06	
Al ₂ O ₃	13.26	22.13	23.03	
Fe ₂ O ₃ *	1.26	1.16	1.11	
MnO	0.06	0.06	0.05	
MgO	0.02	0.04	0.04	
CaO	0.37	0.26	0.25	
Na ₂ O	3.53	3.52	3.49	
K ₂ O	3.88	3.82	3.74	
P ₂ O ₅	0.05	0.05	0.05	
LOI**	8.79	2.84	2.68	
Total	101.53	99.90	100.03	
Ba (ppm)	bd	bd	bd	
Sample # mm from surface	A112-004A			
	0	11	26	38
SiO ₂	71.05	69.78	64.75	67.75
TiO ₂	0.06	0.06	0.06	0.07
Al ₂ O ₃	12.11	17.43	23.26	19.90
Fe ₂ O ₃ *	1.19	1.21	1.14	1.20
MnO	0.06	0.06	0.06	0.06
MgO	0.01	0.04	0.08	0.06
CaO	0.35	0.35	0.34	0.36
Na ₂ O	3.65	3.60	3.26	3.71
K ₂ O	4.01	3.85	3.90	3.81
P ₂ O ₅	0.05	0.05	0.08	0.05
LOI**	6.65	3.00	2.89	3.10
Total	99.20	99.44	99.82	100.05
Ba (ppm)	bd	bd	bd	bd

* Total iron as Fe₂O₃ (Fe³⁺).

** LOI = loss on ignition, a measure of total volatile content.

Oxide data in weight %; Ba in ppm. bd = below detection (100 ppm Ba).

TABLE 12. ANALYSES OF CLAY COAT TRAVERSES.

Sample #	A148-002A			
mm from surface	0	5	20	30
SiO₂	73.55	73.82	73.93	72.95
TiO₂	0.07	0.06	0.07	0.07
Al₂O₃	12.77	14.44	13.58	14.73
Fe₂O₃*	1.38	1.26	1.26	1.20
MnO	0.08	0.06	0.07	0.06
MgO	0.03	0.04	0.02	0.03
CaO	0.30	0.31	0.31	0.31
Na₂O	3.66	3.78	3.69	3.70
K₂O	4.12	4.10	4.06	4.00
P₂O₅	0.05	0.05	0.05	0.05
LOI**	3.21	3.04	2.92	3.11
Total	99.22	100.96	99.95	100.21
Ba (ppm)	bd	bd	bd	bd

Sample #	A148-003-01A			
mm from surface	0	10	15	35
SiO₂	71.81	72.95	71.51	72.99
TiO₂	0.10	0.08	0.10	0.08
Al₂O₃	13.55	13.10	12.52	13.31
Fe₂O₃*	1.62	1.55	1.55	1.48
MnO	0.08	0.08	0.09	0.08
MgO	0.15	0.04	0.08	0.05
CaO	0.46	0.33	0.35	0.33
Na₂O	3.65	3.90	3.82	3.84
K₂O	4.21	4.43	4.38	4.38
P₂O₅	0.10	0.05	0.06	0.05
LOI**	4.03	3.60	3.85	3.69
Total	99.76	100.13	98.29	100.28
Ba (ppm)	bd	bd	bd	bd

* Total iron as Fe₂O₃ (Fe³⁺).

** LOI = loss on ignition, a measure of total volatile content.

Oxide data in weight %; Ba in ppm. bd = below detection (100 ppm Ba).

In Figures 19-25, traverses across vapor-phase crystallization (VPC) surfaces (with as little lichen as possible) are in blue in the “front” of the diagram. Traverses across VPC surfaces with abundant lichen follow in red; traverses across fresh surfaces with lichen (no VPC) are next in green. In the “back” of the diagram are traverses across sooted ceilings in orange and two traverses across clay-coated surfaces in black/gray. The most notable feature of the traverses is that VPC affects the chemical composition of the tuff much more than lichen, soot, or clay.

Variations in SiO₂ across various weathered/altered surfaces are shown in Figure 19. Fresh tuff analyzed in this project has an average SiO₂ concentration of $75.2 \pm 0.98\%$. All of the tuffs in Figure 19 have lower SiO₂ than average fresh tuff, due largely to higher LOI values in the weathered and altered samples. The traverse in samples VPCA-011C is anomalous; it crosses a low SiO₂, high Al₂O₃, high LOI zone at 15 cm from the surface. This is probably a lithic fragment (fragment of subvolcanic crust entrained during eruption). This feature is also seen in traverses Fresh Lichen A010B-09, Sooted Ceiling A112-005, and Sooted Ceiling A112-004 (Figs. 19, 20), although the VPC traverse is the only one to show increased LOI towards the interior of the sample (Fig. 25).

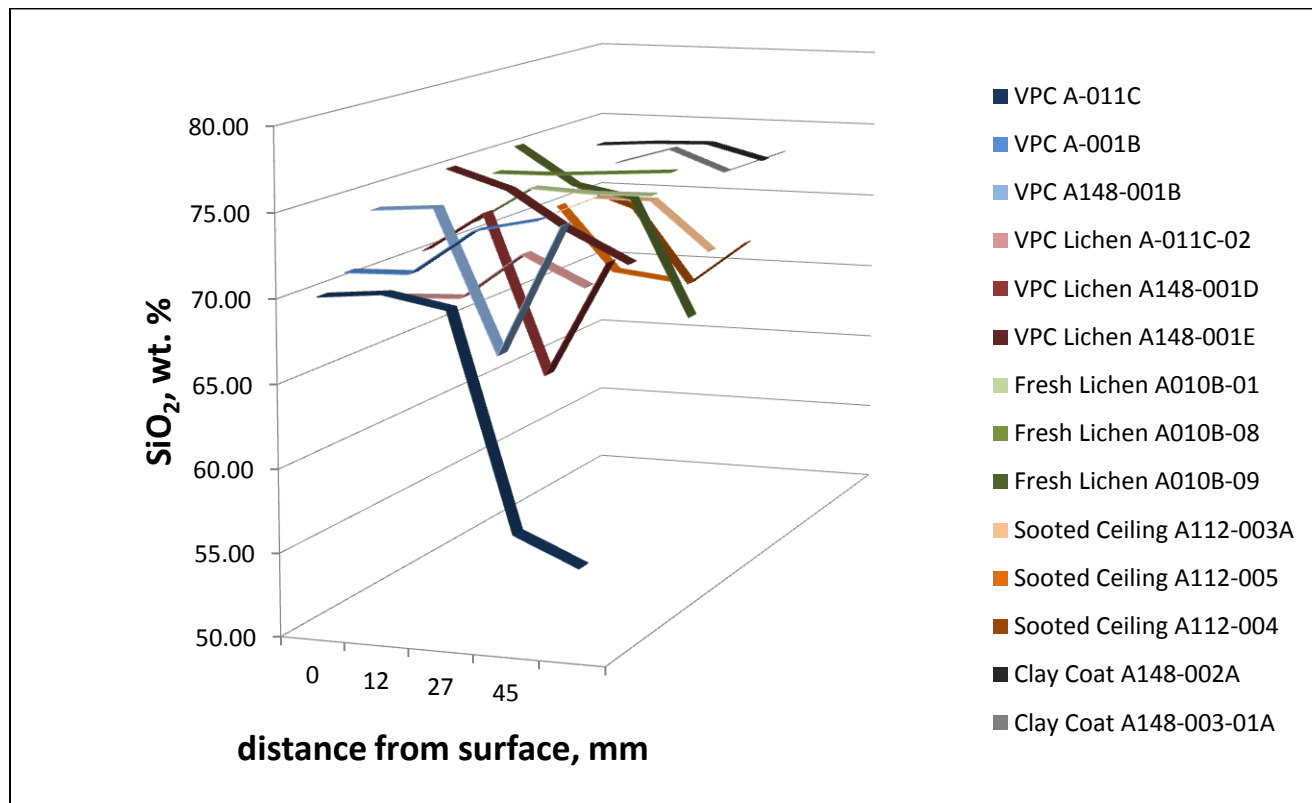


FIGURE 19. VARIATION IN SiO₂ FROM THE SURFACE TOWARDS THE INTERIOR OF TUFF FOR VARIOUS TYPES OF TUFF.

For Al₂O₃ (Fig. 20), the VPC and VPC with lichen samples are again the most variable in composition, reflecting the addition of elements from alkali-feldspar that was observed on glass surfaces in the SEM images. Clay-coating and lichen alone have little effect on Al₂O₃ concentrations. Average fresh tuff has 11.56 ± 0.20 wt% Al₂O₃.

Clay-coating and soot alone have little effect on Fe₂O₃ concentrations (Fig. 21). These traverses have Fe₂O₃ concentrations very close to that of average fresh tuff: 1.33 ± 0.06 . However, VPC and lichen both cause distinct increases in Fe₂O₃ towards the surface, causing the characteristic pinkish tone of the cliff faces in the monument (Figs. 1, 4).

Most of the analyzed traverses show little variation of CaO (Fig. 22), and have CaO concentrations close to average fresh tuff (0.36 ± 0.01 wt%). However, four of the VPC traverses

show higher and more variable concentrations of CaO, probably as a result of precipitation of calcite (CaCO_3) crystals on glass surfaces, as observed in the SEM images.

One might expect the mobile alkali elements Na_2O and K_2O to have highly variable concentrations in the VPC, but this is not observed (Figs. 23, 24), although the VPC traverses do show more variability than lichen, soot, and clay-coating traverses. In addition, the VPC traverses have lower overall Na_2O and K_2O concentrations compared to the others, which are close to the average fresh tuff concentrations at $3.58 \pm 0.25 \text{ wt}\% \text{ Na}_2\text{O}$ and $4.15 \pm 0.04 \text{ wt}\% \text{ K}_2\text{O}$.

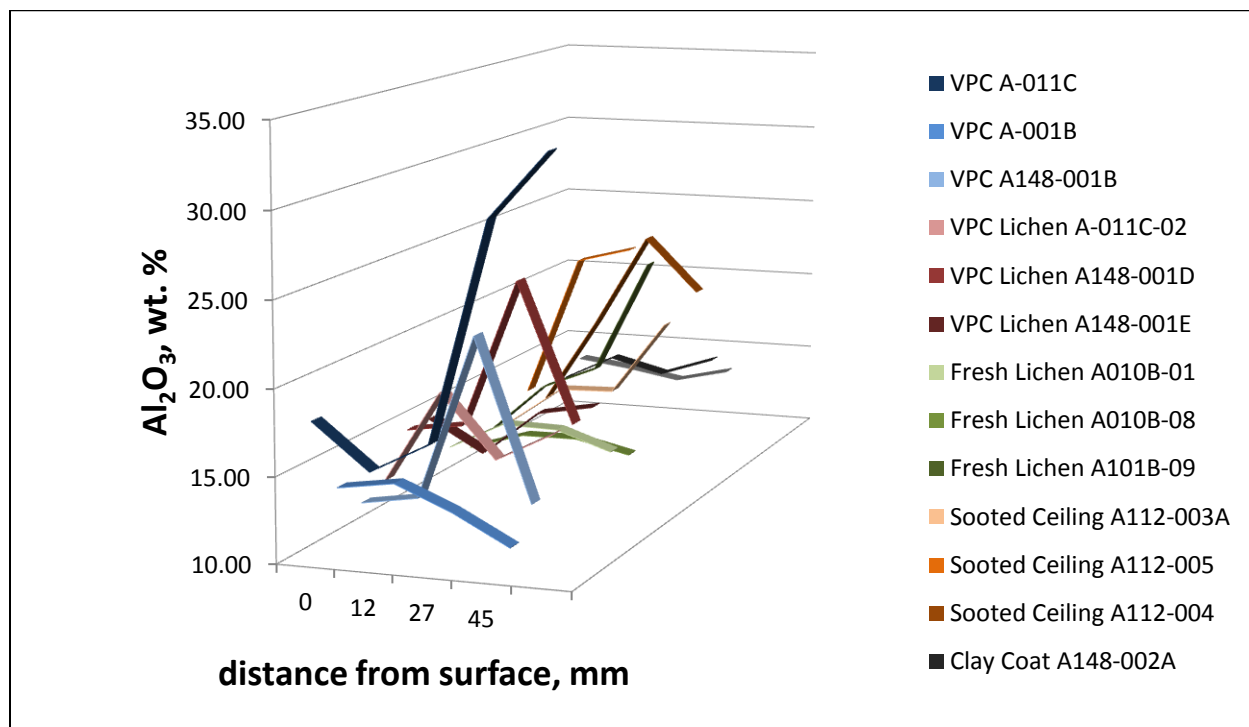


FIGURE 20. VARIATION IN Al_2O_3 FROM THE SURFACE TOWARDS THE INTERIOR OF TUFF FOR VARIOUS TYPES OF TUFF.

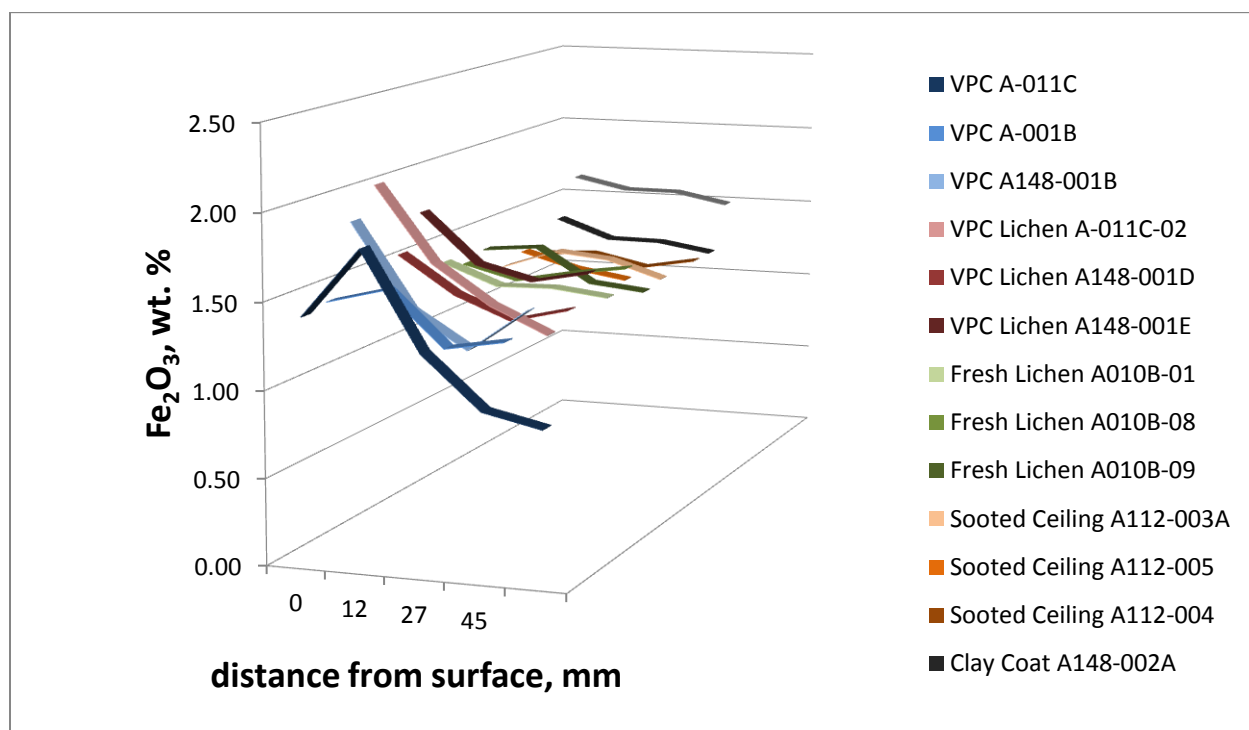


FIGURE 21. VARIATION IN Fe_2O_3 FROM THE SURFACE TOWARDS THE INTERIOR OF TUFF FOR VARIOUS TYPES OF TUFF.

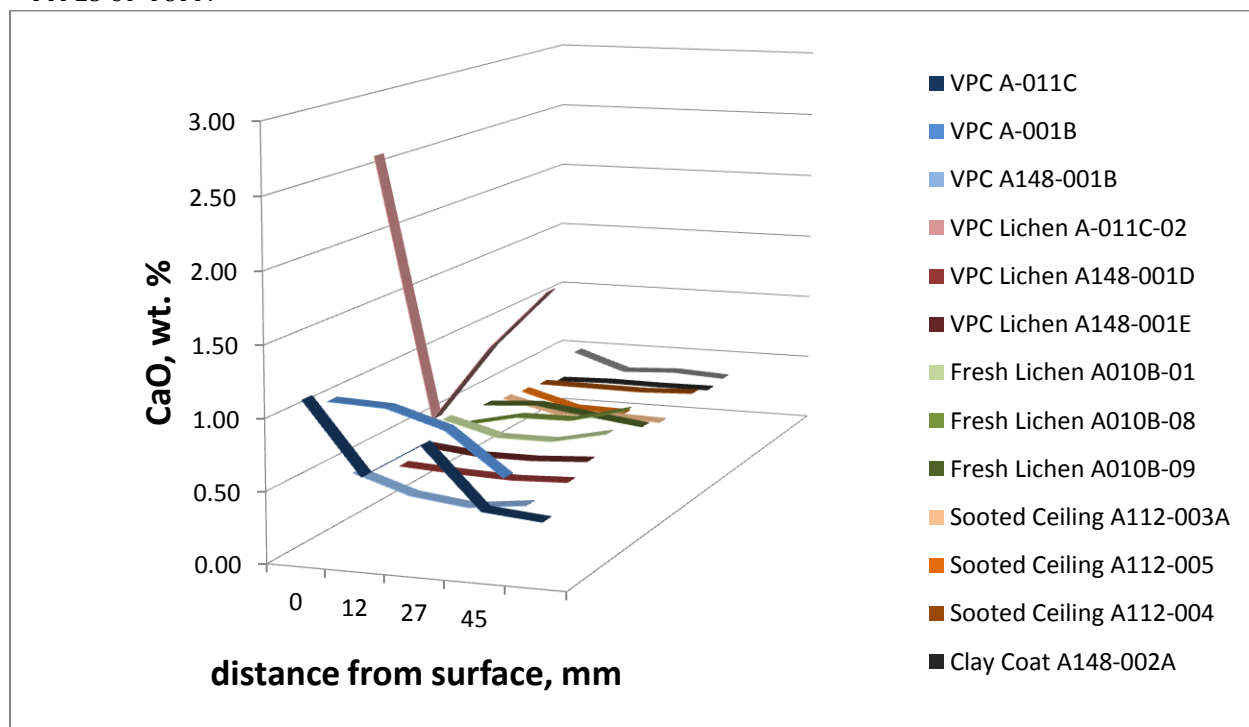


FIGURE 22. VARIATION IN CAO FROM THE SURFACE TOWARDS THE INTERIOR OF TUFF FOR VARIOUS TYPES OF TUFF.

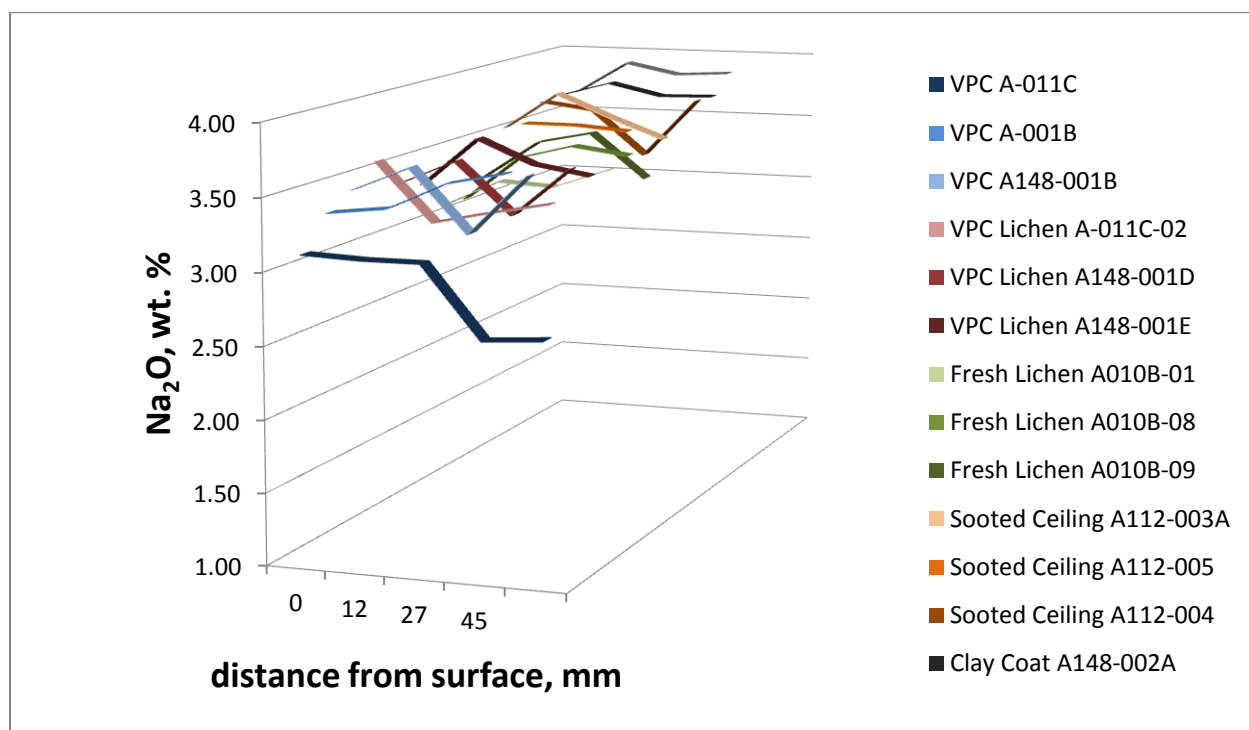


FIGURE 23. VARIATION IN Na_2O FROM THE SURFACE TOWARDS THE INTERIOR OF TUFF FOR VARIOUS TYPES OF TUFF.

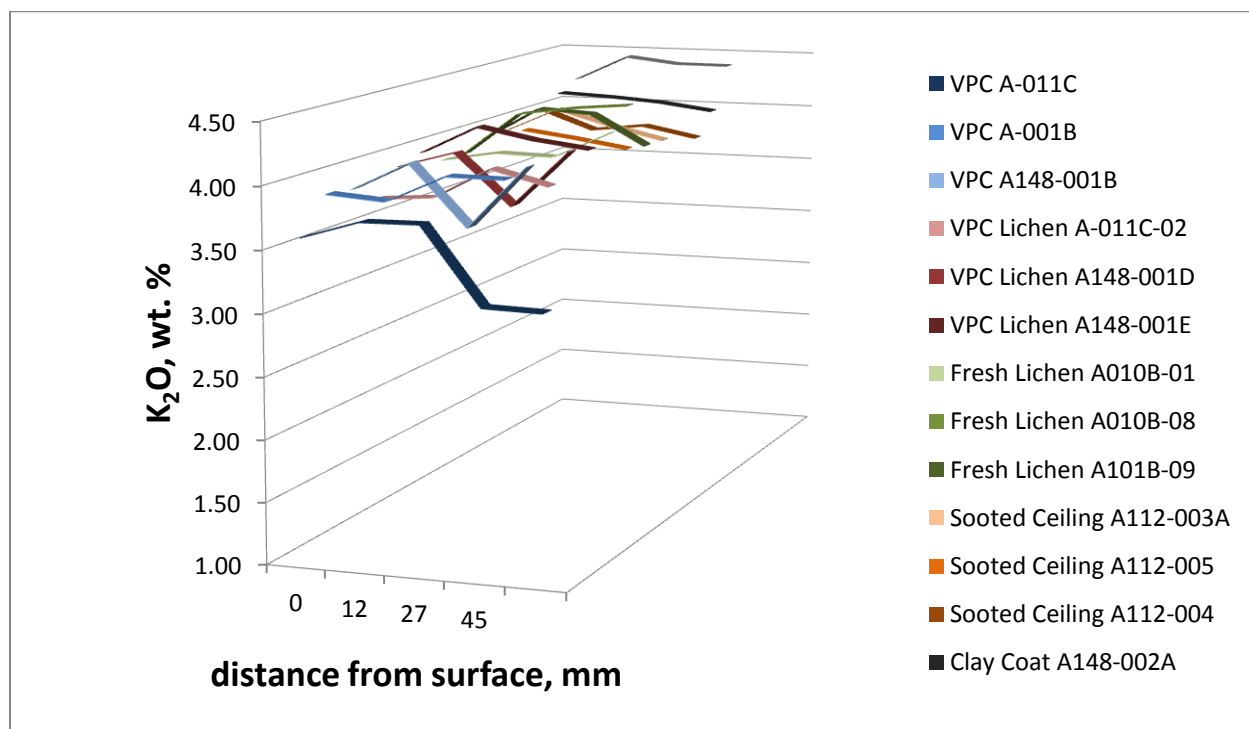


FIGURE 24. VARIATION IN K_2O FROM THE SURFACE TOWARDS THE INTERIOR OF TUFF FOR VARIOUS TYPES OF TUFF.

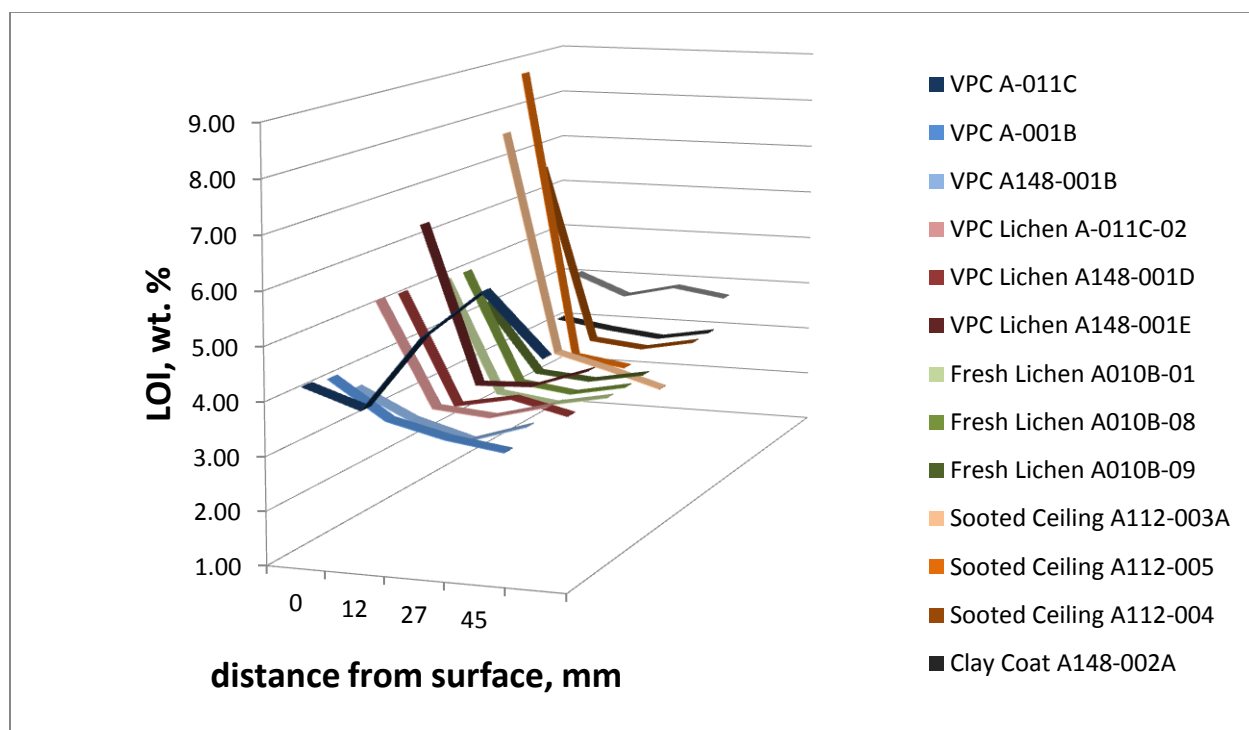


FIGURE 25. VARIATION IN LOI (LOSS ON IGNITION, OR TOTAL VOLATILES) FROM THE SURFACE TOWARDS THE INTERIOR OF TUFF FOR VARIOUS TYPES OF TUFF.

Variations in LOI (Fig. 25) reflect the processes that occur during the various alteration processes. Average fresh tuff has 3.60 ± 0.93 wt% LOI. The two traverses of clay-coated tuff fall within this range and show little variation towards the interior of the tuff, suggesting that the clay and the water that deposited it have little chemical interaction with the tuff particles. The traverses for sooted ceiling have an enormous enrichment of LOI at the surface; the soot is volatilized during analysis. Similarly, all of the lichen-encrusted samples, whether on a VPC or fresh surface, have high LOI at the surface because the lichen itself is volatilized during analysis. Note that the VPC without lichen traverses have lesser increases of LOI at the surface than the VPC with lichen traverses; clearly, the lichen contributes more to LOI than the volatile minerals in the VPC zone (calcite, halite). The chemical effect of lichen penetrates less than 10 mm into the tuff (just a few mm, based on the photomicrograph in Fig. 11).

CHEMICAL EFFECTS OF WATER-TUFF INTERACTION

METHODS

Water-rock interaction accelerates weathering and alteration. Dissolution of soluble minerals, formation of low-temperature minerals, and physical filtering of fine particles from a rock during water seepage are important processes weathering and soil formation. To study the dissolution of tuff in water, a pilot study was performed. Powdered fresh tuff (sample M108-025) was used in this project. Some powder was preserved untreated for analysis; 6 g of powder were immersed in 200 ml of distilled, deionized water and stirred on a magnetic stir plate for 24 hours. Distilled deionized water was used because it should be more reactive with the tuff than rainwater, providing data on the maximum leaching that would occur in nature. The solid material was filtered from the liquids and dried; the water was preserved but not analyzed. Aliquots of untreated powder and treated powder were analyzed by XRF to examine the changes in tuff composition due to water-tuff interaction. This work was a pilot study to determine if this would be a fruitful path for future research.

RESULTS

This test shows that all elements except for Al (and possibly P) dissolve during water-tuff interaction; Al is a highly insoluble element in most geologic environments. The increase in wt % Al_2O_3 is due to the loss of other components. Note that when the analyses are normalized to 100%, compensating for analytical error, the loss of SiO_2 , TiO_2 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , and K_2O is exactly compensated by the gain in Al_2O_3 .

TABLE 13. RESULTS OF WATER-TUFF REACTION EXPERIMENT.

Sample	Raw Data			Normalized to 100%		
	M108-25 untreated	M108-25 treated	Difference*	M108-25 untreated	M108-25 treated	Difference*
SiO_2	77.57	75.78	-1.78	77.30	76.41	-0.89
TiO_2	0.09	0.06	-0.03	0.08	0.06	-0.03
Al_2O_3	12.42	13.76	1.34	12.37	13.87	1.50
Fe_2O_3^*	1.41	1.09	-0.32	1.41	1.10	-0.31
MnO	0.07	0.06	-0.01	0.07	0.06	-0.01
MgO	0.11	0.09	-0.02	0.10	0.09	-0.02
CaO	0.37	0.32	-0.05	0.37	0.32	-0.05
Na_2O	3.95	3.82	-0.13	3.94	3.85	-0.08
K_2O	4.33	4.15	-0.17	4.31	4.19	-0.12
P_2O_5	0.04	0.04	0.00	0.04	0.04	0.00
Total	100.34	99.18	-1.16	100.00	100.00	0.00

* Difference = treated - untreated. Negative values indicate relative loss; positive values indicate relative gain.

RESISTANCE TO ABRASION AND COMPRESSION

METHODS

The purpose of the hardness test is to measure the relative abrasion resistance of the various types of tuff. The minerals on Moh's Hardness Scale (Table 14) were used for reference. Each tuff was scratched with talc (the softest mineral on the scale), then with gypsum, and so on, until the mineral scratched the tuff surface. Samples used are listed in Table 15.

Talc	1
Gypsum	2
Calcite	3
Fluorite	4
Apatite	5
Microcline	6
Quartz	7
Topaz	8
Corundum	9
Diamond	10

TABLE 14. MINERALS IN
MOH'S HARDNESS SCALE

The six types of tuffs were compressed in a hydraulic press to measure their resistance to compression. Samples were placed in the press with the altered surface (VPC, sooted ceiling, etc.) perpendicular to the compressive stress, or vertically, in the press (Fig. 26). Pressure was increased until the sample failed, defined as when a fracture completely crossed the sample. Usually, this resulted in catastrophic failure of the sample. The pressure required to cause failure was measured on three samples of each tuff type and averaged (Table 16). Because the exerted pressures were fairly low and the scale on the press was not sufficiently sensitive, the readings are estimates. However, the relative compressive strengths are reliable.

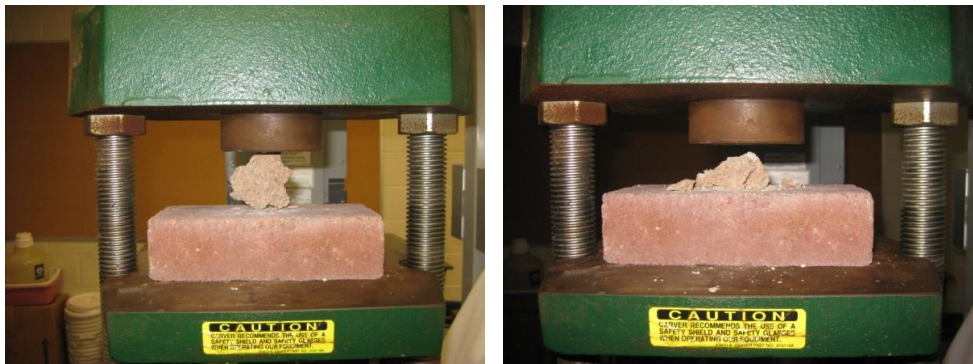


FIGURE 26. COMPRESSIVE STRENGTH TEST OF TUFF, SHOWING THE SAMPLE BEFORE FAILURE (LEFT) AND AFTER FAILURE (RIGHT).

TABLE 15. SAMPLES USED IN HARDNESS AND COMPRESSION TESTS.

Tuff Type	Samples Used in Hardness Test	Samples Used in Compression Test
Fresh tuff	M136-029B	Fresh tuff is too friable to test.
VPC without lichen	A-011N	M-049, M-050, M-052
VPC with lichen	A148-001E	A010B-10, A148-001, A148-001
Lichen	A-010B	A-010B-11, A-010B-05, A010B-04
Sooted Ceiling	A112-003A-01	A114-009, A114-007, M82-021
Clay Coat	A148-002B	A114-011G-01, A114-001G-02, A114-011G-03

RESULTS

Abrasion and compression tests yielded the same results: the VPC and VPC with lichen samples are the hardest and failed at higher pressures in compression tests (Table 11).

TABLE 16. RESULTS OF HARDNESS AND COMPRESSION TESTS. FRESH TUFF IS TOO FRIABLE TO TEST FOR COMPRESSION.

Type of Tuff	Hardness (Moh's scale)	Failure Pressure (psi)
Vapor-Phase Crystallization	3 (softer than fluorite)	510
Vapor-Phase Crystallization with lichen	3 (softer than fluorite)	438
Sooted Ceiling	2 (softer than calcite)	200
Fresh tuff with lichen	1 (softer than gypsum)	200
Clay coated tuff	0 (softer than talc)	200
Fresh tuff	0 (softer than talc)	Fresh tuff is too friable to test.

RESISTANCE TO FREEZE-THAW

METHODS

The climate in Bandelier National Park is conducive to weathering by freeze-thaw. To investigate the strength of tuff to this process, two samples of fresh tuff (Table 17) were immersed momentarily in distilled deionized water and left to freeze overnight. The samples were then thawed at room temperature. This procedure was repeated until the sample failed, defined as losing coherence.

TABLE 17. SAMPLES OF FRESH TUFF USED IN FREEZE-THAW TESTS.

M136-035
M136-037

RESULTS

Two samples of fresh tuff were subjected to freeze-thaw (Fig. 27). One sample disintegrated after the first thaw; the second disintegrated after the sixth thaw. These data and the continued existence of tuff in Frijoles Canyon suggest that freeze-thaw is not a significant weathering factor. An implication of this is that groundwater percolation through the tuff overlying the cavates is not a significant factor in the weathering of the tuffs.

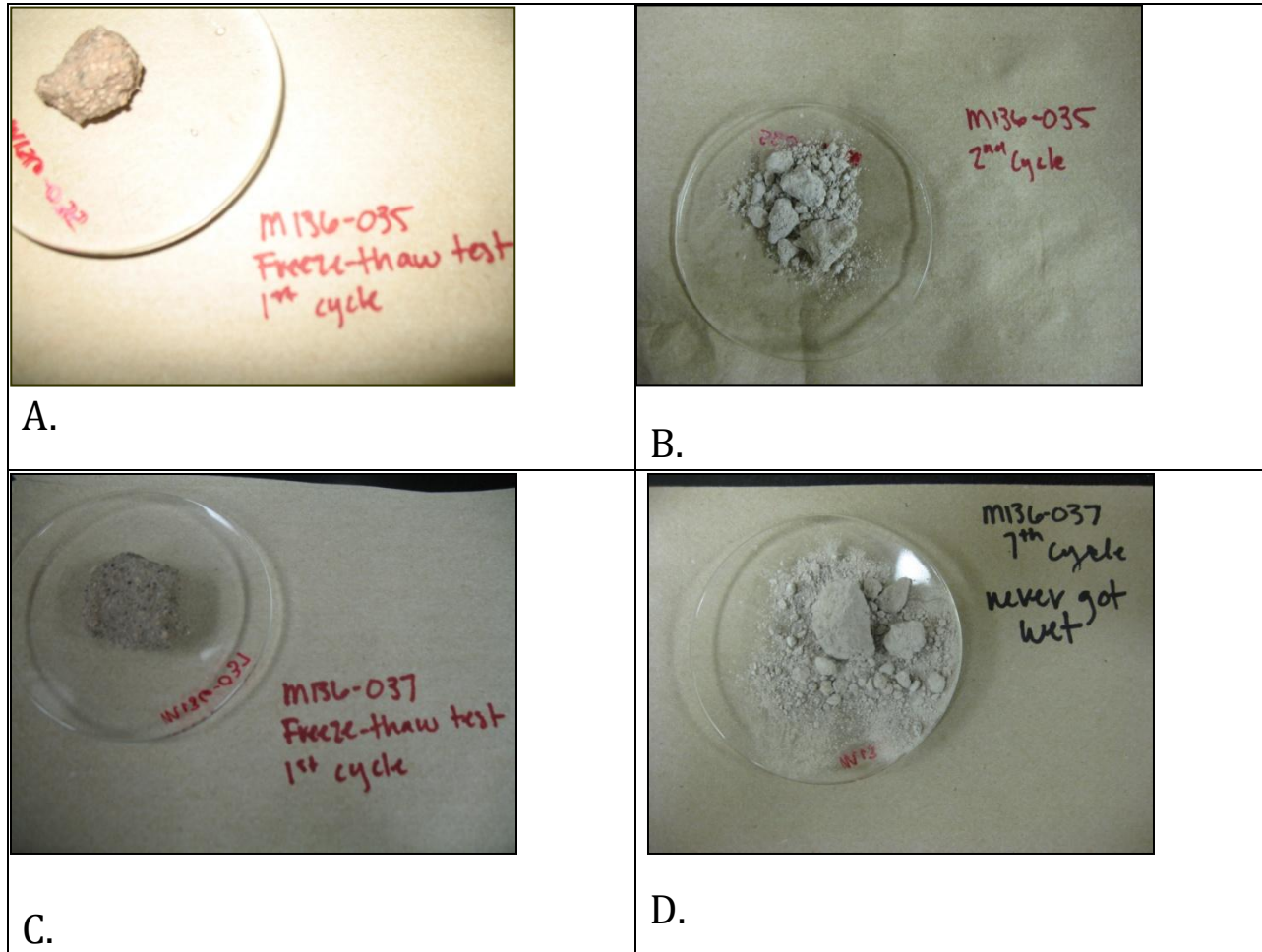


FIGURE 27. RESULTS OF FREEZE-THAW EXPERIMENTS. FRESH TUFF M136-035 SURVIVED ONLY ONE CYCLE; M136-037 SURVIVED SIX CYCLES.

TUFF DETERIORATION AND STRENGTHENING

Fresh, unwelded Bandelier Tuff is very friable. It disintegrates under very little pressure (Table 16). This is the property that made it possible for the cavates to be carved with simple technology. Tuff particles are not bound to each other with any kind of cement; they are also not tightly packed. Several natural processes occurred in what is now Frijoles Canyon to make the

vertical cliff faces stronger than fresh tuff and sufficiently stable to allow human habitation in cavates. These processes are vapor-phase crystallization, encrustation with lichen, and clay coatings from water spilling over the canyon wall.

Vapor-phase crystallization (VPC) occurred during cooling of the pyroclastic flow (Reneau, 2000; Crowe et al., 1978; Broxton et al., 1995). In Frijoles Canyon, fluids escaped from the tuff along vertical fractures. The minerals cristobalite, calcite, halite, and probably alkali-feldspar (Figs. 14-17) crystallized along both fracture surfaces as the fluids cooled. This very thin layer of minerals binds the tuff particles together, creating a hard surface several cm thick (Figs. 1-4). As the stream cut into the tuff, the fresh tuff was rapidly eroded and the stream widened until it reached the VPC zone, which became the vertical cliff face we see today. Through time, lichen colonies established themselves on the VPC zone, further strengthening the cliff faces. This interpretation explains why the cavates could be easily carved beyond the VPC zone and also why the ceilings continue to deteriorate.

Chen et al. (2000) provides an excellent overview of the effects of lichen on rock weathering processes. Lichen colonization increases physical weathering as the lichen hyphae penetrate into the rock along grain surfaces and cleavages. Both the physical intrusion of the hyphae and the associated freeze-thaw are thought to enhance physical weathering. Chemical changes attributed to lichen are variable, depending on the lichen species and the rock type. However, production of acid (oxalic, carbonic, gluconic, and citric) may cause chemical reactions in the rock. One observed reaction product is the precipitation of amorphous silica on the parent material under the lichen. Chen et al. (2000) also note that, in some cases, lichen actually strengthens the surface of the rock by binding it together and protecting it from rain, snow, and hail.

In Bandelier National Monument, it appears that lichen strengthen and protect the tuff surfaces, while also physically changing the surface. Chemically, there is very little change in composition from the lichen-covered surface to fresh tuff 40 mm from the surface (Table 10; Figs. 19-25). Depletion of Si is not observed, contrary to Kerr and Zavada (1989). There is a slight increase of Fe_2O_3 at the surface. Note that LOI (Loss on Ignition, a measure of total volatile content) increases drastically at the surface; this is because there was significant lichen in the sample, which vaporized during heating. Other elements have the same or lower concentrations at the surface as in the interior; this is simply because of the added organic material in the lichen at the surface. Lichen do not appear to be making large chemical changes to the rock.

In some places, a thin layer of clay has been deposited by water spilling or dripping over the cliff face from above (Fig. 7). The clay coating and the water that deposited it have little influence on the chemistry or mineralogy of the tuff (Table 12, Figs. 19-25). Certainly, the tuff under the clay coat does not show the chemical changes expected from water-tuff interaction seen in Table 13. The clay coatings appear to stabilize some tuff surfaces; however, the clay coatings are just as soft as fresh tuff and only slightly more resistant to compression (Table 61).

Groundwater percolation through the Bandelier Tuff from the mesa surface has been considered as an important factor in cavate degradation. This no longer a probable cause, for several reasons. First, some units of the Tshirege Member above unit Qbt 1g are welded to varying degrees (Fig. 1). Welded tuff has much lower permeability than non-welded tuff. Thus, the welded layers will prevent vertical water flow, acting as an umbrella and shielding unit Qbt 1g from excessive groundwater flow. Second, the work in this study indicate that the fresh tuff in Frijoles Canyon is fragile during water-rock interaction. Thus, a steady drip of groundwater through the

tuff would cause disintegration fairly rapidly. Similarly, the tuff is very non-resistant during freeze-thaw cycles. If the tuff contained water during the winter months, disintegration would happen in a few nights. Finally, chemical traverses of tuff from sooted surfaces into the ceiling do not show significant changes in chemical composition, except for higher volatile content on the surface due to the addition of soot. If groundwater had been interacting with the tuff, one would expect to see the leaching of all elements except Al and P, as in the water-rock interaction experiment performed in this work. Instead, very little chemical variation is observed, suggesting that the tuff above cavate ceilings has not interacted with water.

FUTURE WORK

This work suggests that groundwater percolation is not an important erosive process in Bandelier National Monument. However, erosion of cavate interiors after rainy days has been observed. Most likely, this is due to small amounts of water blown into the cavate during storms that causes the tuff in the walls and ceilings to disintegrate. Further investigation into this process could prove fruitful. Chemical analysis of the tuff that has fallen after a rain storm might exhibit the characteristics of water-rock interaction.

Other potential projects include a study of the cause of spalling of the cliff face. Is this result of water percolation into fractures? A detailed SEM study of lichen growth might also prove interesting.

APPENDIX: REPORTS WRITTEN BY UNDERGRADUATE RESEARCHERS

ABRASION TEST

Purpose:

The purpose of this test is to observe the abrasion resistance of unaltered and altered tuff using the minerals from the Moh's Hardness scale to determine the strengths of the different types of tuff.

Hypothesis:

The prediction of this test is that the samples with altered surfaces will have a higher resistance to abrasion in comparison to the unaltered fresh tuff. Another prediction for this test is will our samples of Vapor Phase crystallization(VPC) and Vapor Phase Crystallization with lichen have a similar abrasion resistance to quartz due to the cristobalite on the surface.

Procedure:

The samples used for testing were Vapor Phase Crystallization A-011N, Vapor Phase Crystallization with lichen A148-001F, fire sooted A112-003C, clay coated A148-002B, Fresh with lichen A-010B, and unaltered fresh tuff M136-029B. Each sample was scratched first with the weakest mineral from the Moh's Hardness scale and gradually moving up on the scale of hardness until the sample was abraded by a specific mineral.

Moh's Hardness Scale

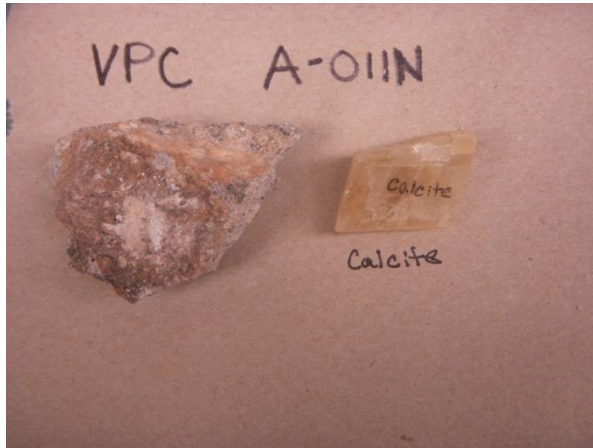
Talc	1
Gypsum	2
Calcite	3
Fluorite	4
Apatite	5
Microcline	6
Quartz	7
Topaz	8
Corundum	9
Diamond	10

Observations:

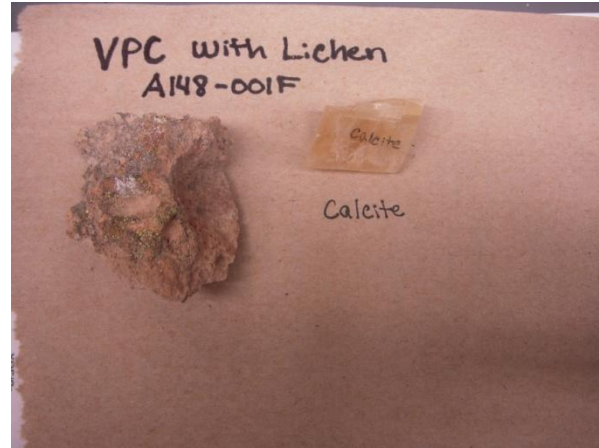
The two samples that were the most resistant to abrasion out of all six samples tested were Vapor Phase Crystallization and Vapor Phase Crystallization with lichen; both of these samples had comparable hardness with calcite, but both of these samples were abraded by fluorite. The next hardest was the fire sooted sample which resisted abrasion by gypsum, but was unable to resist abrasion to calcite. The third hardest of the three samples was fresh with lichen which resisted abrasion from talc, but was easily abraded by gypsum. Lastly both the clay coated sample and the unaltered fresh sample were easily abraded by talc.

Conclusion:

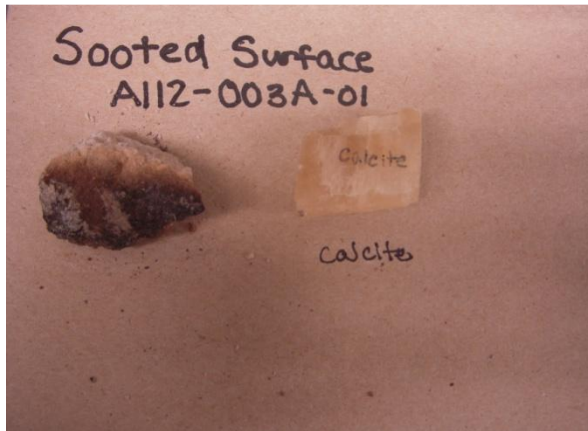
After performing the abrasion test on the six different samples of Bandelier tuff the most resistant to abrasion was Vapor Phase Crystallization and Vapor Phase Crystallization with lichen, however neither of these samples were comparable to the hardness of quartz. This may suggest that the surface of our sample of Vapor Phase Crystallization is not cristobalite or that there is a thin layer of cristobalite that is easily penetrable by the weaker minerals in the Moh's Hardness Scale.



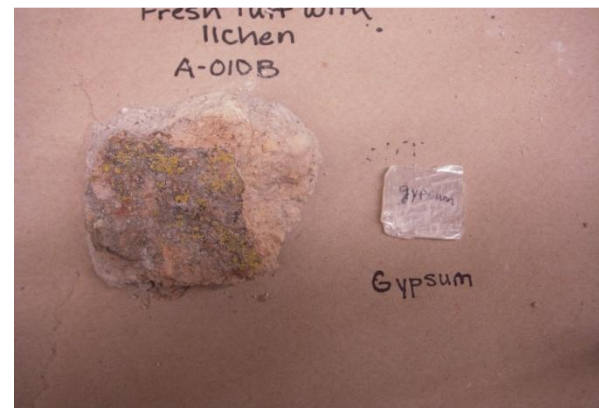
Sample A-011N Vapor Phase Crystallization was abraded by calcite.



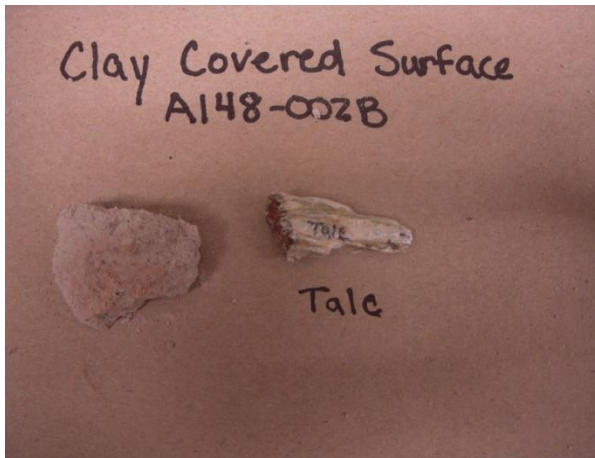
Sample A148-001F Vapor Phase Crystallization with Lichen was abraded by calcite.



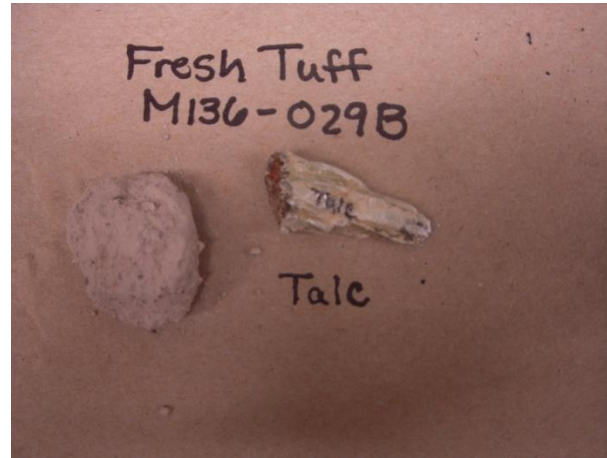
Sample A112-003A-01 Fire Sooted Surface was abraded by calcite.



Sample A-010B Fresh Tuff with Lichen was abraded by gypsum.



Sample A148-002B Clay Covered Surface was abraded by talc.



Sample M136-029B Unaltered Tuff was abraded by talc.

COMPRESSIVE STRENGTH TEST

Purpose:

To determine the pressures at which significant tuff surfaces fail when compressed with a hydraulic press.

Hypothesis:

We predict that the failure pressures for vapor phase crystallization (VPC) and VPC with lichen will be significantly greater than those of the less durable lichen on fresh, sooted ceiling and clay coat surfaces.

Procedure:

Significant tuff surfaces include vapor phase crystallization (VPC), VPC with lichen, lichen on fresh, sooted ceiling and clay coated fresh. Three samples of each surface were used for these tests. Each sample was measured, placed on the hydraulic press with the significant surface oriented vertically (perpendicular to the force) and compressed until failure occurred. For this test, failure is defined as a fracture which bisects the sample.

Data:

Surface	Sample	Dimensions (cm)	Approx. Failure Point (psi)
VPC	M-050	2.5 x 1.5 x .5	415
	M052	2.5 x 2.5 x 1.5	415
	M-049	5 x 5 x 1	700
VPC w/ Lichen	A-010B-10	5 x 5 x 1.5	415
	A148-001E-01	4 x 2.5 x 2	200
	A148-001E-02	8 x 4 x 4	700
Lichen on Fresh	A-010B-11	4.5 x 5 x 1	200
	A-010B-05	2.5 x 3 x 4	200
	A-010B-04	4 x 3.5 x 2	200
Sooted Ceiling	M82-021	4.5 x 3 x 1	200
	A114-007	3 x 3 x 1	200
	A114-009	3 x 3 x .5	200
Clay Coat	A148-011G-01	5 x 5.5 x 7	200
	A148-011G-02	7 x 6 x 9	200
	A148-011G-03	5 x 4 x 7	200

Observations:

The majority of these samples were so easily compressed that the gauge's resolution was not fine enough to give exact failure pressures, therefore the data is given as approximations. In general, surfaces that exhibit a greater hardness and durability have the highest compressive strengths, i.e. VPC and VPC with lichen. The softer, less cohesive samples that are similar to fresh tuff have the lowest failure pressures and were nearly undetectable. The largest VPC and VPC with lichen samples have the highest compressive strengths.

Conclusions:

The surfaces with the highest compressive strengths are VPC and VPC with lichen, which are also the most durable surfaces. Sample size may play a role in compressive strength since that largest VPC and VPC with lichen samples had the highest failure pressures.

Before Compression

After Compression

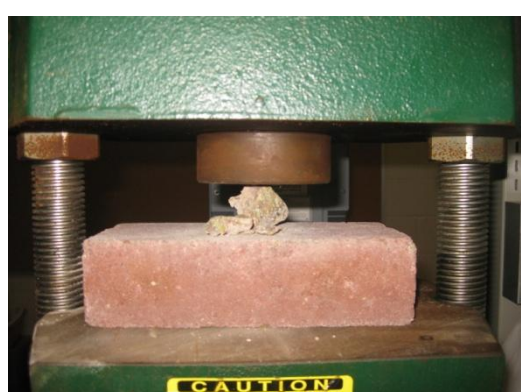
VPC



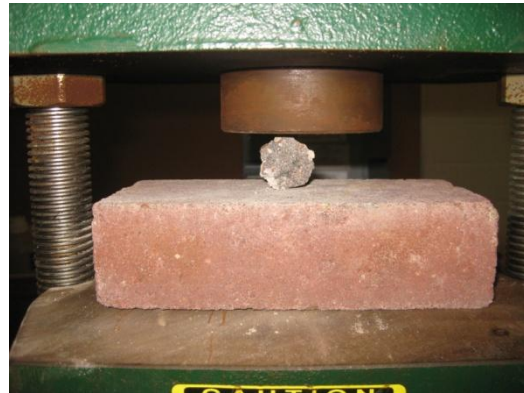
VPC w/ Lichen



Lichen on Fresh



Sooted Ceiling



Clay Coat



FRESH TUFF FREEZE-THAW TEST

Purpose:

The purpose of this experiment is to observe the effects of water and temperature on the cohesiveness of the fresh tuff in order to determine if water and temperature action are reasonable sources of degradation of the cavates.

Hypothesis:

We predict that the combination of wetting and then freezing and thawing will cause severe damage to the tuff in the forms of cracks and loss of cohesion, leading to the eventual total disintegration of the rock.

Procedure:

We selected two samples of fresh tuff, M136-035 and M136-037. We then immersed M136-035 in distilled and deionized water, xxH_2O , and it immediately broke into smaller pieces, one of which was large enough to continue testing. Rather than immerse M136-037 in xxH_2O for a period of time, we quickly submersed it in the water and immediately removed it. We then placed the samples on glass dishes in a freezer for approximately 12-24 hours. Once we removed them from the freezer, the samples were allowed to thaw and come to room temperature (approx. 8 hours). We repeated this process for a total of six cycles.

Observations:

During the first cycle, both samples lost material due to immersion in the water. After removal from the freezer, neither sample showed significant cracks or other signs of damage, other than loose material on the glass dishes. M136-035 crumbled after thawing and prior to immersion in xxH_2O for cycle two. We were able to successfully immerse M136-037 in xxH_2O and continue testing. For every cycle, the sample lost material upon dunking, but no other significant signs of damage were observed. Finally, after thawing and prior to immersion for cycle seven, M136-037 disintegrated when it was picked up.

Conclusion:

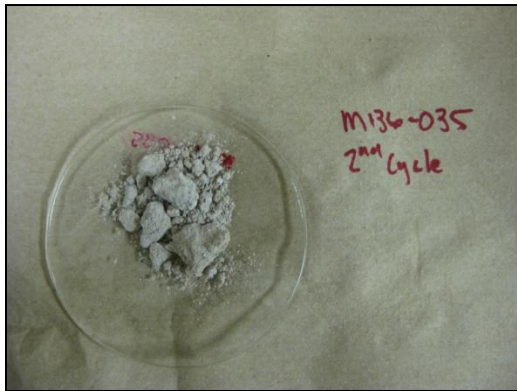
From the information we gathered from this experiment, we believe that water and temperature action are not a leading cause of deterioration of the cavates. Though we found that these factors did have a severe weathering effect, the disintegration of our tuff samples was much too rapid and indicated that these processes could not be happening to the cavates, otherwise total deterioration would already have occurred. We would like to mention, however, that there seems to be a difference in cohesion between our hand samples of fresh tuff and the tuff into which the cavates are carved. Our hand samples were extremely fragile and the smallest motion or pressure could cause them to crumble. The walls of the cavates and cliff faces, though friable and only slightly welded, were not so significantly affected by touch.



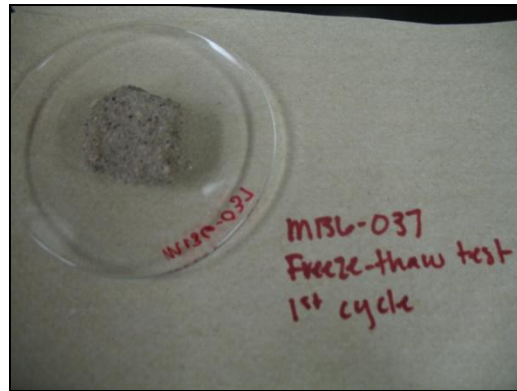
Sample M136-035 after immersion in xxH_2O for the first cycle.



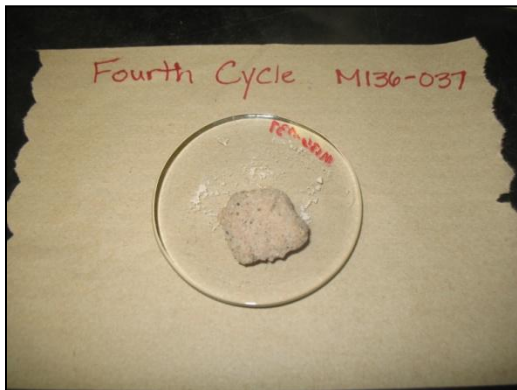
Material lost from sample M136-035 during immersion in xxH_2O for the first cycle.



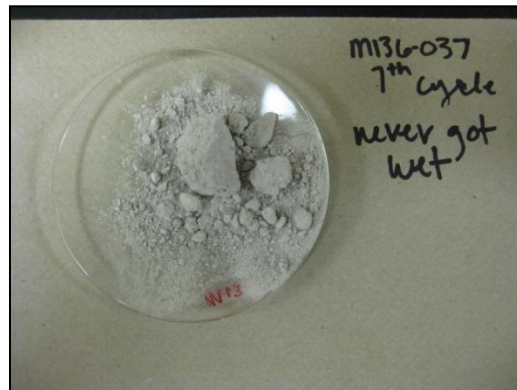
Sample M136-035 prior to immersion in xxH_2O for cycle two. The sample crumbled when we attempted to lift it from the dish.



Sample M136-037 after immersion in xxH_2O for the first cycle.



Sample M136-037 prior to immersion for cycle four. This is approximately half way through the experiment and no significant signs of deterioration were observed.



Sample M136-037 prior to immersion in xxH_2O for cycle seven. The sample crumbled when we attempted to lift it from the dish.

THE POROSITY OF THE BANDELIER TUFF

Introduction

The porosity of the Tshirege member of the Bandelier Tuff is highly variable depending on the composition and texture of the tuff. To observe the porosity of the tuff thin sections were taken from these samples of tuff; the samples included

- Vapor Phase Crystallization
- Hybrid of Vapor Phase Crystallization with lichen

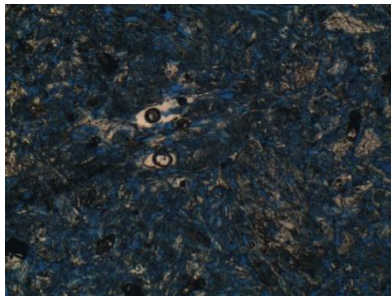
- Lichen covered tuff
- Fire sooted covered tuff
- Unaltered fresh tuff

The Tshirege member tuff contains volcanic glass, quartz, sanidine, clinopyroxene, and small mineral inclusions, as well as large porous pumices and mildly compacted volcanic glass. Parts of the Tshirege member also are extremely variable in texture which affects the amount of porous space in the tuff.

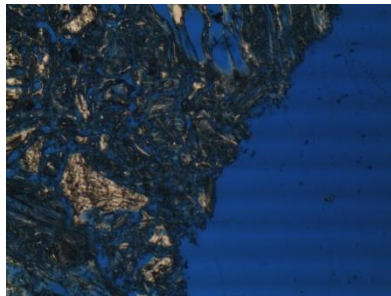
Unaltered tuff

The sample of unaltered tuff has little to no variation in porosity from surface to interior. The porosity of the unaltered tuff resembles the interior of all the other samples observed. The unaltered tuff has extremely high porosity in the pumice pieces found in thin section. All the pumices observed in this sample were unaltered.

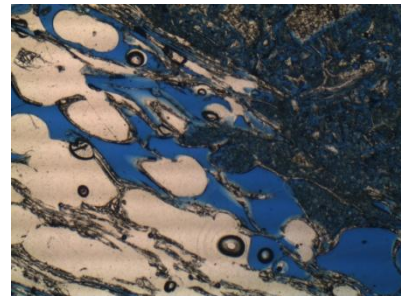
Interior



Surface



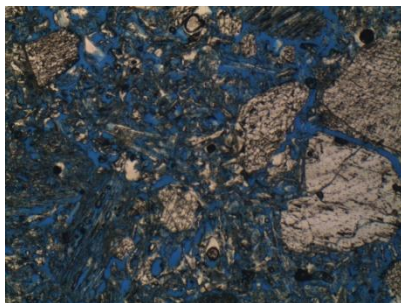
Pumice



Lichen covered surface

The sample of the Lichen covered surface also has small variation in porosity between the surface and interior. The surface is slightly less porous than the interior. The pumice in this sample varies in porosity. Some of the pumice in the rock had the "Smashed" appended where as others had more open pore spaces. The porosity observed in this sample strongly resembled unaltered tuff.

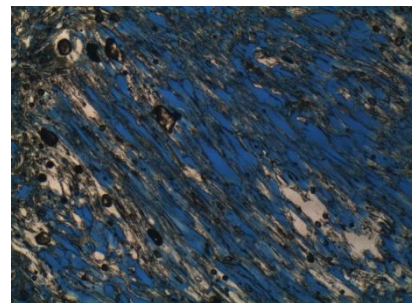
Interior



Surface



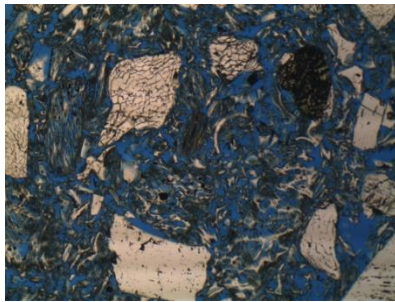
Pumice



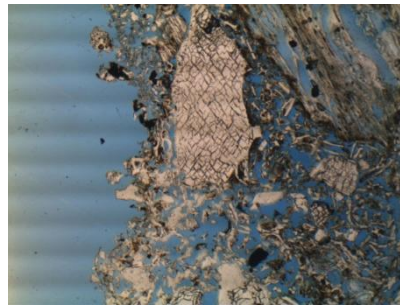
Fire Sooted Surface

The sample taken of the Fire Sooted surface has a consistent porosity from interior to surface. Once again the surface of the sample is slightly less porous than the interior. The pumices in this sample are highly porous, and with less of a “smashed” appearance. The porosity of the Sooted surface sample is closely related to the unaltered fresh samples of tuff. The only apparent difference between the two samples is the soot that coats the surface and fills in some of the pores of the sample.

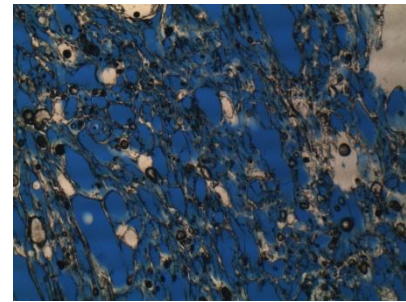
Interior



Surface



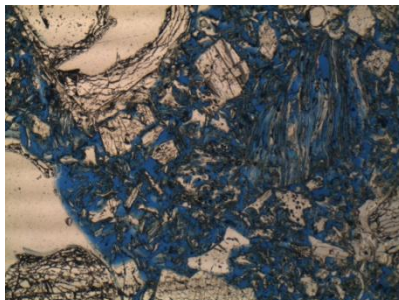
Pumice



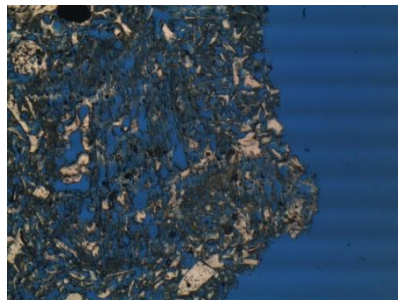
Vapor Phase Crystallization

The sample of Vapor Phase crystallization is less porous at the surface than at the interior and pumice. The surface of the sample had tightly compacted glass shards and microcrystals. The compacted surface of the tuff begins to spread out about 2mm from the surface. The interior or 3 mm depth is slightly more porous than the surface, consisting of less fractured minerals and glass. The pumices in this sample have the highest porosity of the whole composition of the rock. The pumices in most of the samples have big air pockets producing most of the porous space in the tuff. The pumice in the Vapor Phase Crystallization sample have a “smashed,” appearance, making less space in the pores of the pumice compared to other samples of pumices.

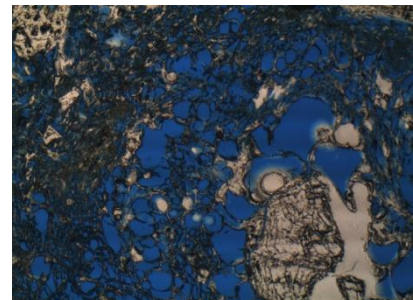
Interior



Surface



Pumice

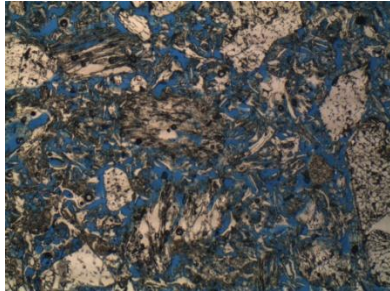


Vapor Phase Crystallization with Lichen

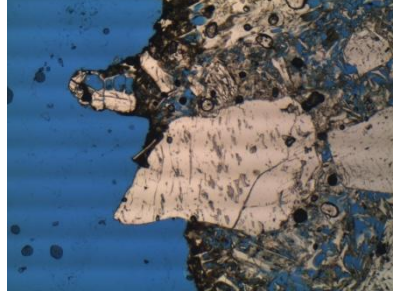
The sample of the hybrid between lichen covered surface and Vapor Phase Crystallization has mostly the same porosity as Vapor phase crystallization. The surface has tightly

compacted glass shards and microcrystals, although the surface has some traces of lichen that has filled in some pores of the sample. The compacted microcrystals and glass shards at the surface are also about 2-3 mm into the sample. The interior has slightly more spaced volcanic glass and minerals. The pumices in this sample are also the most porous part of the tuff.

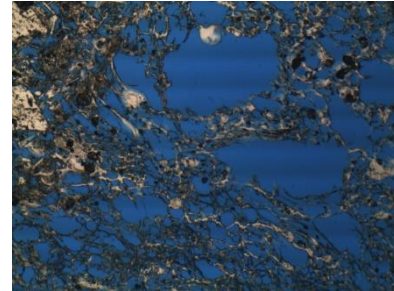
Interior



Surface



Pumice



Conclusion

The porosity of the Tshirege member of the Bandelier tuff is variable depending on the composition and texture of the tuff. Most of the samples revealed lower porosity at the surface vs. the interior and very high porosity in the pumice. The Vapor Phase Crystallization and Vapor Phase crystallization with lichen samples reveal less porous space at the surface compared to the samples of unaltered, fire sooted surface and Lichen covered surface. The interior of all the samples have little to no change in porosity. The pumice in all these samples varied, The Vapor Phase Crystallization and Vapor Phase crystallization with lichen have more of the “Smashed,” pumices where as the unaltered, fire sooted surface and Lichen covered surface had mostly the unaltered pumices.