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*Risk Reduction and Environmental  
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# 13391

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*Symbol:* RRES-GWPP:02-005  
*Date:* September 25, 2002

**SUBJECT: STRATIGRAPHY OF THE TUFFS FROM BOREHOLE 49-2-700-1 AT  
TECHNICAL AREA (TA) 49, LOS ALAMOS NATIONAL LABORATORY  
(LANL), NEW MEXICO**

Enclosed is a copy of the Stratigraphy of The Tuffs from Borehole 49-2-700-1 at TA 49,  
LANL, New Mexico. This report documents work completed under the Environmental  
Characterization and Remediation Group (ECR).

If you have any questions, please call Dave Broxton at the above phone number.

DB  
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Enclosure: Stratigraphy of the Tuffs from Borehole 49-2-700-1 at Technical Area 49,  
Los Alamos National Laboratory, New Mexico (ER2002-0482)

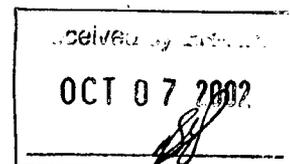
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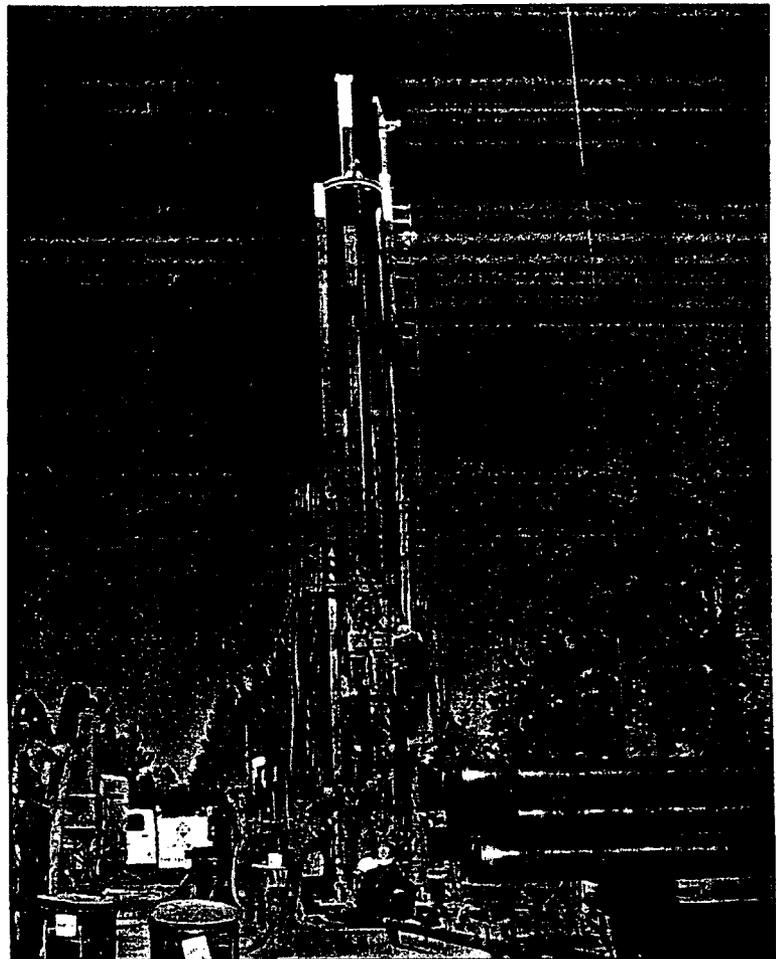
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*Stratigraphy of the Tuffs from  
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Technical Area 49,  
Los Alamos National Laboratory,  
New Mexico*



  
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*Stratigraphy of the Tuffs from Borehole 49-2-700-1 at  
Technical Area 49, Los Alamos National Laboratory,  
New Mexico*

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## Table of Contents

ABSTRACT .....	1
1.0 INTRODUCTION .....	2
2.0 METHODS.....	3
3.0 RESULTS AND DISCUSSION .....	5
3.1 Lithologies.....	5
3.2 Moisture Distribution .....	7
3.3 Fractures and Alteration.....	8
3.4 Chemistry.....	8
3.5 Mineralogy.....	8
4.0 ACKNOWLEDGEMENTS .....	12
5.0 REFERENCES.....	12

APPENDIX A. BULK-ROCK CHEMICAL COMPOSITIONS FOR BOREHOLE 49-2-700-1

APPENDIX B. INAA RESULTS FOR BOREHOLE 49-2-700-1

APPENDIX C. BULK-TUFF MINERALOGY FOR BOREHOLE 49-2-700-1

**STRATIGRAPHY OF TUFFS FROM BOREHOLE 49-2-700-1 AT TECHNICAL AREA 49,  
LOS ALAMOS NATIONAL LABORATORY, NEW MEXICO**

by

J.A. Stimac, D.E. Broxton, E.C. Kluk, S.J. Chipera, J.R. Budahn

**ABSTRACT**

This report presents the stratigraphy of tuffs encountered in borehole 49-2-700-1 located at TA-49. The primary methods of investigation included hand-sample observation (hand lens and binocular microscope), supplemented by limited scanning electron microscopy. Selected samples were analyzed by X-ray fluorescence (XRF) and instrumental neutron activation analyses (INAA) for major and trace element composition. Additional samples were analyzed by quantitative X-ray diffraction (QXRD) to determine mineralogy. This investigation provides necessary data to develop conceptual models for the hydrogeology of the site, evaluate potential transport pathways and processes, and provide a stratigraphic framework for numerical models evaluating migration of water and contaminants.

Geologic field observations in adjacent canyons helped verify the thickness and character of the stratigraphic units in the upper portion of the borehole. The exposed bedrock stratigraphic sequence in Water Canyon is restricted to units of the Tshirege Member of the Bandelier Tuff. The Tshirege Member is a multiple-flow, ash-flow sheet that forms a series of step-like vertical cliffs and sloping ledges along canyon walls. Canyon exposures immediately north of the borehole consist of, in ascending order, Qbt 1g, Qbt 1v, Qbt 2, Qbt 3, and Qbt 4 of the Tshirege Member.

Because the borehole extended beneath the level of adjacent canyon floors, a number of unexposed units were encountered, including, in descending order, the Tsankawi Pumice Bed, tephra and volcanoclastic sediments of the Cerro Toledo interval, and the Otowi Member of the Bandelier Tuff. The borehole bottomed in the upper part of Otowi Member.

The Otowi Member and units Qbt 1g through Qbt 3 of the Tshirege Member are high-silica rhyolites (77% SiO<sub>2</sub>, on a volatile-free basis). Qbt 4 of the Tshirege Member is significantly less silicic (74% SiO<sub>2</sub>) than underlying tuffs. Major element abundances for these units show relatively little variability (except for Qbt 4), but both the Otowi and Tshirege Members are compositionally zoned with respect to their trace elements.

The pre-eruptive phenocryst assemblage of both the Tshirege and Otowi Members is dominated by alkali feldspar and quartz. The post-eruptive mineralogy is dominated by volcanic glass in the Otowi Member, in the Cerro Toledo interval, and in Qbt 1g of the Tshirege Member. Units Qbt 1v, Qbt 2, Qbt 3, and Qbt 4 of the Tshirege Member are devitrified and vapor-phase altered, and their post-eruptive mineralogy is dominated by feldspar + quartz ± cristobalite ± tridymite ± smectite ± hematite.

Examination of moisture contents suggests some lithologic control. The most prominent features of the moisture data are abrupt increases in moisture content at the transition from glassy (Qbt 1g) to devitrified (Qbt 1v) Tshirege Member and at the Tsankawi Pumice Bed.

## 1.0 INTRODUCTION

This investigation describes the stratigraphy, lithology, mineralogy, and chemistry of the tuffs that underlie TA-49, based on detailed logging of core from borehole 49-2-700-1. TA-49 is located in the south-central portion of Los Alamos National Laboratory (LANL), north of State Highway 4 (Figure 1). This study was part of work that the Environmental Restoration (ER) Project performed at TA-49.

Drilling of borehole 49-2-700-1 began on November 17, 1993, and was completed January 25, 1994. The borehole was drilled by air-rotary methods and achieved its target depth of 700 ft. Continuous core was collected using a 3.25-in. diameter rock barrel from 0-50 ft and a 2.4-in. diameter rock barrel from 50-700 ft. ODEX casing (10-in. inner diameter [ID]) was set in the hole from 0-50 ft and grouted. From 10-700 ft, ODEX casing telescopes to 8-in. ID. The core was stored at the ER Sample Management Facility.

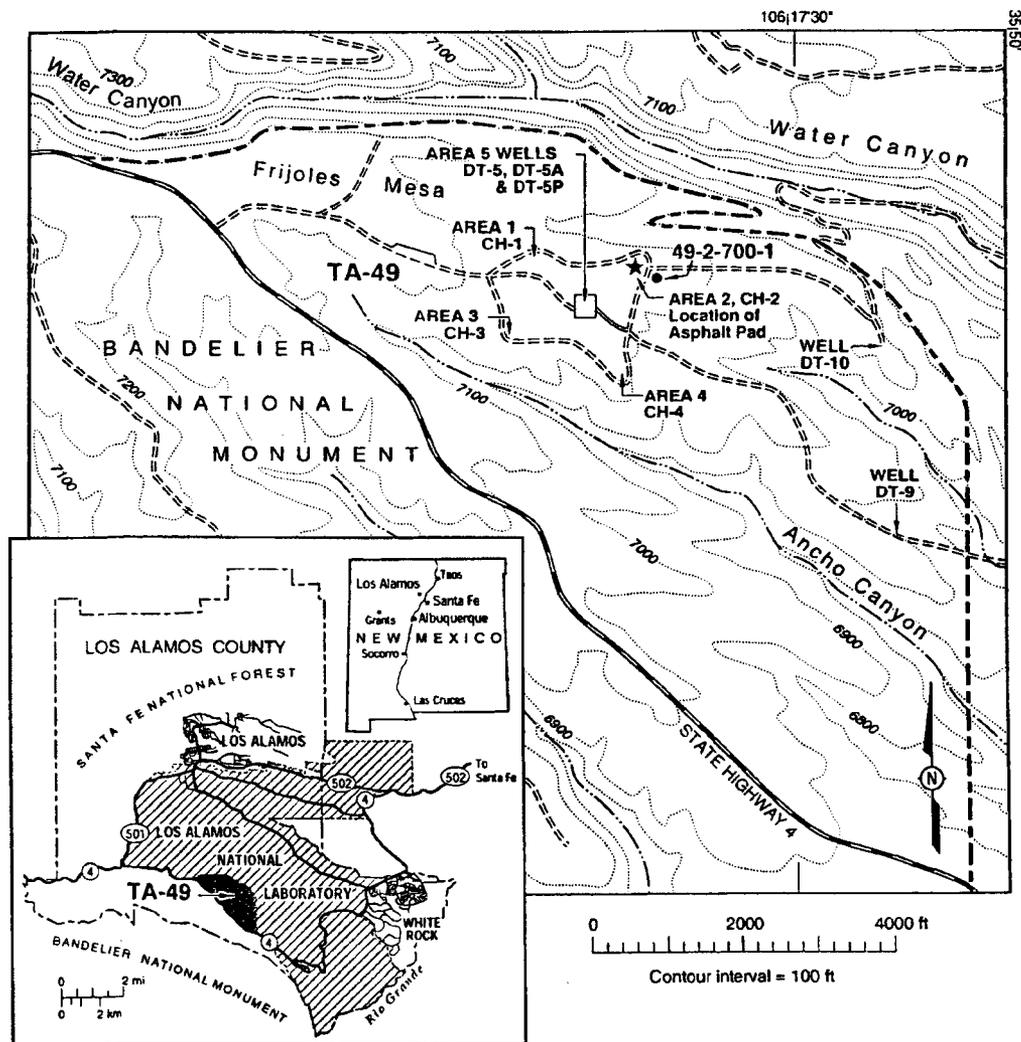


Figure 1. Map of the TA-49 area showing the location of borehole 49-2-700-1

This report provides geological data to develop and test hydrogeological conceptual models for the site and to evaluate potential transport pathways and processes. The data constrain numerical models for groundwater flow and contaminant transport, and they provide a geological framework for evaluating various types of remediation that could be applied at the site. Furthermore, this study delineates lithologic changes that may control the movement of moisture and contaminants.

The general stratigraphy of the Pajarito Plateau has been described by numerous authors (Griggs 1964; Smith and Bailey 1966; Broxton et al. 1995a; Broxton and Reneau 1995; and Goff 1995). Weir and Purtymun (1962) describe local geologic and hydrologic investigations conducted at TA-49 on Frijoles Mesa from 1959 to 1960. The purpose of the Weir and Purtymun investigation was to provide geologic information about the TA-49 site and to define the direction and rate of groundwater movement. Weir and Purtymun divided the Tshirege Member into six lithologic subunits as part of mapping and borehole studies. They determined the distribution of subsurface lithologic units by correlating lithologic and geophysical logs for borehole DT-5P, test wells DT-5, DT-5A, DT-9, and DT-10, and core holes CH-1, CH-2, CH-3, and CH-4 (Figure 1).

## **2.0 METHODS**

A detailed graphic log was prepared for borehole 49-2-700-1 at the ER Project's Field Support Facility. This log can be obtained from the authors or through the Project's Record Processing Facility. A summary of the major lithologies in the borehole was prepared from the detailed graphic log and is presented as Figure 2.

The graphic log includes descriptions of lithology, mineralogy, and abundances, sizes, and compositions of lithic fragments and pumice. Fractures and alteration patterns critical to assessing hydrologic flow paths are also described. Additional information recorded includes a summary of samples taken from the core and the state of core preservation.

Major and trace elements were analyzed in 64 samples using an automated Rigaku wavelength-dispersive X-ray fluorescence (XRF) spectrometer. Samples were prepared by crushing and homogenizing 15–20 g of the sample in a tungsten-carbide shatter box according to Yucca Mountain Project procedure LANL-EES-DP-130 (Geologic Sample Preparation). Sample splits were heated at 110°C for 24 hrs, and then 4-g splits were fused at 1100°C with 8 g of lithium metaborate/lithium tetraborate flux. Elemental concentrations were calculated by comparing X-ray intensities for the samples to those for 21 standards of known composition. A fundamental parameters program was used for matrix corrections (Criss 1980) in accordance with Yucca Mountain Project procedure LANL-EES-DP-111.

Splits of 39 XRF samples were sent to the US Geological Survey and analyzed for major and trace elements by instrumental neutron activation analysis (INAA). Baedeker and McKowen (1987) describe the INAA method and levels of precision and accuracy.

The mineralogy of the tuffs was determined by analyzing 63 samples using X-ray diffraction (XRD). Samples were first powdered in a tungsten-carbide shatter box and then mixed with an internal standard of 1  $\mu\text{m}$  metallurgical grade  $\text{Al}_2\text{O}_3$  (corundum) powder in a ratio of 80% sample to 20% internal standard by weight. The samples were then ground under acetone in an automatic Brinkmann-Retsch mill fitted with an agate mortar and pestle to produce an average particle size of less than 5  $\mu\text{m}$ . This fine particle size is necessary to ensure adequate particle statistics and to minimize primary extinction (Klug and Alexander, 1974). Particle-size distributions have been verified in our laboratory for similar samples using a Horiba CAPA-500 centrifugal particle-size distribution analyzer calibrated with Duke Scientific

glass microsphere standards. X-ray diffraction data were collected on a Siemens D-500 theta-theta diffractometer using copper-K $\alpha$  radiation, incident- and diffracted-beam Soller slits and a KeveX solid-state (SiLi) detector. Data were typically collected from 2.0 to 50.0° 2 $\theta$  using a 0.02° step size and at least two seconds per step.

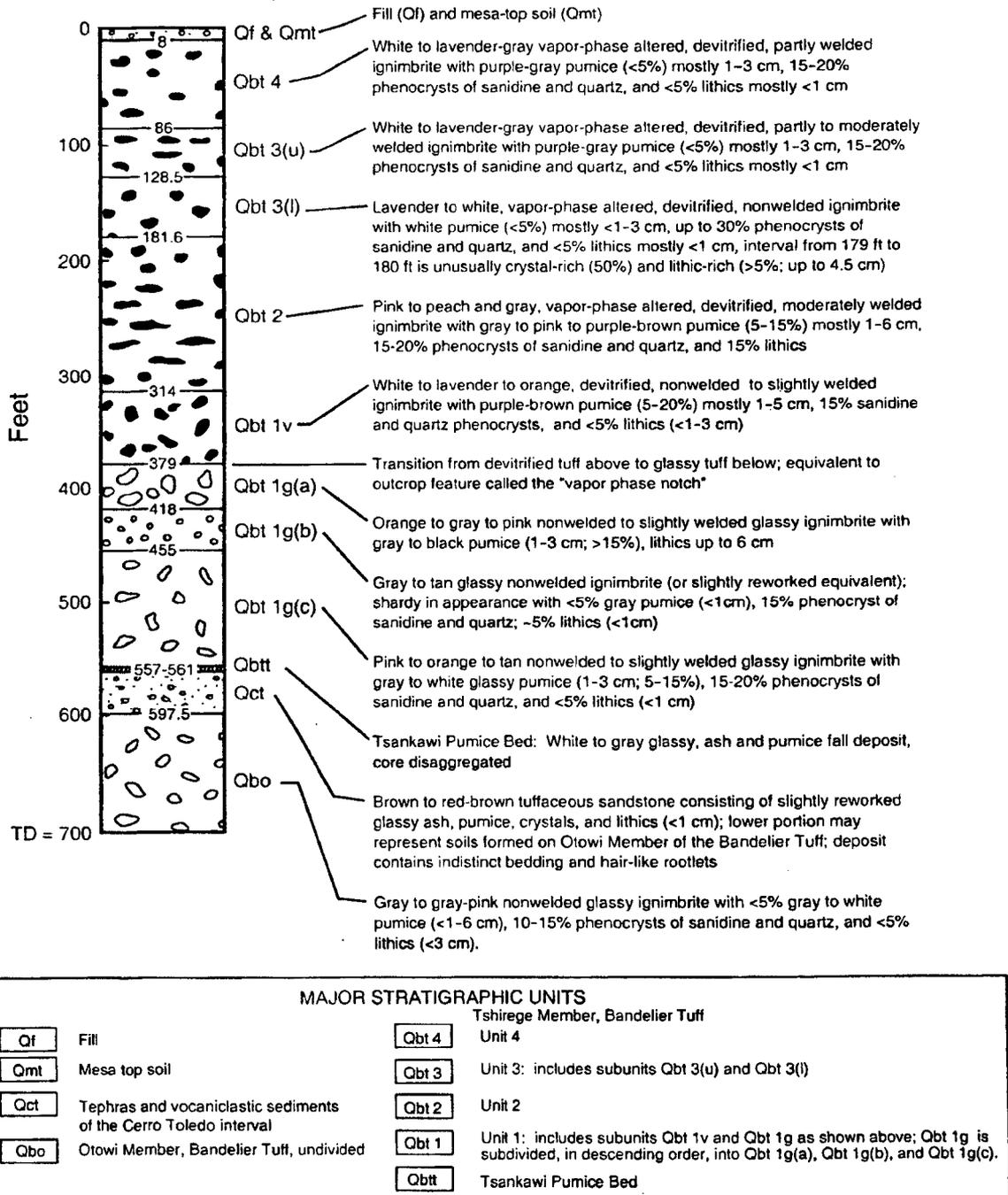


Figure 2. Summary of major lithologies in borehole 49-2-700-1

Quantitative mineral analyses employed the internal standard or matrix-flushing method of Chung (1974a,b). Details of this method can be found in Bish and Chipera (1988; 1989). In addition, the following Yucca Mountain Project procedures were used for sample preparation and analysis of XRD samples: LANL-EES-DP-130 (Geologic Sample Preparation); LANL-EES-DP-56 (Brinkmann Automated Grinder Procedure); LANL-EES-DP-16 (Siemens X-Ray Diffraction Procedure); and LANL-EES-DP-116 (Quantitative X-Ray Diffraction Data Reduction Procedure). Yucca Mountain Project quality assurance requirements are comparable in rigor to those used by the LANL ER Project.

Moisture contents were determined gravimetrically on 128 samples collected at a nominal spacing of 5 ft. Samples were sealed in plastic bags as soon as possible after being collected from the borehole to prevent moisture loss. Samples from 0–468 ft were analyzed at an on-site mobile radiological laboratory. These samples were transferred to a clean container in a moisture analyzer where they were automatically weighed, dried at 200°C until they reached a constant mass, and weighed again. The remaining samples were analyzed by a fixed-base laboratory at CST-3. These samples were weighed, heated overnight in an oven at 100°C, and weighed again. The moisture data from the on-site mobile radiological laboratory and the fixed-base laboratory appear to be comparable based on the measured moisture contents and moisture trends for the entire borehole.

### **3.0 RESULTS AND DISCUSSION**

#### **3.1 Lithologies**

Major lithologic units in the core are summarized in Figure 2, which uses the same symbol notation as the more detailed graphic log of Figure 1. The stratigraphic nomenclature follows the suggested usage of Broxton and Reneau (1995). Figure 3 compares the unit nomenclature used in this report with that used by Weir and Purtymun (1962), and it compares the stratigraphy of borehole 49-2-700-1 with nearby borehole DT-5P (see Figure 1 for location).

In descending order, the major units encountered in borehole 49-2-700-1 are as follows: (1) Qf (fill) and Qmt (mesa top soil); (2) units Qbt 4, Qbt 3, Qbt 2, Qbt 1v, Qbt 1g, and the Tsankawi Pumice Bed (Qbt) of the Tshirege Member of the Bandelier Tuff; (3) Qct, tephra and volcaniclastic sediments of the Cerro Toledo interval; and (4) Qbo, the Otowi Member of the Bandelier Tuff.

A few lithologic variations encountered in the core are open to interpretation, and ongoing study of core samples may require making minor modifications to the above unit designations. Of particular interest are variations in core designated as Qbt 1g of the Tshirege Member and Qct, the Cerro Toledo interval. In Figure 2 we divided Qbt 1g into three portions with distinctive features. Qbt 1g(a) is about 20 ft thick and similar to Qbt 1g at TA-21 (see Broxton et al. 1995a). It is nonwelded and grades in color from orange to gray; the pumices range in size mainly from 1–3 cm. Qbt 1g(b) is a distinctive facies consisting of about 37 ft of gray to tan, very fine-grained tephra and crystals; pumices are generally less than 1 cm. Qbt 1g(c) is similar to Qbt 1g(a) but with a slightly smaller average pumice size. It is likely that Qbt 1g(b) is a distinct facies that is not described elsewhere in the literature on the Bandelier Tuff. The origin of the fine-grained facies is not known at this time. Qct is mostly red-brown, fine-grained vitric tephra and crystals, which we currently interpret as a sequence of bedded tuffs, reworked tuffaceous sediments, and immature soils formed on a paleosurface incised into the top of the Otowi Member.

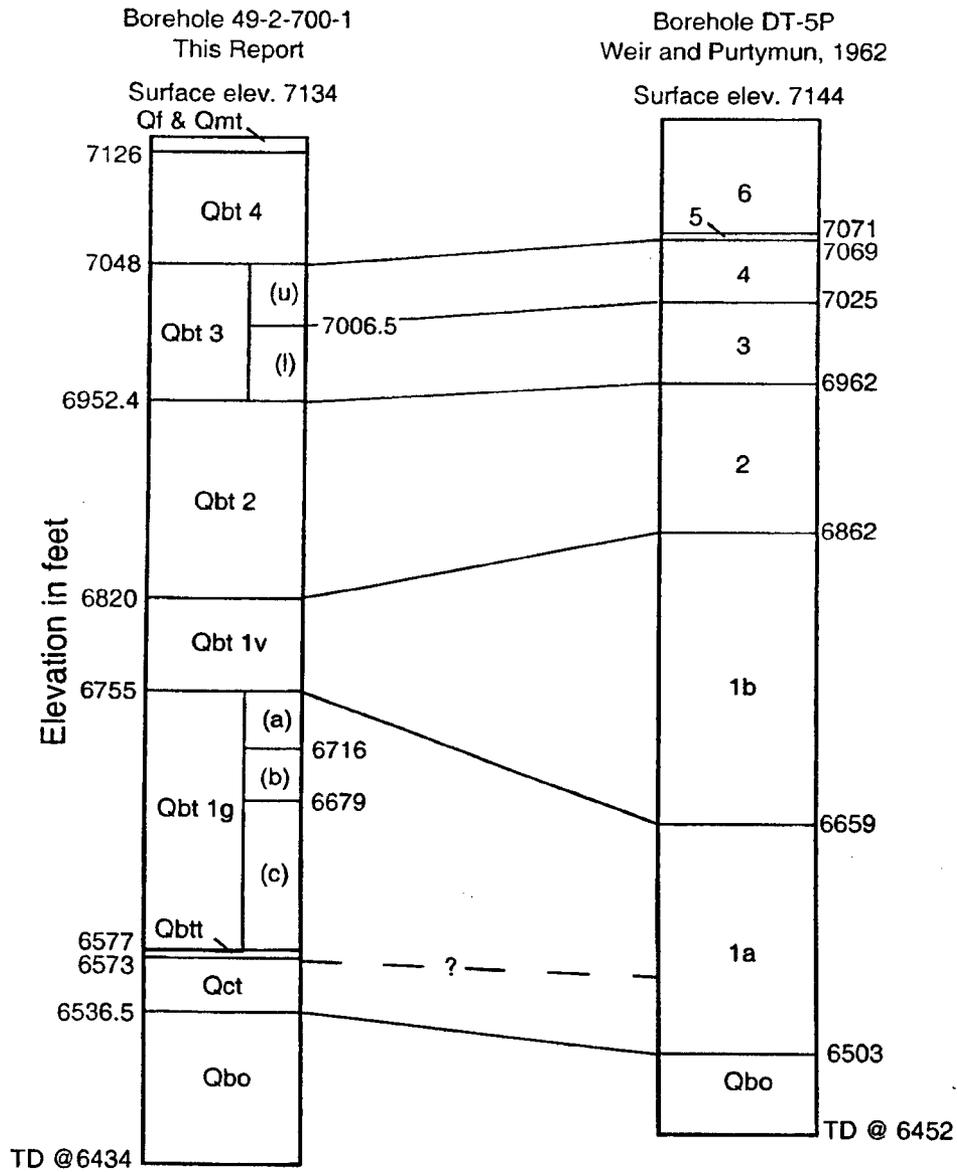


Figure 3. Correlation of stratigraphic units in borehole 49-2-700-1 with those described by Weir and Purtymun (1962) in nearby borehole DT-SP (unit correlations based on descriptions by Weir and Purtymun)

### 3.2 Moisture Distribution

Examination of moisture variations with depth in borehole 49-2-700-1 suggests some lithologic control. Gravimetric moisture contents are relatively high (11%) in fill material and soil (Qf and Qmf) near the surface, but they decrease abruptly to 1–4% in the upper tuff units of the Tshirege Member (Figure 4). Moisture contents are relatively constant in units Qbt 4, Qbt 3, Qbt 2, and the upper part of Qbt 1v, but they systematically increase in the central and lower part of Qbt 1v, culminating in a prominent moisture spike of 15% at the Qbt 1v/Qbt 1g contact (equivalent to the vapor phase notch in surface exposures). A similar moisture spike occurs at the Qbt 1v/Qbt 1g contact in borehole LADP-4 at TA-21 (Broxton et al. 1995b) and may represent a zone of preferential groundwater accumulation.

Below the moisture spike associated with the Qbt 1v/Qbt 1g contact, moisture contents generally range between 8–10% in subunits of Qbt 1g (Figure 4). Another prominent moisture spike begins in the lower part of Qbt 1g(c) and reaches a maximum of 16.5% in the Tsankawi Pumice Bed. This pattern of moisture distribution was also found in borehole LADP-4 (Broxton et al. 1995b). Below the Tsankawi Pumice Bed, moisture contents are somewhat erratic but typically range from 10–11%. The top of the main aquifer was not penetrated in borehole 49-2-700-1, but it is expected to be about 1163 ft deep based on nearby borehole DT-5A (Weir and Purtymun 1962).

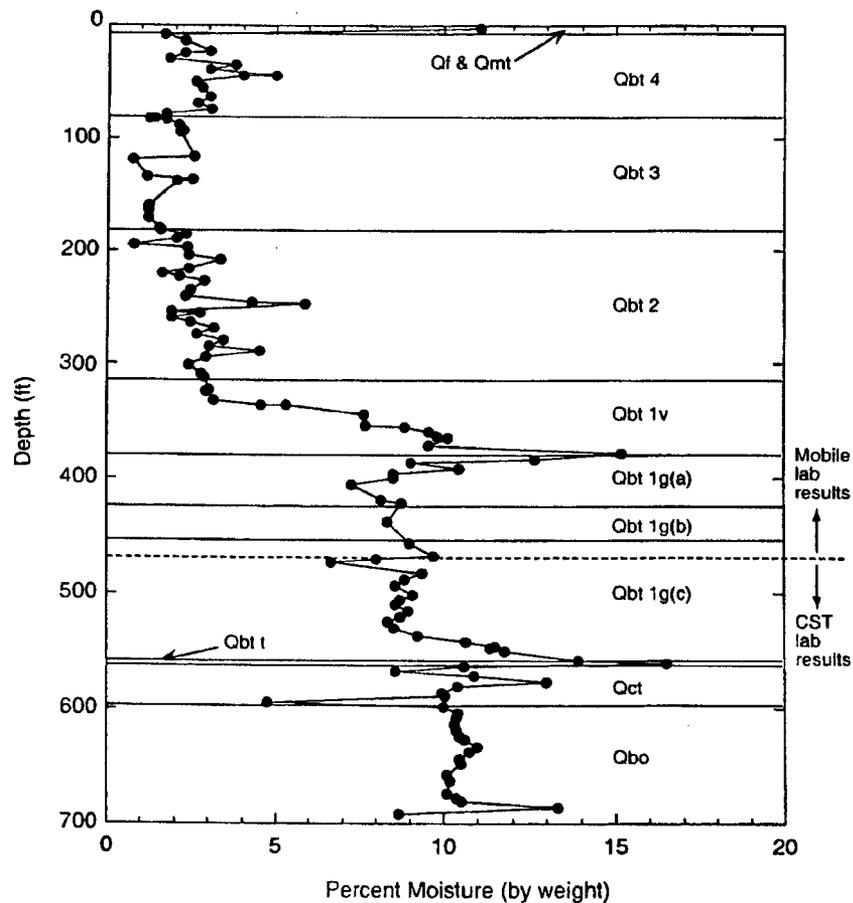


Figure 4. Comparison of moisture content with stratigraphic units of borehole 49-2-700-1

### **3.3 Fractures and Alteration**

Only a few fractures were documented in the core, some of which lacked mineral coatings and may have been caused by drilling and sampling (e.g., fractures at 90 ft and 283 ft). A few irregular fractures with orange colored (limonitic?) staining are present in the first 35 ft of the core, and may influence hydrologic flow near the surface. At depths of >35 ft, only one region of the core, from 243 to 255 ft, showed four subvertical fractures with mineral coatings. The coatings consist primarily of smooth, orange-colored material 1–5 mm thick, which has tentatively been identified as a mixture of very fine-grained clays and Fe-oxides. Scanning electron microscopy indicates that the coatings consist primarily of Si, Al, and variable Fe, with lesser amounts of K and Ca, consistent with the tentatively identified mineralogy.

### **3.4 Chemistry**

Bulk-rock chemical compositions for tuffs in borehole 49-2-700-1 by XRF are given in Appendix A, and INAA results are given in Appendix B. The Otowi Member and units Qbt 1g through Qbt 3 of the Tshirege Member are high-silica rhyolites (77% SiO<sub>2</sub>, on a volatile-free basis), whereas Qbt 4 of the Tshirege Member is significantly less silicic (74% SiO<sub>2</sub>). Major element abundances for these units show relatively little variability (except for Qbt 4), but both the Otowi and Tshirege Members are compositionally zoned with respect to their trace elements (Figure 5). Petrologic studies of the Bandelier Tuff have shown that these compositional zonations reflect the systematic withdrawal of magma from a chemically zoned magma chamber (Smith 1979). Compositional gaps occur at some unit boundaries, and they probably represent gaps in the depositional record of the Tshirege Member in this area. These gaps may represent the nondeposition of some tuffs at TA-49 because the runout of some ignimbrites from their source in the Valles caldera was limited to the western part of the Pajarito Plateau. Additionally, some ignimbrites from the Valles caldera may have flowed in directions other than towards the Pajarito Plateau.

The chemical data presented in Appendix A were combined with data from other sites across the Pajarito Plateau to establish whole-rock background elemental concentrations for the Bandelier Tuff. These background values were published as part of a separate report that summarizes a LANL-wide study to establish background levels for the ER Project (Ryti et al. 1998). It should be noted that the data presented in Appendix A are total elemental concentrations (as opposed to acid extractable concentrations), and their use for background concentrations is valid only if the analytical data being compared are also total elemental concentrations. The chemical data for the Bandelier Tuff show that its background chemistry varies as a function of stratigraphic position, particularly for trace elements (Figure 5).

The chemical data are also useful for establishing stratigraphic correlations of tuff units across the Pajarito Plateau. In drill holes, compositional gaps provide a means for recognizing unit boundaries (Figure 5). For example, Qbt 4 was not recognized during logging of the drill core for this borehole until the chemical data became available. Using chemical data in conjunction with the core logs increased the accuracy of our unit identifications. Correct placement of unit boundaries is critical for interpreting subsurface data and for selecting instrument locations in monitoring wells that target specific horizons.

### **3.5 Mineralogy**

The pre-eruptive phenocryst assemblage of both the Tshirege and Otowi Members is dominated by alkali feldspar and quartz (generally from 10–25 vol %), with lesser amounts (<2 vol %) of Fe-rich pyroxene, Fe-Ti oxides, and fayalite, but they also contain other minerals at trace abundances (Warshaw and Smith 1988; Stimac 1996). Broxton et al. (1995a) provide more detailed information on the general modal petrography of the Bandelier Tuff and associated units.

Stratigraphy of Tuffs from Borehole 49-2-700-1 at TA-49

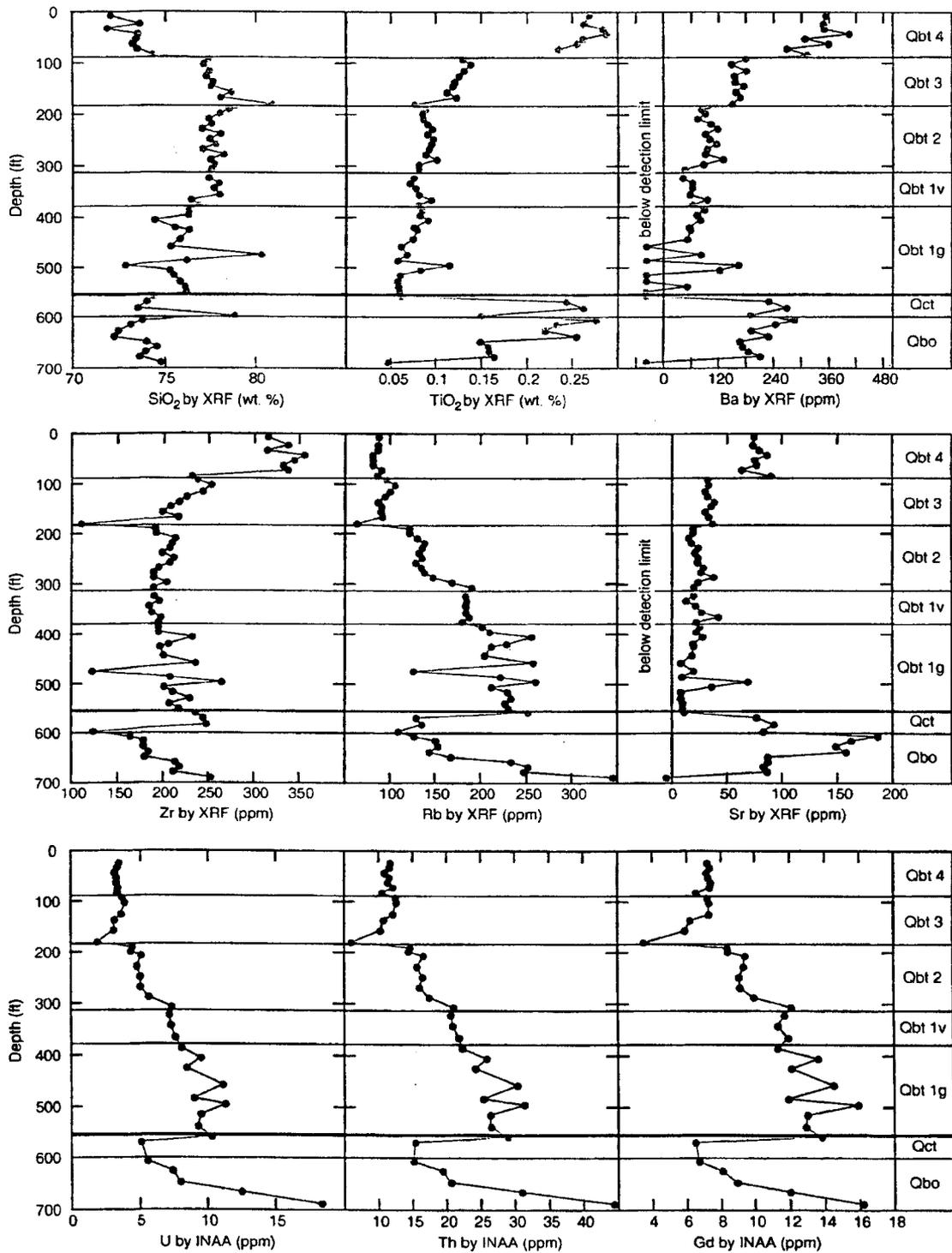


Figure 5. Comparison of chemical data with preliminary stratigraphic units of borehole 49-2-700-1

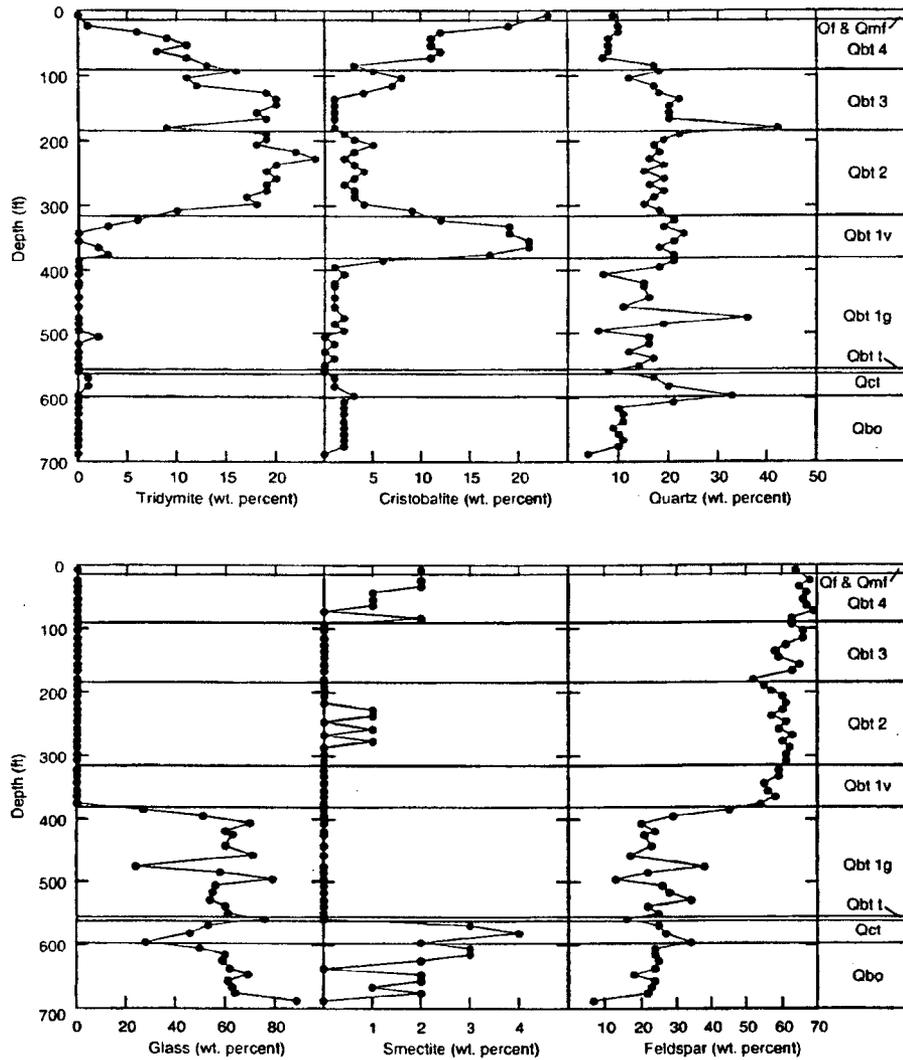
The bulk-tuff mineralogy of tuffs at TA-49 is relatively simple, consisting primarily of alkali feldspar + quartz ± cristobalite ± volcanic glass ± tridymite (Appendix C). These four minerals and the volcanic glass make up over 95% of nearly all tuff samples, although their relative proportions vary as a function of stratigraphic position (Figure 6). Minor constituents of the tuffs include smectite and hematite. Trace amounts of mica, hornblende, clinoptilolite, and kaolinite were also detected in a few of the samples.

Alkali feldspar and silica minerals have relatively poor ion-exchange properties and probably provide little in the way of natural mineralogic barriers to contaminant migration. On the other hand, the surfaces of these minerals have high affinities ( $K_d$ s >1000 ml/g) for elements such as Am, Cm, Nb, REE, Sn, Th, Zr, and Pu (Allard et al. 1982; Beall and Allard 1981; Thomas 1987; Brandberg and Skagius 1991; Meijer 1992), and they may provide retardation by surface complexation.

Smectite, hematite, and Mn oxide are potentially important trace minerals because they are sorptive of certain radionuclides and could provide important natural barriers to their migration. Smectites are highly selective for cationic radionuclides (Grim 1968). Magnetite and its alteration products such as hematite have an affinity for uranium and actinide species through surface complexation (Hsi and Langmuir 1985; Ho and Miller 1986; Allard and Beall 1979; Beall and Allard 1981; and Allard et al. 1982). Mn oxides intergrown with clay minerals have an affinity for Pu, Ce, Ga, Nb, Pb, Y, Ca, Ti, and Zn (Duff et al. 2001). The clay-Mn oxide trace mineral assemblage has been identified in the Bandelier Tuff (both in the tuff matrix and as a fracture-filling material) and in overlying soils (Vaniman et al. 2002). Although the trace minerals described above occur in small quantities, they are disseminated throughout the stratigraphic sequence and may provide significant retardation potential over long groundwater flow paths.

Volcanic glass is the dominant mineralogic component of tuffs in Qbo, Qct, and Qbt 1g (Figure 6). The glass occurs as pumices, shardy tuff matrix, and fine ash. The presence of abundant glass and paucity of low-temperature alteration minerals such as smectites and zeolites indicate that the tuffs of Qbt 1g have had limited contact with groundwater since their deposition. Smectite is slightly more abundant (1 to 4% by weight) at the top of Qbo and in Qct (Figure 6), suggesting that a greater degree of low-temperature diagenetic alteration or soil clay development (possibly eolian) occurred in these units. The alteration in these tuffs and sediments may reflect incipient soil development resulting from a long period (~400,000 y) of surface exposure and weathering. The smectites abruptly disappear in Obtt, above Qct, suggesting that these clays formed prior to the deposition of the Tshirege Member.

Alkali feldspar, cristobalite, quartz, and tridymite are the main constituents of tuffs above the Qbt 1g/Qbt 1v contact (Figure 6). Alkali feldspar and cristobalite occur mainly in the tuff matrix as fine-grained (micron-size), high-temperature devitrification products that replaced the original volcanic glass as the tuff cooled. The tridymite and some alkali feldspar were deposited in open pore spaces by vapors released during outgassing of the tuff after emplacement. The stratigraphic association of tridymite and cristobalite with units Qbt 1v through Qbt 4 is similar to that reported for surface outcrops in Los Alamos Canyon (Broxton et al. 1995a). Tridymite is most abundant in Qbt 2 and Qbt 3, whereas cristobalite is most abundant in Qbt 1v and Qbt 4 (Fig. 6). Cristobalite and tridymite abundances vary inversely, suggesting that the occurrence of these minerals is controlled by a thermal or thermal-kinetic transition.



**Figure 6. Comparison of mineralogical data with preliminary stratigraphic units of borehole 49-2-700-1**

Tridymite is an indicator mineral for vapor-phase alteration, and its abundance in Qbt 2 and Qbt 3 suggests that post-emplacement vapor phase crystallization was greater in these tuffs relative to Qbt 1v and Qbt 4. The repetition of this alteration pattern over regional distances suggests that the eruptive hiatuses between units of the Tshirege Member were relatively brief, allowing the entire assemblage of units to devitrify together in a single stage. However, significant differences in degree of welding for adjacent units (e.g., Qbt 2 and Qbt 3[1]) indicate that eruptive hiatuses were of sufficient duration for distinct cooling breaks to develop.

Most of the alkali feldspar and quartz detected by XRD in the vitric tuffs of Qbo and Qbt 1g is coarse-grained (1–3 mm) phenocrysts that grew in the magma chamber prior to eruption (Broxton et al. 1995a). In Qbt 1v and higher units, the abrupt increase in alkali feldspar abundances over Qbt 1g and lower units reflects devitrification and vapor-phase crystallization (Figure 6). Quartz abundances are little affected by

the transition from vitric to devitrified tuffs in the Tshirege Member, suggesting that most or all of the quartz occurs as phenocrysts. The slight increase in quartz upsection through the Tshirege Member probably reflects the tendency for the unit to become more phenocryst-rich upsection (Broxton et al. 1995a). The abrupt decrease of quartz in Qbt 4 represents a fundamental change in the phenocryst assemblage of these uppermost tuffs, including a significant decrease in the quartz-to-alkali feldspar ratios (Figure 6).

Minor smectite and hematite occur in the devitrified tuffs of the Tshirege Member (Figure 6). Smectite is slightly more abundant at the top of Qbt 4 and may reflect post-Bandelier soil development. Although low in abundance, both minerals are widely disseminated through the tuffs and may inhibit the migration of radionuclides.

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