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**Detailed Mineralogical Characterization  
of the Bullfrog and Tram  
Members in USW-G1, with Emphasis  
on Clay Mineralogy**

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DETAILED MINERALOGICAL CHARACTERIZATION OF THE BULLFROG AND TRAM MEMBERS  
IN USW-G1, WITH EMPHASIS ON CLAY MINERALOGY

by

David L. Bish

ABSTRACT

The detailed mineralogy of the Bullfrog and Tram Members of the Crater Flat Tuff from drill hole USW-G1 has been examined, primarily to characterize fully the amounts and types of clay minerals in the tuffs and the possible effects clay minerals have on rock properties. Results of bulk sample x-ray diffraction analyses agree closely with previous determinations, although slightly higher clay mineral contents were found in this study. X-ray diffraction analysis of fine fractions revealed that the clay minerals in the tuffs are sodium-saturated montmorillonite-beidellites with typical layer charges and no high-charge layers. These smectites are found in virtually all samples of the Bullfrog and Tram, and there is no correlation between the amounts of smectites and the amounts of zeolite, quartz, and feldspar. Smectites are present in both welded and nonwelded horizons and are scarce in some zones with slight-to-absent welding. The montmorillonite-beidellites are all randomly interstratified with a small amount (about 10%) of illite, and there is no consistent trend in the degree of interstratification with depth, contrary to what is commonly found in pelitic sediments. This observation, together with the lack of smectites in some zeolitized zones, suggests that clay mineral formation occurred after zeolite crystallization and under conditions similar to those in the rocks today (35-45°C). It is also likely that the ground water in the tuffs has inhibited the smectite-to-illite reaction.

The montmorillonite-beidellites exist in a 12.6 Å form under room conditions, and their basal spacings can range from 10 Å at 0% relative humidity or slightly elevated temperatures to approximately 20 Å in a 100% relative humidity atmosphere. Further increases in water:clay ratio cause additional expansion. In view of the possible significant variations in montmorillonite-beidellite molar volume and water content with small changes in temperature and relative humidity, it is important that we understand the present conditions existing in the rocks and appreciate the changes

in rock and mineral properties expected when altering these conditions, either in a repository or in a laboratory test.

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## I. INTRODUCTION

The tuffs of the Nevada Test Site (NTS) region have been and are currently under investigation as repository media for high-level radioactive waste. Under these studies, a detailed exploration program began in 1979 at Yucca Mountain, and several exploration holes were drilled. Data from the drill holes UE25a-1 and USW-G1, including geophysical, stratigraphic, structural, and petrographic information, are reported by Sykes et al. (1979), Spengler et al. (1979, in preparation), Bish et al. (1981), and Carroll et al. (1981). Bish et al. (1981) concluded that four horizons in the USW-G1 hole have favorable characteristics for a waste repository: the lower cooling unit of the Topopah Spring Member of the Paintbrush Tuff; the lower cooling unit of the Bullfrog Member of the Crater Flat Tuff; the Tram Member of the Crater Flat Tuff (Spengler et al. in preparation); and the Lithic-rich tuff (Spengler et al. in preparation). The latter unit has been tightly sealed by recrystallization during burial metamorphism, and the three other units contain thick densely welded and zeolite-free horizons.

Carroll et al. (1981) focused on the details of the Topopah Spring Member of the Paintbrush Tuff and the Lithic-rich tuff and included a discussion of the clay mineralogy in the Topopah. They found that interstratified montmorillonite/illites were ubiquitous throughout the Topopah in hole UE25a-1, occurring in both welded and nonwelded horizons in amounts ranging from several per cent to approximately 20%. There was little variation in the degree of interstratification, and all of the clays examined were at least 80% smectitic (swelling). Optical petrographic examination demonstrated that the clays occurred in the groundmass and were concentrated along shard boundaries and pumice tube walls. Bish et al. (1981) reported the detailed petrography and mineralogy of the USW-G1 core, but they presented only a preliminary discussion of the clay mineralogy. Selected samples from the Bullfrog and Tram Members contained dioctahedral smectites randomly interstratified with less than 20% illite.

Because the data presented by Bish et al. (1981) concerning the clay mineralogy of the Bullfrog and Tram Members were of a preliminary nature, it is the purpose of this report to describe the clay mineralogy in detail and to briefly discuss the possible effects of clays on rock properties. Although clay minerals are commonly present in low concentrations within the tuffs at Yucca Mountain, they are ubiquitous and can profoundly affect element sorption, rock strength, and the porosity and permeability of tuff. Erdal et al. (1980) and Smyth et al. (1980) emphasize that it is possible for a minor phase to completely dominate the sorption properties of a rock, and the results of Smyth et al. (1980) suggest that clay minerals control sorption in granites. The numerous papers in Longstaffe (1981) demonstrate the very important effect clay minerals, especially swelling clays, have on rock porosity and permeability. Minor changes in temperature and ground-water chemistry can dramatically lower the porosity and permeability. Finally, as a result of the swelling nature of smectites, small changes in temperature, pressure, and humidity can release water and lead to major volume changes. Because the clay minerals in the tuffs can have such a substantial effect on the chemical and mechanical behavior of the rocks, it is essential to examine the mineralogy in detail and to elucidate the effects of temperature and humidity on the clay minerals. For the present work, most samples examined in Bish et al. (1981) have been studied, and an additional suite of samples has been collected and examined. Because large samples were used in the clay mineral separations, x-ray diffraction patterns of homogeneous bulk samples were obtained routinely before performing the clay mineral separations.

## II. STRATIGRAPHY

The stratigraphy of the Bullfrog and Tram Members in USW-G1 has been described in detail by Spengler et al. (in preparation) and Bish et al. (1981), and only a brief description of these units will be presented here. The stratigraphic position of the Bullfrog and Tram Members in USW-G1 is shown in Fig. 1. The Bullfrog Member of the Crater Flat Tuff is approximately 144 m thick and is composed of two major units, an upper unit (BF-I) containing two tuff sheets and a lower unit (BF-II) containing five different tuff sheets. These two units are separated by a thin bedded tuff. The BF-I is nonwelded and is composed of two ash flows that appear to have cooled as a single unit. The

# YUCCA MOUNTAIN GEOLOGIC UNITS

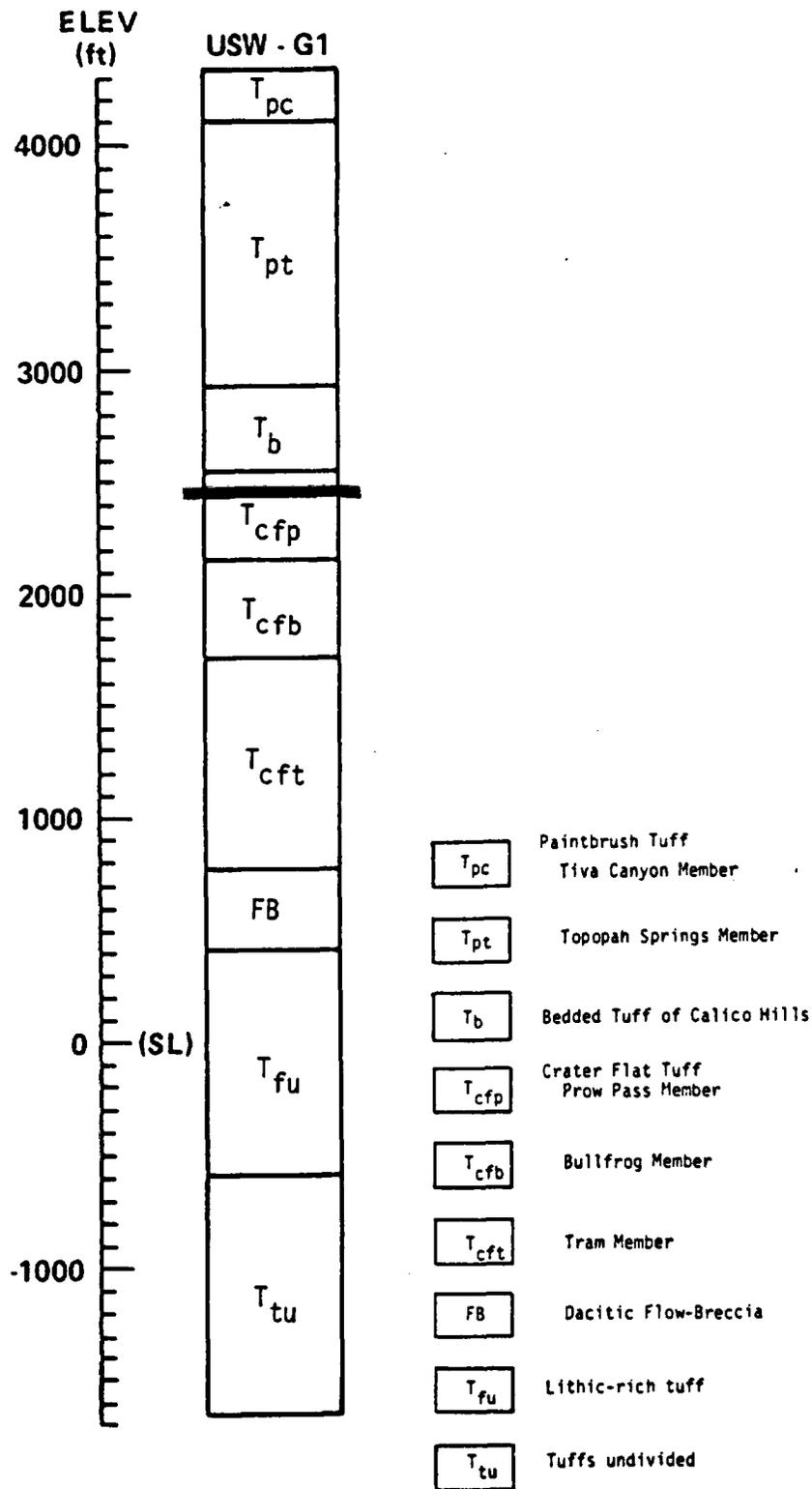


Fig. 1.

Stratigraphic column for drill hole USW-G1 showing the positions of the Bullfrog and Tram Members. The heavy black line is the static water level in the hole.

BF-II is a single cooling unit ranging from slightly welded at the top and bottom to moderately welded within the interior.

In BF-I, all glass shards are pseudomorphed by zeolites, and clays are slightly more abundant in the groundmass than in BF-II. Zeolites also replace glass shards and fill void spaces in the bottom of BF-II, reflecting the absence of welding and original high permeability. Above the zeolitized section of BF-II, the degree of welding increases and the alteration phases decrease in abundance, reflecting the decreased permeability in the central and upper sections of BF-II.

The Tram Member of the Crater Flat Tuff is composed of five units, a basal bedded tuff and four ash-flow sheets. Petrographically, the Tram can be divided into two units, an upper, single, largely devitrified cooling unit, and a lower unit composed of three ash flows and a reworked tuff. The upper unit is zeolitized near the top and has a densely welded lower portion showing devitrification to quartz and alkali-feldspar. The lowermost ash flow in the lower Tram exhibits the transition from clinoptilolite to analcime (Bish et al. 1981). The second ash-flow unit of the lower Tram is nonwelded, zeolitized, and oxidized. The uppermost ash-flow unit of the lower Tram is partially welded and is zeolitized.

### III. REVIEW OF SMECTITE MINERALOGY

Smectites very commonly form as alteration products of volcanic rocks, including tuffs and volcanic ash, and montmorillonite can form from clinoptilolite (Ames et al. 1958). The term smectite is used as a group name for the swelling 2:1 clay minerals including montmorillonite, beidellite, nontronite, saponite, hectorite, and saucnite (Brindley et al. 1975; Table I, Deer et al. 1966). All smectites possess a structure similar to talc or pyrophyllite, with ionic substitutions creating negatively charged layers (Fig. 2). The silicate layers are composed of an octahedral sheet between two tetrahedral sheets; thus the notation 2:1 layer silicates. Octahedral sheets can have either two out of three or three out of three octahedral sites occupied yielding, respectively, dioctahedral or trioctahedral layers. The negative charge on the 2:1 layers can arise through the substitution of aluminum for tetrahedral silicon and/or the substitution of magnesium for octahedral aluminum. In the smectites, cations are present between the layers to balance the negative charge on the 2:1 layers; these "interlayer cations" may include

TABLE I  
IDEALIZED SMECTITE, PYROPHYLLITE, AND TALC COMPOSITIONS

	<u>Diocahedral</u>		
	<u>Z</u>	<u>Y</u>	<u>X</u> (exchange cations)
Pyrophyllite	Si <sub>8</sub>	Al <sub>4</sub>	--
Montmorillonite	Si <sub>8</sub>	Al <sub>3.34</sub> Mg <sub>0.66</sub>	(1/2Ca,Na) <sub>0.66</sub>
Beidellite	Si <sub>7.34</sub> Al <sub>0.66</sub>	Al <sub>4</sub>	(1/2Ca,Na) <sub>0.66</sub>
Nontronite	Si <sub>7.34</sub> Al <sub>0.66</sub>	Fe <sub>4</sub> <sup>+3</sup>	(1/2Ca,Na) <sub>0.66</sub>
	<u>Triocahedral</u>		
Talc	Si <sub>8</sub>	Mg <sub>6</sub>	--
Saponite	Si <sub>7.34</sub> Al <sub>0.66</sub>	Mg <sub>6</sub>	(1/2Ca,Na) <sub>0.66</sub>
Hectorite	Si <sub>8</sub>	Mg <sub>5.34</sub> Li <sub>0.66</sub>	(1/2Ca,Na) <sub>0.66</sub>
Sauconite	Si <sub>6.7</sub> Al <sub>1.3</sub>	Zn <sub>4-5</sub> (Mg,Al,Fe <sup>=3</sup> ) <sub>2-1</sub>	(1/2Ca,Na) <sub>0.66</sub>

any of the alkali or alkaline earth cations. The compositions of smectites are such that their negative layer charge is low, approximately -0.33 per Si<sub>8</sub>O<sub>20</sub>(OH)<sub>4</sub> formula unit. This compares with layer charges of about -0.66 for vermiculites, -1.0 for micas, and -2.0 for brittle micas.

Because the electrostatic attraction between layers is small and the interlayer cations interact with water, smectites can expand in a direction perpendicular to the layers. The exact nature of the expansion in water is thus related to the type of interlayer cation (for example, charge, size, hydration energy) and, depending on conditions, smectites can have layer thicknesses ranging from 10 Å to > 20 Å. An additional consequence of the weak interlayer attraction and hydrated interlayer cations is the phenomenon of cation exchange. Smectites typically have cation exchange capacities ranging from 70 to 130 meq/100 g of clay, and sodium, calcium, magnesium, and hydrogen are the most common interlayer cations (Weaver et al. 1975). Large univalent cations such as potassium and cesium can be "fixed," that is, irreversibly exchanged, onto smectites with above average layer charge if the interlayer attraction

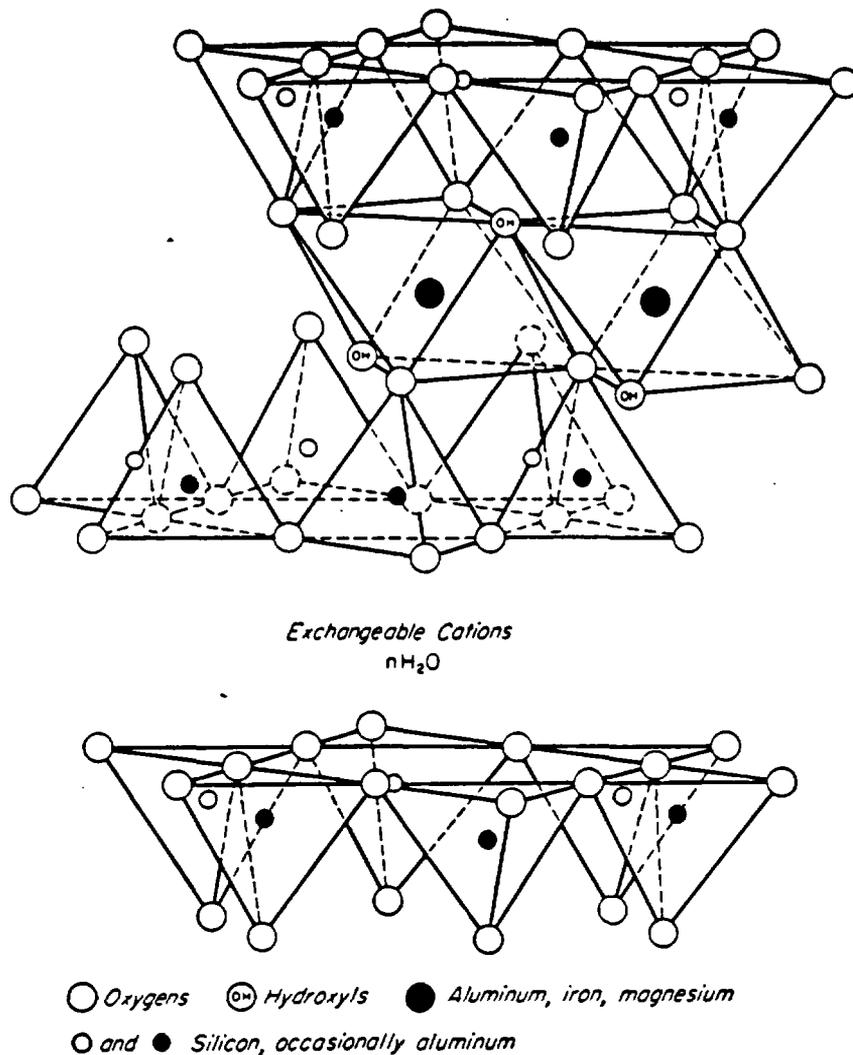


Fig. 2.  
Diagrammatic sketch of the structure of montmorillonite (after Grim 1953).

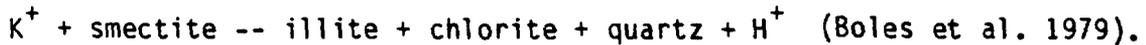
exceeds the cation hydration energies. Cation fixation thus occurs more readily in high-charge smectites or those containing scattered high-charge layers. In addition, divalent cations are generally preferred in exchange reactions over univalent cations of similar hydrated size.

Numerous authors (Burst 1959; Perry et al. 1970, 1972) have shown that smectites undergo a transition to a mica-like mineral with increasing depth or temperature. This reaction involves both compositional and structural changes; there is a gain in interlayer potassium and additional substitution of aluminum for silicon in the tetrahedral layers, thereby increasing the net

negative charge, fixing potassium, and collapsing the layers to 10 Å. The overall reaction may be



or



Structurally, this reaction involves a complex intermediate clay phase in which layers are randomly collapsed to 10 Å throughout a single crystal. In the initial stages of the reaction, a smectite is formed with 10 Å, or illite, layers randomly dispersed throughout. This phase is termed a randomly interstratified illite/smectite and is a common product of low-grade diagenesis of smectites. A randomly interstratified illite/smectite (Fig. 3c) is distinctly different from a physical mixture of illite and smectite (Fig. 3b) or a regular interstratification (Fig. 3a), and care should be taken not to confuse the two. Higher grade diagenesis yields complex ordered interstratifications that are common in Gulf Coast sediments but have not been found at the Nevada Test Site. The diagenetic reaction to an interstratified mineral has important consequences on the physical and chemical properties of the clay. The

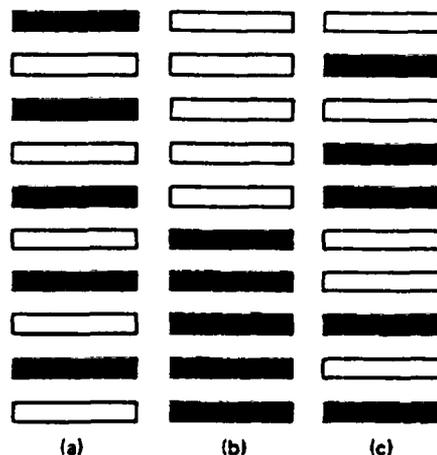


Fig. 3.

Types of interstratification: (a) alternating ABAB..., "regular;" (b) segregated AAA...BBB...; (c) "random," (after MacEwan et al. 1975).

cation exchange capacity gradually decreases from values typical of pure smectites to approximately 15 meq/100 g, and the amount of swelling in water and organic liquids is gradually reduced. Ormsby et al. (1954) demonstrated that a linear relation exists between the cation exchange capacity and per cent expandable layers in illites and interstratified illite/smectites.

#### IV. EXPERIMENTAL METHODS

The investigation of samples in this work involved standard x-ray powder diffractometer techniques and examination of clays separated by sedimentation and centrifugation. Bulk samples were crushed to approximately -300 mesh and mounted in cavities in glass slides. The cavities were large enough so that the sample area fully contained the x-ray beam at the lowest angle of interest. This technique ensured that clay mineral contents in the bulk samples would not be underestimated. Relative percentages of the different phases were determined by comparison with standard patterns.

More accurate clay mineral identification involved first dispersing the crushed bulk samples in distilled water in an ultrasonic bath. The large size fraction (greater than 10  $\mu\text{m}$ ) was sedimented out and a finer fraction was obtained via centrifugation. Through x-ray analysis of the fine fraction, it is possible to identify very small amounts of clay minerals. Oriented sample mounts were prepared for x-ray diffraction by dropping an aqueous suspension of the fine fraction onto a glass slide and allowing it to dry. These mounts were then x-rayed after the following treatments: (1) air dried, 30% relative humidity, (2) dried at 100°C for at least 6 h, (3) ethylene glycol solvation, (4) heated to 200°C with subsequent ethylene glycol solvation, and (5) solvation with water. In addition, the fine fraction from G1-3500 was saturated with lithium and potassium in LiCl and KCl solutions, heated to 200°C, and solvated with ethylene glycol.

Heating a lithium-saturated smectite fixes the lithium into available interlayer and octahedral vacancies and is useful in distinguishing between tetrahedral and octahedral charge deficiencies in smectites (Greene-Kelley 1955). Dioctahedral smectites with octahedral charge deficiencies (montmorillonites) will not expand in ethylene glycol after lithium saturation and heating. Smectites with the layer charge originating in the tetrahedral sheet (beidellites) will expand to approximately 16.9 Å after lithium saturation and heating. Potassium saturation of smectites yields information on the

magnitude of the layer charge deficiencies. Expandable layers with sufficiently high negative charge will collapse to 10 Å after potassium saturation.

The air dried, 100°C dried, and water solvated samples provide information on the type of interlayer cation present and on the behavior of the clay with changes in temperature and humidity. Sodium-saturated smectites commonly exhibit basal spacings of approximately 19.5, 15.6, 12.6, and 10 Å with decreasing humidity, demonstrating the existence, respectively, of three, two, one, and no layers of water between the smectite layers. Calcium- and magnesium-saturated smectites exist predominantly in the two-layer hydrate form (14-15 Å), and potassium smectites occur in 10 Å (no-water layers) and 12.6 Å (one-water layer) forms (Gillery 1959; Suquet et al. 1975).

The x-ray patterns of ethylene-glycol-solvated smectites provide additional useful information. Solvation of smectites with ethylene glycol produces a stable complex yielding more easily interpretable x-ray patterns. Using the methods of Reynolds et al. (1970) and Srodon (1980) and comparing the observed x-ray patterns to hypothetical patterns calculated for a given type of interstratification, it is possible to determine accurately the presence and nature of interstratification. Figure 4 illustrates the calculated changes that take place in the diffraction patterns going from pure smectite through randomly interstratified smectite/illite to pure illite.

## V. RESULTS AND DISCUSSION

Bish et al. (1981) described the bulk mineralogy of the Bullfrog and Tram Members from core samples from USW-G1. However, because several additional samples of core were obtained and because large homogeneous samples were required for the clay mineral separations, I repeated bulk sample x-ray diffraction analyses (Table II).

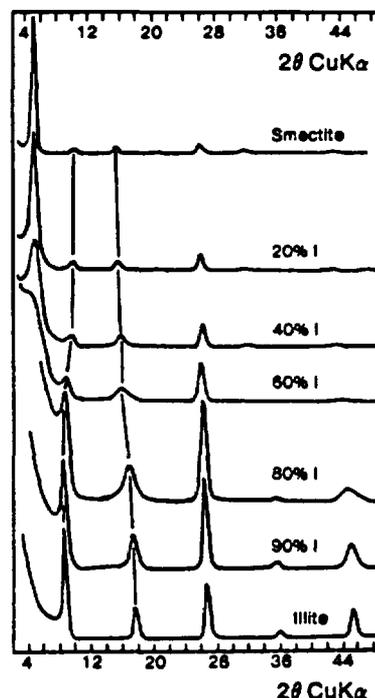


Fig. 4.  $(00\ell)_I/(00\ell)_S$  diffraction profiles of randomly interstratified illite/glycol-smectite. Lines connect the  $(001)_{10}/(002)_{17}$  and  $(002)_{10}/(003)_{17}$  combined reflections (Hower 1981).

TABLE II  
X-RAY DIFFRACTION ANALYSIS OF BULK SAMPLES OF THE BULLFROG  
AND TRAM MEMBERS FROM USW-G1

SAMPLE	(m)	Smectite	Mica	Clinop- tilolite	Mordenite	Analcime	Quartz	Cristo- balite	Alkali Feldspar
G1-2176	663.2	<5%	5-10	30-50	5-15	--	5-10	5-20	15-30
G1-2198	670.0	5-15	5-10	50-70	--	--	--	5-15	10-20
G1-2247	684.9	<5%	~5	40-60	5-15	--	10-20	5-15	20-40
G1-2318	706.5	15-30	10-20	--	--	--	10-20	--	50-70
G1-2349	716.0	~5	~5	--	--	--	30-50	--	40-60
G1-2436	742.5	5-10	~5	--	--	--	30-50	--	40-60
G1-2467	751.9	<5	~5	--	--	--	30-40	5-15	40-60
G1-2486	757.7	<5	5-10	--	--	--	30-50	--	40-60
G1-2525	769.6	<5	<5	--	--	--	30-50	--	40-60
G1-2555	778.8	<1	<5	25-45	25-45	--	5-10	10-20	10-20
G1-2587	788.5	<1	5-10	30-50	30-50	--	--	5-10	5-15
G1-2600	792.5	--	5-10	25-45	15-35	--	5-10	--	10-30
G1-2613	796.4	<5	~5 <sup>a</sup>	<5	20-40	--	20-40	~5	30-50
G1-2622	799.2	<5	5-10	20-40	10-20	--	20-40	<5	20-40
G1-2633	802.5	~5	5-10	30-50	15-30	--	20-40	5-10	5-15
G1-2641	805.0	5-10	10-20	20-40	--	--	10-20	5-20	25-40
G1-2715	827.5	~5	~5	30-50	--	--	10-20	10-30	10-20
G1-2748	837.6	~5	~5	5-15	<5	--	20-40	10-30	20-40
G1-2781	847.7	5-10	~5	--	--	--	40-60	5-10	30-50
G1-2804	854.7	<5	5-10	--	--	--	40-60	0-10	40-60
G1-2820	859.5	5-10	<5 <sup>a</sup>	--	--	--	40-60	--	40-60
G1-2868	874.2	<5	5-10	--	--	--	30-50	--	40-60
G1-2884	879.0	<2	~5	--	--	--	40-60	--	40-60
G1-2932	893.7	<2	~5	--	--	--	40-60	--	40-60
G1-2981	908.6	<2	~5	--	--	--	40-60	--	40-60
G1-3001	914.7	5-10	~5	--	--	--	40-60	--	40-60
G1-3039	926.3	<2	5-10	15-30	5-15	--	30-50	--	20-40
G1-3099	944.6	5-10	5-15	15-30	--	5-10	30-50	--	20-40
G1-3137	956.2	5-15	5-10	--	<5	5-15	25-45	--	15-35
G1-3196	974.1	5-10	~5	10-20	<5	<5	30-50	--	15-30
G1-3238	986.9	5-15	<5	10-20	--	<5	30-50	--	15-30
G1-3258	993.0	10-20	~5 <sup>a</sup>	10-20	--	--	25-45	--	20-40
G1-3321	1012.2	5-15	~5	5-15	--	<5	30-50	--	15-30
G1-3345	1019.6	5-15	~5	10-20	--	<5	20-40	--	25-45
G1-3371	1027.5	5-15	~5	--	--	10-20	30-50	--	30-50
G1-3468	1057.0	10-20	~5	5-15	--	<5	30-50	--	15-30
G1-3500	1066.8	15-30	~5	--	--	<5	30-50	--	15-30

<sup>a</sup> Broad peak, possibly oxidized.

There are no major differences between these results and those presented in Bish et al. (1981), although Bish et al. commonly estimated lower smectite contents than I found in this study. This minor discrepancy is possibly due to differences in sample preparation technique; Bish et al. did not ensure that the full x-ray beam was contained within the sample area at low angles where the main smectite peak occurs. The results for the remaining phases are in excellent agreement.

All samples in the upper cooling unit of the Bullfrog Member (Bullfrog I) are zeolitized, and smectites are ubiquitous but in low concentrations. The upper portion of the Bullfrog II (706.5-769.6 m) is not zeolitized, but smectites are present in all samples. Clinoptilolite and mordenite are present in all lower samples of the Bullfrog II (778.8-802.5 m), however, unlike all other Bullfrog samples, there is a narrow range (778.8-792.5 m) in which smectites are virtually absent. Clinoptilolite is present in the upper portion (805.0-837.6 m) of the Tram, is absent from 847.7-914.7 m, and sporadically distributed throughout the remainder of the unit. Analcime first appears at 944.6 m and is present in all but one of the lower samples.

Smectites are present in all samples of the Tram examined here; the upper part (805.0-914.4 m) contains small amounts of smectites, but below 914.4 m, the Tram is fairly rich (up to 30%) in smectites. There are no consistent correlations in the Bullfrog and Tram Members between the amounts of smectites and the amounts of zeolites, quartz, and alkali feldspar. In some intervals, zeolitized zones are the poorest in smectite (Bullfrog), while in others (lower Tram), relatively abundant smectites and zeolites occur together. Smectites are present equally in welded and nonwelded horizons and, contrary to expectation, are scarce in some zones with absent or slight welding and probable high original permeability (Bullfrog Member, 762.0-792.5 m). The absence of smectites in nonwelded, zeolite-rich horizons may be due to lowering of permeability by zeolites. If so, this indicates that the formation of the smectites postdates zeolite growth in the tuffs.

Using the fine-fraction material separated from bulk samples, it is possible to identify the type of smectite and its reaction to changes in humidity and temperature. X-ray diffraction patterns of  $< 2 \mu\text{m}$  material in cavity mounts yield an (06 $\bar{1}$ ) reflection from the smectites with a spacing of about 1.49 Å, very characteristic of the dioctahedral smectites montmorillonite and beidellite. Trioctahedral smectites typically have (06 $\bar{1}$ ) reflections at about

1.53 Å. The smectites in the Bullfrog and Tram Members are thus montmorillonite-beidellites. The fine-fraction from G1-3500 was lithium-saturated in an effort to distinguish between montmorillonite and beidellite. The sample was saturated, deposited on a glass slide, heated to 220°C, and ethylene-glycol solvated. The smectite still expanded to about 16.9 Å after this treatment, suggesting that the site of the negative charge is in the tetrahedral sheets and that the smectite is beidellite. However, the lithium-saturation test can yield incorrect results when heating samples on glass slides, possibly as a result of lithium-for-sodium exchange. (This information was discussed with D. Eberl in July, 1981). For this reason, and because the properties of montmorillonite and beidellite are so similar, I will refer to the clays in the Bullfrog and Tram as montmorillonite-beidellites.

Under room conditions (20-50% relative humidity, 20-25°C), all of the smectites examined have one layer of interlayer water yielding a basal spacing of approximately 12.6 Å. These conditions certainly do not represent those occurring in the rocks because both the Bullfrog and Tram Members are in the saturated zone with temperatures ranging from approximately 35 to 45°C (Bish et al. 1981). Solvating the montmorillonites with water and allowing them to dry while x-raying reveals that all of the montmorillonites examined expand to approximately 20 Å in a 100% relative humidity atmosphere and, as they dry, contract to approximately 12.6 Å, going through a 15 Å intermediate state. The behavior of these montmorillonites is typical of sodium-saturated smectites and is depicted by Fig. 5 (Gillery 1959; Suquet et al. 1975). There are, however, minor fluctuations in the spacings of the different hydrates, probably because of variations in layer charge and interlayer cation. Depending on the exact conditions present in the rocks, the montmorillonites can have a large variation in basal spacing and consequently in molar volume. As stated above, from 0 to 100 % relative humidity, the basal spacings vary from 10 Å to approximately 20 Å, and the swelling pressure is approximately  $4 \times 10^9$  dyne/cm<sup>2</sup> (Norrish, 1972). With increasing water content (g water/g clay), sodium-montmorillonites become plastic and disperse in a manner depicted in Fig. 6. The swelling pressure in the plastic region (region 2) is from  $10^5$  -  $10^7$  dyne/cm<sup>2</sup>. Finally, with additional water (> 20 g water/g clay), sodium-montmorillonites disperse completely with a swelling pressure of  $< 10^5$  dyne/cm<sup>2</sup>. Obviously, knowing the natural hydration state of the montmorillonites is very important in understanding the effects of changing conditions

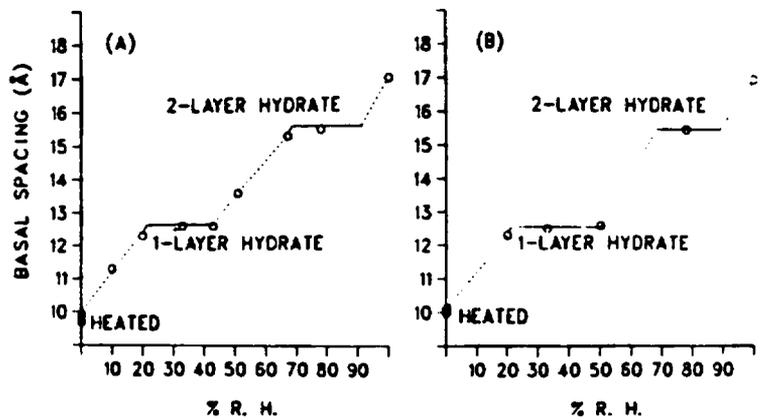


Fig. 5.

Basal-spacing relative-humidity relations (R. H.). (a) Natural sodium-montmorillonite, (b) synthetic sodium-beidellite (after Gillery 1959).

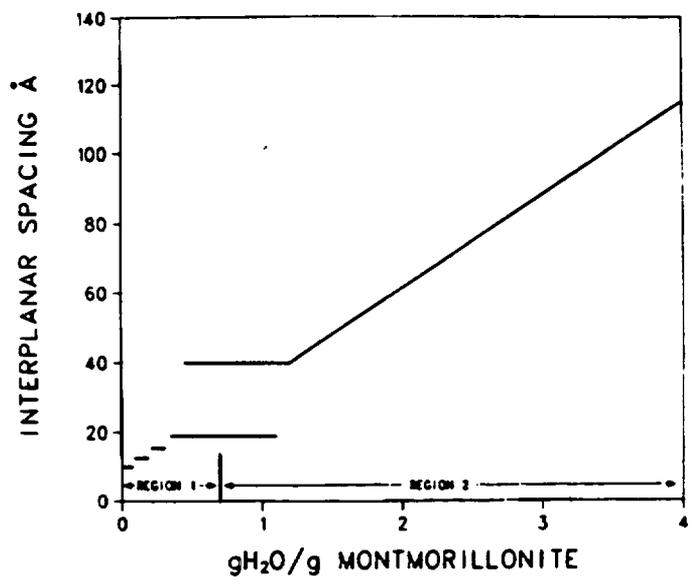


Fig. 6.

Swelling of sodium-montmorillonite (after Norrish 1972).

on the montmorillonites and ultimately on rock properties. It is thus imperative that we understand the present conditions existing in the rocks and appreciate the changes in rock and mineral properties expected when altering these conditions, either in a repository or in a laboratory test.

Further information on the behavior of the montmorillonite-beidellites when heated can be obtained by heating samples to 200°C and re-solvating with ethylene glycol. Samples with high-charge layers and appreciable interlayer potassium will expand only partially, or not at all, after this treatment. Sample G1-3196 was the only sample to be affected by heating, only partially expanding in ethylene glycol. Heating this sample to 100°C had no effect on the expansion behavior. In addition, potassium saturating and heating the montmorillonite-beidellite in G1-3500 had no effect on the expansion properties. The montmorillonite-beidellites in the Bullfrog and Tram Members have typical layer charges (about 0.33) and few or no high-charge layers. This suggests that the cation exchange capacities will not be substantially altered by heating up to 200°C.

As noted above, during diagenesis smectites commonly undergo an irreversible transition to illite through an interstratified illite/smectite intermediate. The extent of this reaction in pelitic sediments can be used as an approximate geothermometer (Hoffman et al. 1979), and it is thus essential to examine the extent of this reaction in the tuffs at the Nevada Test Site. The degree of interstratification in the montmorillonite-beidellites was examined using the techniques of Reynolds et al. (1970) and Srodon (1980). Table III lists the results of these determinations, along with the approximate ethylene-glycol-complex layer thickness. The montmorillonite-beidellites are all randomly interstratified with a small proportion of illite, and no ordered interstratifications are present. In all samples with low clay mineral contents, I estimated the degree of interstratification using the relative intensity of the low-angle scattering. However, this technique is beset by numerous problems connected with crystallite size and instrumental factors (Reynolds 1968; Ross 1968), and these results are only qualitative. I applied Srodon's (1980) methods to samples with more than 5% smectite, and these results are considerably more accurate; the uncertainties applied in Table III for these smectites are conservative. It is obvious from these results that there is no consistent trend in the degree of interstratification with depth, and the amount of illite is fairly uniform throughout the Bullfrog and Tram

TABLE III

X-RAY DIFFRACTION RESULTS FOR RANDOMLY INTERSTRATIFIED  
ILLITE/SMECTITES IN USW-G1

Sample Number	Depth (m)	Per cent Illite in Illite/Smectite	Ethylene Glycol Complex Thickness (Å)
G1-2198	670.0	20±10	16.90
G1-2318	706.5	20±10	16.80
G1-2349	716.0	25±10	16.70
G1-2436	742.5	20±10	16.75 <sup>b</sup>
G1-2467	751.9	20±20 <sup>a</sup>	n.d.
G1-2486	757.7	20±20 <sup>a</sup>	n.d.
G1-2525	769.6	25±20 <sup>a</sup>	16.70
G1-2613	796.4	30±20 <sup>a</sup>	16.75
G1-2622	799.2	30±20 <sup>a</sup>	n.d.
G1-2641	805.0	30±10	16.80
G1-2715	827.5	30±20 <sup>a</sup>	n.d.
G1-2748	837.6	10±10	16.80
G1-2804	854.7	30±20 <sup>a</sup>	n.d.
G1-2820	859.5	10±10	16.70
G1-2868	874.2	30±20 <sup>a</sup>	n.d.
G1-2884	879.0	30±20 <sup>a</sup>	n.d.
G1-2932	893.9	30±20 <sup>a</sup>	n.d.
G1-2981	908.6	30±20 <sup>a</sup>	n.d.
G1-3001	914.7	10±10	16.70
G1-3039	926.3	30±20 <sup>a</sup>	n.d.
G1-3099	944.6	5±5	16.75
G1-3137	956.2	15±10	16.75
G1-3196	974.1	20±10	16.75
G1-3238	986.9	10±10	16.85
G1-3258	993.0	25±10	16.90
G1-3321	1012.2	10±10	16.90
G1-3345	1019.6	5±5	16.90
G1-3371	1027.5	15±10	16.90
G1-3468	1057.0	5±5	16.85
G1-3500	1066.8	5±5	16.90

<sup>a</sup> Estimated from low-angle scattering.

<sup>b</sup> n.d. not determined.

Members, averaging about  $10 \pm 10\%$ . There is some variation in the thickness of the ethylene glycol complex reflecting changes in the layer charges of the montmorillonite-beidellites.

In the tuffs, the diagenetic transformation from smectite to illite has proceeded only slightly, if at all, and this is contrary to expectations based on the maximum paleogeotherm (Bish et al. 1981) and observations in pelitic sediments. Bish et al. reported that zeolite zone boundaries suggested temperatures between 75°C at the top of the Bullfrog Member and 110°C at the bottom of the Tram Member. The temperature currently ranges from 35-45°C. It thus appears that either (a) the reaction kinetics in the tuffs are significantly slower than in typical pelitic sediments, or (b) the smectites in the tuffs result from later alteration at temperatures more closely approaching

the current geotherm than the maximum paleogeotherm. Roberson et al. (1981) have shown that the reaction of smectite to interstratified illite/smectite is significantly inhibited by sodium, calcium, and magnesium in solution in addition to potassium. Indeed, Wolfsberg et al. (1979) report considerably more calcium (13 meq/l) and sodium (50 meq/l) than potassium (4.7 meq/l) in the water from J-13 well. It is therefore probable that the solution chemistry in the tuffs has a pronounced effect on the rate of the smectite to illite/smectite reaction. Considering the relatively steep paleogeotherm, it is equally likely that the smectites formed under conditions more closely approaching the present; Perry et al. (1970) showed that smectites are typically only 20% expandable by 100°C in Gulf Coast sediments. It appears certain that the zeolites and smectites formed under separate conditions and at different times in the tuffs at the Nevada Test Site.

#### VI. SUMMARY AND CONCLUSIONS

The results of a detailed examination of the mineralogy of the Bullfrog and Tram Members in USW-G1 agree closely with the bulk mineralogies determined by Bish et al. (1981), although I found slightly higher smectite contents in this study. Smectites are ubiquitous in both units, but a narrow range in the Bullfrog contains virtually no clay minerals. There are no apparent correlations between the amounts of smectite and the amounts of zeolite, quartz, and alkali feldspar, nor does the amount of smectite appear to be related to the degree of welding in the tuffs. In the Bullfrog, the zeolitized zones are poorest in smectite, and relatively abundant smectites and zeolites occur together in the lower Tram. The slightly welded to unwelded zone near the bottom of the Bullfrog contains very small amounts of smectites, suggesting that zeolitization may have lowered the initial high permeability. If so, this implies that smectite formation postdates zeolite crystallization in tuffs.

The montmorillonite-beidellites are randomly interstratified with typically  $10 \pm 10\%$  illite, and there is no increase in degree of interstratification with depth. It is likely that the sodium, calcium-rich ground water inhibited the diagenetic smectite-to-illite transformation, but it is also probable that the smectites formed under conditions close to those in the rocks today (35-45°C) rather than under those suggested by the zeolite zone boundaries (75-110°C).

The smectites in the Bullfrog and Tram are all dominantly sodium-saturated montmorillonite-beidellites with typical layer charges and no high-charge layers. Sodium-saturated smectites exhibit a large variation in basal spacing (from 10 Å to 20 Å) with minor changes in temperature and humidity, and under room conditions, the basal spacings typically are 12.6 Å. Conditions in the saturated zone in situ are very likely considerably different, yielding smectites with basal spacings appreciably larger than 12.6 Å.

In view of the large possible variations in montmorillonite-beidellite volume and water content with small changes in temperature and relative humidity, it is imperative that we understand the present conditions (temperature and water pressure) in the tuffs and appreciate the changes in rock and mineral properties expected when altering these conditions, either in a repository or in a laboratory test. The effects of varying conditions on rock strength, porosity, and permeability should be carefully examined, and a detailed study of the effects of varying temperature and water pressure on the zeolites and clay minerals in the tuffs should be undertaken. Minor heating of the tuffs and concomitant collapse of the smectites could lead to the opening of fractures and release of free water, but the highly expandable sodium-smectites disseminated throughout the rocks could equally act as efficient barriers to fluid flow, immediately swelling in a hydrous atmosphere and effectively controlling permeability. Clearly, we should examine the expansion-collapse behavior of the montmorillonite-beidellites in environments closely approaching those in the tuffs, that is, heating in hydrous atmospheres rather than under room humidity conditions. It is also important to know the mode of occurrence of the smectites in tuffs and the minerals occurring in the pore spaces. The clays will have quite varying effects depending upon whether they occur in fractures, lining pores in the groundmass, or as massive alteration products of pumice fragments.

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