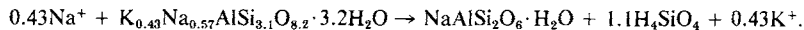


## ZEOLITE REACTIONS IN THE TUFFACEOUS SEDIMENTS AT TEELS MARSH, NEVADA

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**Abstract**—The most prominent authigenic reaction in Holocene tuffaceous sediments at Teels Marsh, Nevada, is the hydration of rhyolitic glass by interstitial brines and the subsequent formation of phillipsite. This reaction has the form: rhyolitic glass + H<sub>2</sub>O → hydrous alkali aluminosilicate gel → phillipsite. Phillipsite is the most abundant authigenic phase in the tuffaceous sediments (>95%), analcime is the next most abundant phase, and clinoptilolite occurs as a trace mineral in the <2-mm fraction. Analcime forms by the reaction of phillipsite and Na<sup>+</sup>. Gaylussite and searlesite also are common authigenic phases at Teels Marsh. The concentration of silica in the interstitial brines is controlled by one or more of the authigenic reactions at less than 100 ppm. A stoichiometric equation for the reaction of phillipsite to analcime at Teels Marsh is:



Sodium and potassium activities of brines associated with both phillipsite and analcime were used to estimate the equilibrium constant for this reaction as  $3.04 \times 10^{-5}$ . The  $\Delta G^0$  value for the reaction is +6.2 kcal/mole at 25°C and 1 atm pressure. The estimated  $\Delta G^0$  value of phillipsite, using this reaction, is -1072.8 kcal/mole at 25°C and 1 atm.

**Key Words**—Analcime, Diagenesis, Gel, Phillipsite, Playa lake, Volcanic ash, Zeolites.

### INTRODUCTION

Studies of zeolites in saline-lake environments have examined the alkalic zeolites (phillipsite, clinoptilolite, erionite, mordenite, and chabazite) that commonly form by the reaction of volcanic glass with saline, alkaline solutions (Sheppard and Gude, 1968, 1969, 1973; Hay, 1966, 1970; Surdam and Parker, 1972; Surdam and Eugster, 1976). Investigations of ancient alkaline lake deposits have established paragenetic sequences for the formation of alkalic zeolites from volcanic glass (Surdam and Sheppard, 1978). However, a complete understanding of the reactions between the volcanic glass and the saline, alkaline solutions requires some knowledge of the initial composition of the glass and composition of the reacting solutions. Surdam and Eugster's (1976) study of modern and ancient environments at Lake Magadi, Kenya, documented several zeolitic reactions and provided data for the reaction between volcanic glass and saline, alkaline brines.

The present study concentrated on reactions taking place in the upper ash bed at Teels Marsh, Mineral County, Nevada (Figure 1). This ash bed generally occurs approximately 30 cm below the surface and varies in thickness from 1.3 to 5.1 cm. Teels Marsh is similar to Lake Magadi in that it is also a modern saline, alkaline-lake environment, and it contains tuffaceous sediments. It is a typical discharge playa with interior drainage of both ground water and surface water. Teels

Marsh represents an almost ideal natural laboratory in which to study the reactions between volcanic glass and alkaline brines because of its limited areal extent (21 km<sup>2</sup>) (Drew, 1969) and because the geology (Ross, 1961) and water chemistry (Everts, 1969; Smith, 1974; Smith and Drever, 1976) have been studied extensively. The purpose of this report is to describe the reactions taking place in the tuffaceous sediments at Teels Marsh and to provide a better understanding of the reactions that can occur between volcanic glass and saline, alkaline solutions.

#### *Previous work*

Two theses from the University of Wisconsin have added significantly to understanding Teels Marsh. C. H. Everts (1969) described the evolution of the brines at Teels Marsh in detail. Everts drilled 28 holes to approximately 40 feet each, and P. A. Drew studied several cores from this drilling. Drew's investigation involved iron-sulfur-carbon reactions in the playa and the correlation to stratigraphic color changes. Drew (1969) also identified clinoptilolite in the lowermost ashes at Teels Marsh.

### GENERAL GEOLOGY

Teels Marsh is located in a block-faulted valley typical of the Basin and Range geomorphic province. Detailed geological studies of Teels Marsh were made by Vanderburg (1937), Ferguson *et al.* (1954), and Ross (1961, see Figure 1). The west-southwest trending Excelsior Range is to the north of Teels Marsh, and Tertiary age intermediate to felsic volcanic rocks form the

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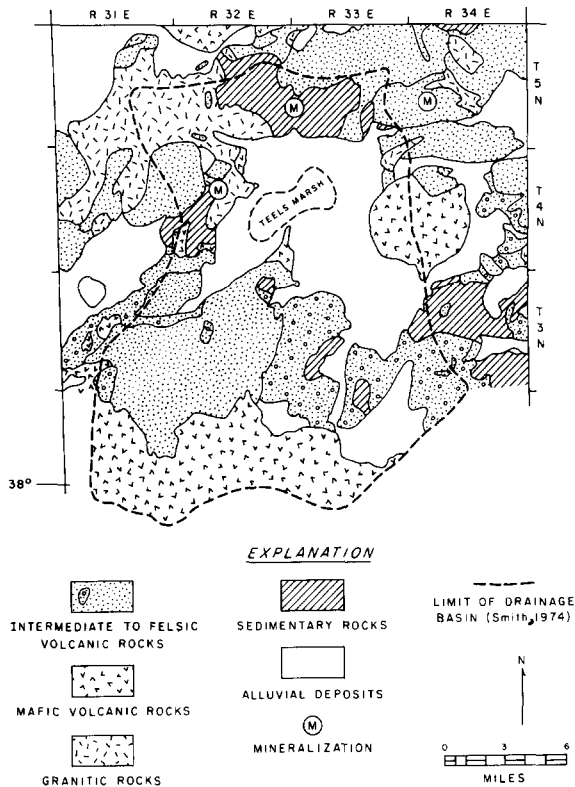


Figure 1. Generalized geologic map of the area surrounding Teels Marsh, Nevada; "M" indicates areas of mineralization (after Ross, 1961).

mountains to the south. The surrounding mountains provide solutes to the basin. The average precipitation in the mountains is higher than the 15 cm/yr for the valley floor, and the high evaporation rate of 127 cm/yr (Everts, 1969) yields a high evaporation to inflow ratio which is typical for an ephemeral lake such as Teels Marsh (Hardie *et al.*, 1978).

The closed basin in which Teels Marsh is located fits the general description of the characteristics of the saline lake deposits of Hardie *et al.* (1978). The "sub-environments" found at Teels Marsh as described by Hardie *et al.* (1978) are: (1) alluvial fan, (2) sandflat, (3) dry mudflat, (4) ephemeral saline lake, (5) dune field, and (6) springs.

*Source of the upper ash bed*

Although the upper ash bed at Teels Marsh has not been dated, its age may be estimated and a source suggested. Hay (1966) cited a  $C^{14}$  date of gaylussite from Teels Marsh at  $10,760 \pm 400$  years B.P. The gaylussite was collected from a depth of 5.5 m which is 1.2 m below the lowest tuff indicating possible zeolitization in the lowest tuff in less than 10,000 years. Hay suggested an age for the uppermost ash bed of about 1000 years.

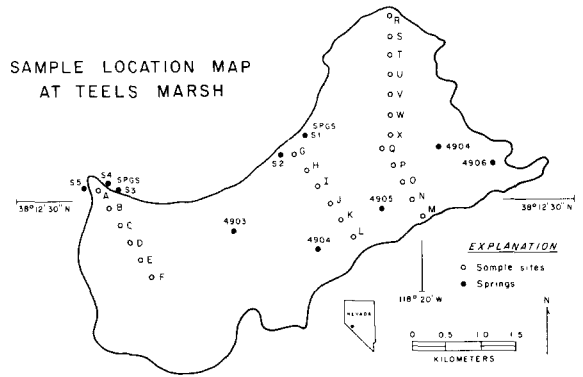


Figure 2. Map showing ash, sediment, and spring locations at Teels Marsh, Nevada.

This age can be correlated to the ages of recent volcanism in the vicinity of Teels Marsh. Wood (1977) described a tephra having an age of  $1190 \pm 80$  B.P. that is associated with the Mono Craters in southeastern California. Although the easternmost extent of this tephra has not been determined, Wood suggested that it may extend into the Great Basin. He reported several tephtras as far east as Hawthorne, Nevada, 48 km northwest of Teels Marsh, but these have not yet been positively correlated with the tephra Z that he described. Based on age association, this tephra could be the same as the upper ash bed at Teels Marsh. Wood suggested that Panum Crater, 68 km southeast of Teels Marsh, is the most likely source of this tephra. The age and geographical location also indicate that Panum Crater is the most likely source for the upper ash bed at Teels Marsh.

**SAMPLING AND SAMPLE LOCATIONS**

Samples were obtained from 24 locations spaced at 305-m intervals along 4 traverses (see Figure 2). At each sample location, a shallow pit (1–2 m deep) was dug exposing the upper ash bed. Samples from the ash bed, the sediment above, and the sediment below the ash bed were collected in plastic pipe 15.5-cm long and 6.5 cm in diameter. The interstitial brine was squeezed into a syringe using a technique similar to that described by Smith (1974). The brine was squeezed in the original plastic cylinder so that contact with the atmosphere was held to a minimum. The pH and the temperature of the brine were recorded as it was being squeezed into the syringe. The pH was measured using a Sargent-Welch S-30070-10 Glass Combination Electrode. The squeezing apparatus included two 0.45-mm Millipore filters which filtered the brine before it entered the syringe. The samples were transferred from the syringe directly into plastic bottles and sealed with plumber's tape. Samples A–F were squeezed in the field; however, due to adverse surface conditions on the playa, samples G–X were sealed in plastic pipe and refriger-

ated until they were squeezed. All samples were squeezed within 12 hr of collection. Eighteen samples were collected in March 1977, and the remaining 54 samples were collected in June 1977. Samples of several springs along the fringes of the lake were also collected in 1-liter polyethylene bottles. The temperature and pH of the samples were measured in the field, and the samples were then sealed until analysis.

#### ANALYTICAL METHODS

All ash samples were examined by standard X-ray powder diffraction (XRD) methods (Carroll, 1970) using a GE XRD-5 instrument and Ni-filtered  $\text{CuK}\alpha$  radiation. The clay mounts were made using the membrane-peel technique of Drever (1973). Selected samples were also examined in thin sections and by scanning electron microscopy (SEM) using a JEOLCO instrument. The amount of calcium carbonate in the sediments was determined by a colorimetric method using acid decomposition (S. W. Boese, Department of Geology, University of Wyoming, Laramie, Wyoming, personal communication). Near-monomineralic separates for chemical analysis were prepared by gravity separation, using diluted heavy liquids. XRD patterns and optical examination in immersion oil showed less than 5% impurities in these fractions; however, corrections were not made for these impurities.

The major elements, total Fe, Ca, Na, Mg, K, and Al, were determined using a Perkin Elmer Model 403 Atomic Absorption Spectrophotometer. Alkalinity, as defined by Stumm and Morgan (1970), was measured in the brine by titration with 0.0206 M HCl using a Brinkman (Metrohm) Automatic Titrator. A Buchler-Cotlove Chloridometer Automatic Titrator was used to determine the amount of chloride. Fluoride was determined using an Orion fluoride ion selective electrode. A colorimetric procedure (American Public Health Association, 1971) was used to determine phosphate using a Varian 635D UV-VIS spectrophotometer. Boron was determined by titration with NaOH and Mannitol (Jeffery, 1970). Silica was determined colorimetrically (Fanning and Pilson, 1973) and sulfate was determined by X-ray fluorescence.

Estimates of the precision for the various techniques are as follows: (1) sediments and ash beds (absolute precision), Mg and Ca =  $\pm 0.03\%$ ;  $\text{SiO}_2$  =  $\pm 0.2\%$ ; Al =  $\pm 0.2\%$ ; Fe, Na, and K =  $\pm 0.1\%$ ; inorganic calcium carbonate =  $\pm 0.05\%$ ; (2) brine samples (relative precision), Na, Cl, alkalinity, and  $\text{CO}_3$  =  $\pm 1\%$ ; K =  $\pm 2\%$ ; Ca =  $\pm 10\%$ ; Mg and  $\text{HCO}_3$  =  $\pm 5\%$ ;  $\text{SiO}_2$  and P =  $\pm 2\%$ ; F and B =  $\pm 5\%$ ; and Al =  $\pm 1$  ppm; (3) water samples, K, Ca, and  $\text{SiO}_2$  =  $\pm 2\%$ ; Na, Cl, alkalinity,  $\text{HCO}_3$ , and P =  $\pm 1\%$ ; Mg, F, and B =  $\pm 5\%$ ; and pH =  $\pm 1$ . Charge balance for all samples, except those specified, is within 5%. Brine and sediment samples A-F and all spring samples were analyzed by S.

W. Boese. All other samples were analyzed by the authors under his direction.

#### WATER CHEMISTRY

Table 1 gives the compositions of the interstitial brines that are associated with the tuffaceous sediments at Teels Marsh. Table 2 gives the composition of the springs, surface waters, lake brines, and interstitial brines that are associated with nontuffaceous sediments at Teels Marsh. The chemistry of the springs was discussed by Smith and Drever (1976), and the brine chemistry and the evolution of the brines were discussed by Everts (1969) and Smith (1974). Discussions on the evolution of the brines similar to those found at Teels Marsh can be found in Jones (1966), Garrels and Mackenzie (1967), Hardie and Eugster (1970), and Eugster (1970). Smith (1974) also described the distribution and the controls on the trace elements in the brines at Teels Marsh.

The brines are essentially sodium chloride waters with carbonate and sulfate the next most abundant constituents. The pH in the brines ranges from 9.0 to 10.1, and the total dissolved solids have a wide range from 20,000 to 300,000 mg/liter. The density of the brines ranges from 1.01 to 1.22  $\text{g/cm}^3$ . The activity of sodium in the brines was determined using a specific-ion electrode. Figure 3 shows a map of the distribution of total dissolved solids at Teels Marsh. The distribution in this map is similar to the concentric pattern of the total dissolved solids during 1972-1973 (Smith, 1974). The general trend is one of increasing concentration into the center of the lake as would be expected in a closed basin where evaporation exceeds inflow. The chemistry of the interstitial brines is controlled by evaporative concentration and the precipitation of minerals from solution (Smith, 1974).

Everts (1969) suggested three stages in the evolution of the brines: (1) Hydrolysis of silicates from silica-rich volcanic and granitic rocks releases alkali and alkaline earth cations and bicarbonate. The bicarbonate then precipitates along with Ca and Mg near the playa margin using the mechanism previously suggested; (2) The loss of some sulfate takes place by evaporative precipitation of burkeite [ $\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$ ] or by the reduction of sulfate to sulfide in the muds by bacteria; (3) Halite and other alkali chlorides precipitate. This evolution scheme seems to fit the path of a sodium/carbonate/sulfate/chloride-rich brine of Eugster and Hardie (1978).

In summary, the brines in the Teels Marsh basin are very rich in Na, bicarbonate-carbonate, chloride, and sulfate, but they are conspicuous by the near absence of Ca and Mg.

#### MINERALOGY

The mineralogy of the tuffaceous rocks and mudstones at Teels Marsh can be characterized by several

Table 1. Composition of the interstitial brines associated with the tuff bed (mg/liter).

Sample number	Temp. (°C)	Field pH	Lab pH	SiO <sub>2</sub>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	Total alkalinity (meq/liter)
2A	24	9.2	9.25	52	60,000	1720	0	1100	45,700	37
2B	17	9.8	9.65	54	80,000	2160	866	7690	13,100	271
2C	13	9.9	9.70	61	70,000	1820	2400	7650	9910	294
2D	20	9.7	9.70	66	114,000	3180	4940	19,200	19,000	721
2E	20	9.85	9.70	52	94,000	2800	4450	13,100	10,000	510
2F	19	9.5	9.60	63	108,000	3040	4950	14,500	11,400	564
2G	34	9.25	9.10	72	38,000	2520	2790	1540	4390	97
2H	32	9.6	9.50	44	112,000	6200	2470	14,800	14,900	534
2I	32	9.7	9.45	68	94,000	3460	6220	11,300	10,200	479
2J	30	9.7	9.50	65	96,000	3700	6220	11,300	22,900	479
2N	30	10.1	9.75	95	66,000	3176	3110	16,400	16,500	598
2O	29	9.7	9.55	67	112,000	6250	0	15,100	24,600	503
2P	27	10.0	9.65	42	106,000	3300	622	19,800	30,600	670
2Q	28	9.6	9.45	52	116,000	4100	0	14,800	30,600	493
2V	27	9.6	9.50	75	102,500	2690	6	10,400	15,900	347
2W	27	9.6	9.50	55	104,000	2490	3100	10,700	12,300	407
2X	29	9.7	9.45	68	110,000	3680	622	13,200	20,000	450

Sample number	Cl <sup>-</sup>	F <sup>-</sup>	B	PO <sub>4</sub> <sup>3-</sup>	Al	Total dissolved solids (ppm)	Density (g/cm <sup>3</sup> )	Chg. bal. error	a <sub>Na</sub> <sup>+</sup>
2A	79,500	125	470	0	<1	189,000	1.12	<5	29,670
2B	91,600	235	440	384	<1	197,000	1.14	<5	42,780
2C	85,600	228	270	398	2.8	178,000	1.13	<5	33,810
2D	114,000	465	360	657	<1	276,000	1.20	<5	64,480
2E	104,000	330	310	588	14	230,000	1.18	<5	49,680
2F	124,000	420	440	636	12	267,000	1.20	<5	63,710
2G	52,700	110	214	66	<1	102,000	1.04	<5	13,800
2H	131,000	223	719	1318	<1	284,000	1.21	<5	54,740
2I	116,000	235	505	800	0.83	243,000	1.18	<5	40,480
2J	107,000	245	427	508	1.25	248,000	1.18	<5	40,700
2N	52,200	225	466	348	0.5	160,000	1.14	<5	18,860
2O	115,000	250	893	1049	0.38	275,000	1.20	<5	39,790
2P	93,000	405	816	627	1	255,000	1.19	<5	36,800
2Q	118,000	310	816	710	<1	285,000	1.22	<5	44,390
2V	122,000	350	583	1017	0.63	256,000	1.20	<5	42,320
2W	120,000	330	544	786	<1	254,000	1.18	<5	42,320
2X	124,000	250	699	800	<1	273,000	1.20	<5	43,240

groups of minerals: (1) detrital silicates, (2) saline minerals, (3) calcite, dolomite, and gypsum, (4) quartz, (5) searlesite, and (6) authigenic zeolites. Table 3 shows the distribution of the mineral assemblages that are associated with the tuffaceous rocks at Teels Marsh. Na-rich plagioclase and microcline are the two common detrital silicates at Teels Marsh. The sources of these silicates are probably the andesite, felsic rhyolite, and quartz monzonite in the area. The clay minerals at Teels Marsh are illite, montmorillonite, chlorite, kaolinite, and mixed-layer clays that probably formed by the weathering of silicates (Smith, 1974), although some of the clays may be authigenic.

The saline minerals at Teels Marsh are generally efflorescent crusts formed from the brines through evaporative concentration. These minerals are halite, trona, burkeite, and mirabilite, with halite being the dominant saline mineral. Crystal casts of halite also are present

in the mudstones. Gaylussite (Na<sub>2</sub>CO<sub>3</sub>·CaCO<sub>3</sub>·5H<sub>2</sub>O) occurs at Teels Marsh, generally as rhombs (Figure 4) in the sediment samples.

Calcite, dolomite, and gypsum were identified in several samples. Some of the calcite may be detrital, but most of it, along with the dolomite and gypsum, probably precipitated near the alluvial fans and at the edge of the lake (Smith and Drever, 1976). Calcite rhombs were observed in thin sections of some of the ash samples. Quartz is ubiquitous in the samples from Teels Marsh and is associated with the authigenic zeolites. Searlesite (NaBSi<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O) also occurs at Teels Marsh mainly in the mudstone, although traces are in the upper ash bed.

The authigenic zeolites at Teels Marsh are phillipsite, analcime, and clinoptilolite. The distribution of phillipsite and analcime at Teels Marsh is shown in Figure 5. Phillipsite in the form of laths (Figure 6) is the predom-

Table 2. Composition of springs, surface water, lake brines, and interstitial brines (mg/liter).

Sample number	Temp. (°C)	Field pH	Lab pH	SiO <sub>2</sub> (mg/liter)	Na <sup>+</sup> (mg/liter)	K <sup>+</sup> (mg/liter)	HCO <sub>3</sub> <sup>-</sup> (ppm)	CO <sub>3</sub> <sup>2-</sup> (ppm)	SO <sub>4</sub> <sup>2-</sup> (mg/liter)
<i>Springs</i>									
S1	12		7.65	70	240	22	109	—	176
S1	14		7.50	75	320	36	161	—	182
S3	14		8.20	59	2040	51	750	22	754
S4	16		8.25	66	330	10	49	4.0	225
S5	14		8.25	79	290	14	51	3.0	199
S6	12		8.25	16	280	29	406	—	564
S7	8		8.55	29	580	71	738	22	38
S8	18		8.15	40	490	56	781	—	179
S9	14		8.70	79	200	27	263	11.0	83
<i>Surface water</i>									
S1			9.05	43	2800	124	—	214	680
S11			9.2	42	1800	56	—	94	453
<i>Lake brines</i>									
B			9.40	38	88,000	2300	12,220	8060	11,400
G			9.15	54	24,000	1240	—	2706	2990
I			9.5	50	124,000	3660	2477	15,800	14,990
J			9.5	53	116,000	3900	1861	15,800	20,000
K			9.5	40	82,000	6300	3099	9455	11,200
N			9.6	48	69,000	4000	1238	12,590	14,700
Z			9.8	95	11,000	663	—	1891	1420
<i>Interstitial brines</i>									
1A	20	9.1	9.05	66	82,000	1720	—	1340	32,500
3A	22	9.2	9.25	76	62,000	2320	—	1440	20,500
1B	17	9.8	9.60	74	84,000	1280	1340	8000	14,800
3B	15	9.8	9.60	43	76,000	2140	1950	6420	7010
1C	14	9.7	9.60	76	90,000	2420	2500	10,900	8420
3C	14	9.9	9.65	56	72,000	2060	1950	7690	5760
1D	20	9.55	9.70	88	108,000	3180	3840	18,100	11,300
3D	20	9.7	9.55	37	98,000	3080	5920	12,700	11,900
1E	19	9.8	9.70	66	108,000	3240	5800	14,500	9060
3E	20	9.8	9.60	36	100,000	3140	4820	12,200	12,100
1F	20	10.0	9.65	86	102,000	3180	2990	17,500	7220
3F	20	9.5	9.60	61	110,000	3240	3110	14,200	9060
1G	34	9.45	9.15	80	68,000	4200	3510	5140	10,300
3G	33	9.4	9.10	74	22,000	1320	689	2070	2510
1H	32	9.7	9.5	48	105,000	4875	3690	15,700	10,800
3H	33	9.7	9.45	53	104,000	6200	2470	14,500	14,900
1I	36	10.0	9.45	75	90,000	3100	14,200	8180	2890
3I	31	10.0	9.55	51	105,000	3600	4330	12,600	15,200
1J	30	10.0	9.5	63	97,000	3880	5550	11,000	25,700
3J	29	10.0	9.5	57	94,000	3300	6160	11,000	21,300
3K	29	9.8	9.5	93	76,000	6540	9270	10,100	10,900
3L	29	10.0	9.55	167	9850	764	2260	1180	1610
3M	31	9.65	9.4	126	7600	560	976	465	1360
1N	33	10.0	9.6	87	82,000	3920	549	1950	18,500
3N	25	10.1	9.65	73	44,700	2280	4330	7870	8260
3O	29	9.7	9.5	26	90,000	6000	2650	12,200	17,200
1P	27	10.0	9.7	85	110,000	3680	0	22,000	66,500
3P	27	9.85	9.6	48	102,000	3420	0	19,800	23,300
1Q	27	9.75	9.5	64	103,000	4060	0	15,400	33,300
3S	24	9.6	9.45	27	43,000	1670	278	3600	3580
3T	19	9.6	9.45	19	104,000	3340	0	12,300	11,400
1U	22	9.7	9.5	64	94,000	4000	0	12,900	9890
3V	27	9.65	9.45	72	98,000	2680	1240	10,700	5940
3W	28	9.9	9.4	64	101,000	2650	3100	10,700	15,300
1X	22	9.55	9.45	58	100,000	2740	0	12,300	15,100
3X	22	9.7	9.55	60	86,000	2140	622	9110	13,000

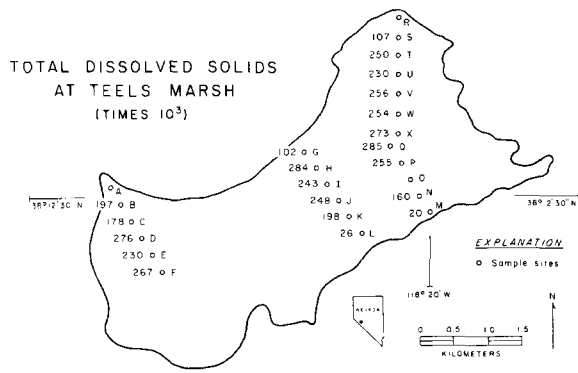


Figure 3. Distribution of total dissolved solids in interstitial brines at Teels Marsh. Numbers are in mg/liter  $\times 10^3$ .

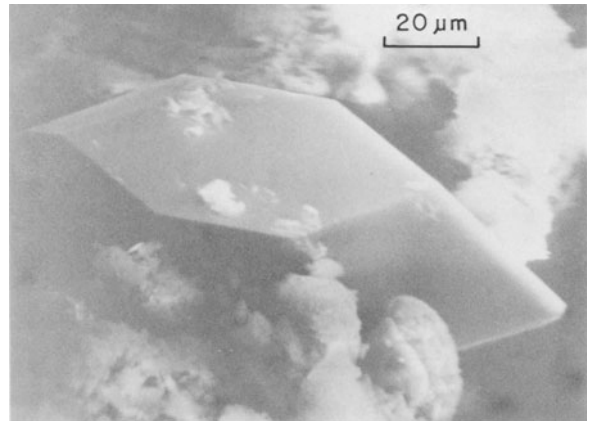


Figure 4. Scanning electron micrograph of a gaylussite crystal from sample 2L.

inant zeolite in the upper ash bed, and it occurs in all ash samples. Analcime also is present in the tuffaceous sediments in the upper ash bed and is associated with phillipsite and quartz. Clinoptilolite occurs in trace amounts and is associated with phillipsite and locally with analcime. Altered and unaltered rhyolitic glass shards are associated with phillipsite in the tuff beds. According to Everts (1969), the glass at Teels Marsh contains 70% SiO<sub>2</sub>. A gelatinous material is also associated with phillipsite and rhyolitic glass at Teels Marsh (Figure 7).

### FORMATION OF AUTHIGENIC MINERALS

#### Phillipsite

Phillipsite is the predominant zeolite at Teels Marsh. Figure 8 shows that the brines at Teels Marsh are relatively low in silica as compared with Lake Magadi brines. However, the question arises as to why a high-silica rhyolitic glass precursor yields phillipsite, a low-silica zeolite. Hay (1966) noted a relationship between

Table 3. Mineral assemblages associated with the tuffaceous rocks at Teels Marsh.

Sample	Ph	An	Cl	H	S	Ga	Q	Cc	D	Gy	F	G
2A	C	C	N	C	T	T	C	N	N	C	C	T
2B	C	C	N	C	T	N	C	T	N	T	T	T
2C	C	C	T	C	T	T	C	T	N	T	C	T
2D	C	C	N	C	T	C	C	N	N	N	C	T
2E	C	C	N	C	T	C	C	N	N	N	C	T
2F	C	C	N	C	T	T	C	N	N	N	C	T
2G	C	C	N	C	T	C	C	N	C	N	N	T
2H	C	C	N	C	T	N	C	N	N	N	N	T
2I	C	N	T	C	T	N	C	N	N	N	T	T
2J	C	N	N	C	N	N	C	N	N	N	T	T
2K	C	N	N	C	T	T	C	C	N	N	C	C
2L	C	N	N	C	T	T	C	T	T	T	T	C
2M	C	C	T	C	T	T	C	T	N	N	C	T
2N	C	N	T	C	T	T	C	T	N	N	C	C
2O	C	C	T	C	T	C	C	N	N	N	C	T
2P	C	C	N	C	T	N	C	N	N	N	C	C
2Q	C	N	T	C	T	T	C	T	N	N	C	C
2R	C	C	N	C	T	T	C	N	N	N	C	T
2S	C	N	T	C	T	C	C	C	N	N	N	T
2T	C	C	N	C	T	C	C	C	N	N	C	T
2U	C	N	T	C	T	T	C	C	N	T	C	C
2V	C	C	N	C	T	T	C	T	N	N	C	T
2W	C	C	N	C	T	T	C	N	N	N	N	T
2X	C	C	N	C	T	C	C	T	N	N	C	N

C = common, T = trace, N = none; Ph = phillipsite, S = searlesite, D = dolomite, An = analcime, Ga = gaylussite, Gy = gypsum, Cl = clinoptilolite, Q = quartz, F = feldspar (see text), H = halite, Cc = calcite, G = glass.

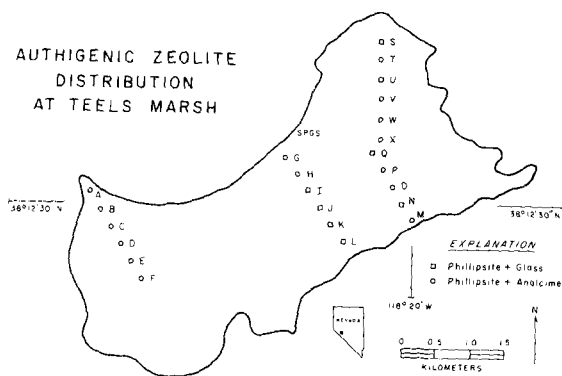


Figure 5. Distribution of authigenic zeolites in the upper ash bed at Teels Marsh.

the Si/Al ratio of the zeolites formed in modern environments and the alkalinity of the solutions in which the zeolites form. Mariner and Surdam (1970) suggested that the relationship between the Si/Al ratio and the pH is the result of the reaction between silicic glass and alkaline solution whereby (1) a gel forms whose Si/Al ratio is controlled by the Si/Al ratio of the solution, and (2) a zeolite forms from the gel whose Si/Al ratio is controlled by the composition of the gel. They also demonstrated experimentally that the solubility of rhyolitic glass increases with increasing pH (see also Surdam and Sheppard, 1978) and that the concentration of dissolved Al increases with increasing pH but the Si/Al ratio decreases with increasing pH. This second point indicates that at high pH, zeolites such as phillipsite, which has a relatively low Si/Al ratio, are favored over zeolites with high Si/Al ratios such as clinoptilolite.

Surdam and Mariner (1971) were able to separate the gel phase from Teels Marsh samples and, upon heating it to 80°C at autogenous pressures, found that it crystallized to phillipsite. This relationship is illustrated in Figure 9. Figure 10 shows the lath-like phillipsite that formed in close proximity to the gel. Figure 11 is an SEM photograph showing the dissolution texture of a glass shard and phillipsite that has grown on the outside of the shard. Note the absence of textures that suggest that phillipsite directly replaced the glass.

#### Analcime

Analcime commonly is found in saline, alkaline-lake deposits (Hay, 1966; Sheppard and Gude, 1969; Hay, 1970; Surdam and Parker, 1972). Data from studies of tuffaceous sediments indicate that analcime does not form from the alteration of glass because glass and analcime have not been found in association (Surdam and Eugster, 1976). Analcime has been found, however, in association with many alkalic zeolites. Surdam and Eugster (1976) reported evidence that erionite altered to analcime at Lake Magadi, and Sheppard and Gude

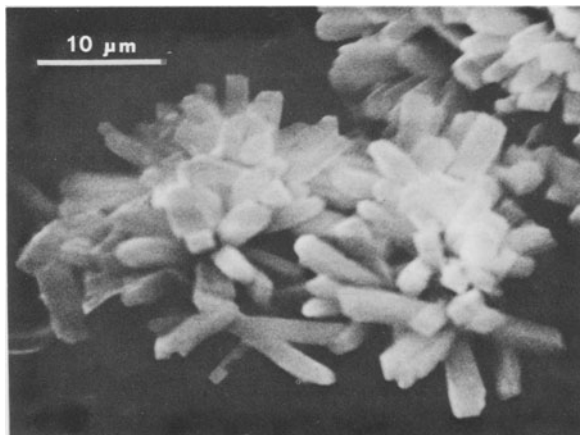


Figure 6. Scanning electron micrograph of lath- or rod-shaped phillipsite crystals from Teels Marsh, Nevada.

(1969) reported evidence that clinoptilolite and phillipsite altered to analcime. At Teels Marsh analcime is always associated with phillipsite, indicating that phillipsite may be the precursor to analcime. Analcime was not found in association with glass or gel in any of the thin sections or XRD patterns of samples from Teels Marsh.

#### Other authigenic silicates

Clinoptilolite occurs in trace amounts in some of the samples from the upper ash bed. In addition, searlesite is common in the sediments at Teels Marsh, and gaylussite occurs in the tuffaceous sediments.

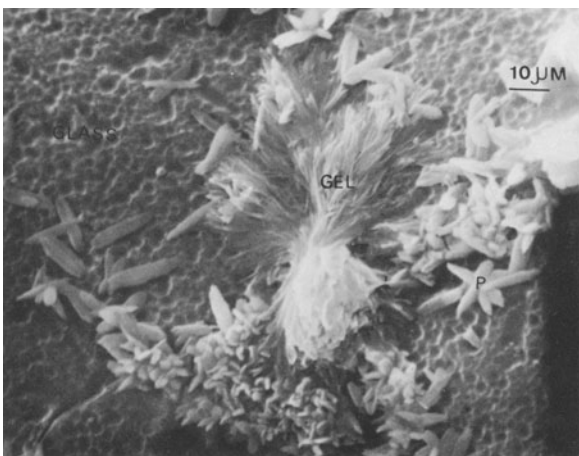


Figure 7. Scanning electron micrograph showing the lath-like crystal habit of phillipsite (p). Laths are approximately 10 to 12  $\mu\text{m}$  in length. Note the radiating fibrous material in the center of the photograph from which the phillipsite laths appear to be forming. This material is a precursor gel phase.

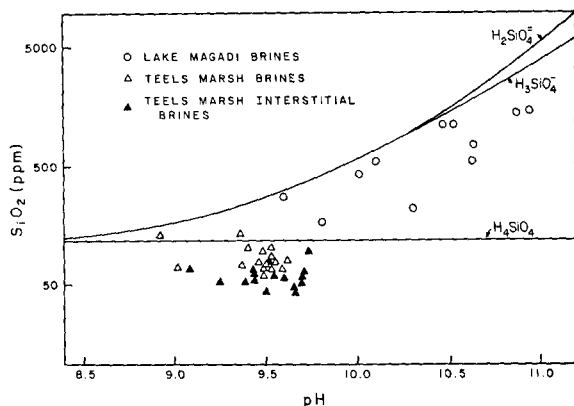


Figure 8. Relationship between silica (ppm) and pH in the brines (modified from Surdam and Sheppard, 1978).

### CHEMICAL PETROLOGY

Several authors have studied the chemistry of the phillipsite and rhyolitic glass at Teels Marsh. Table 4 shows the analyses of Hay (1966) and Surdam and Sheppard (1978). Table 4 also shows the composition of the phillipsite and rhyolitic glass calculated to the Barth Standard Cell. The phillipsite composition from Hay (1966) was derived from a chemical analysis of phillipsite from the third youngest tuff bed at Teels Marsh which occurs at a depth of 2.3 m. The composition of phillipsite and rhyolitic glass (Surdam and Sheppard, 1978) are from microprobe analyses of these materials from the upper tuff bed at Teels Marsh. Based on Barth Standard Cell calculations, the reaction of rhyolitic glass to phillipsite at Teels Marsh involves a loss of silica and calcium and a gain of sodium and potassium.

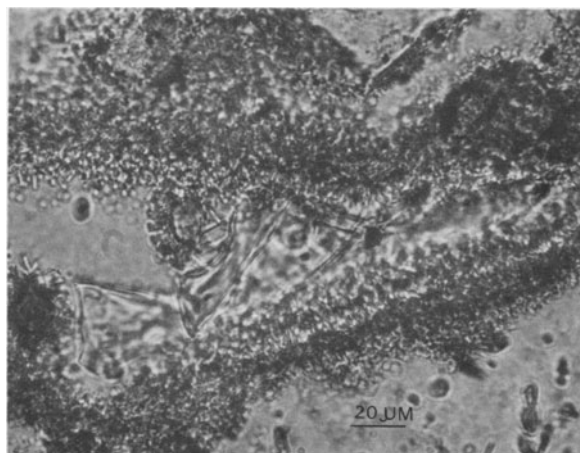


Figure 9. Photomicrograph of glass shard (center of picture) surrounded by gelatinous material (ropy texture, isotropic, density less than 2) and phillipsite apparently growing from gel (lath-like crystals). Unpolarized light.

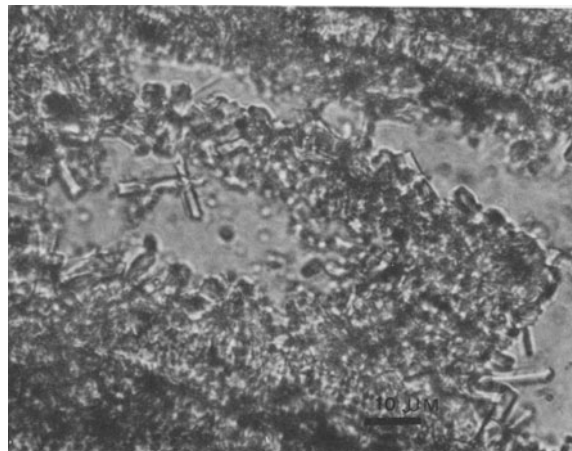


Figure 10. Photomicrograph of phillipsite (laths) apparently growing from gelatinous material (ropy texture). Unpolarized light.

The phillipsite from Teels Marsh examined in this study has an average Si/Al atomic ratio of 3.3 to 3.4. This phillipsite occurs in association with brines ranging in pH from 9.1 to 10.1. Hay (1964, 1966) described phillipsite from Teels Marsh with an average Si/Al ratio of 3.0 in association with brines ranging in pH from 9.1 to 9.4. The phillipsite synthesized by Mariner and Surdam (1970) came from a gel with a Si/Al ratio of 3.4 in a solution having a pH of 9.1.

### Silica solubility

The brines at Teels Marsh are high in alkalis ( $\text{Na}^+$ ,  $\text{K}^+$ ) and low in alkaline earths and silica (Surdam and Sheppard, 1978; Taylor, 1978, Figure 8). The low silica concentration in an alkaline brine is noteworthy, es-

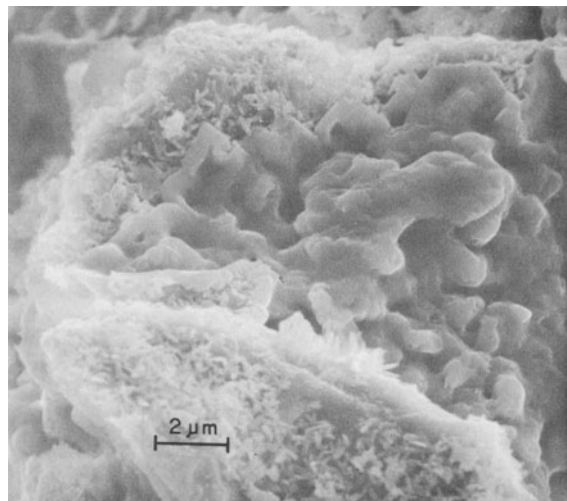


Figure 11. Scanning electron micrograph of a partially dissolved glass shard. Phillipsite laths on outside of the shard.

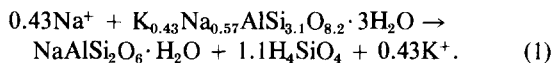


pecially because the alkaline brines involved in hydrating the rhyolitic glass release silica into solution (Table 4). The lack of silica in the brines has been explained by the presence of abundant boron in the brines and the presence of searlesite in the sediments. Surdam and Sheppard (1978) suggested that the boron content of the brines at Teels Marsh is high enough that the precipitation of searlesite effectively controls the silica content of the brines.

THERMODYNAMIC DATA

The equilibrium constant (K<sub>eq</sub>) for the reaction phillipsite → analcime and the free energy value (ΔG) for phillipsite can be estimated using the chemical data and mineral reaction described in this paper. Figure 12 shows the activity ratios of brine samples that are associated with the upper tuff bed at Teels Marsh plotted on a stability-field diagram of phillipsite and analcime. An important factor in dealing with supersaline solutions is the increased possibility of complexing. For this reason, a computer program was written to calculate the molalities and activities of several ions correcting for complexing in the brines.<sup>2</sup>

A linear regression on the hydrogen-normalized sodium vs. potassium data for phillipsite and analcime determined the stability-field boundary between phillipsite and analcime (Figure 12). The slope of the line is 1.0, and the γ-intercept is 2.94. A stoichiometric equation for the reaction phillipsite → analcime is:



The equilibrium constant (K) for this reaction is:

$$K = [a(\text{H}_4\text{SiO}_4)^{1.1}][a_{\text{K}^+}^{0.43}]/[a_{\text{Na}^+}^{0.43}] \quad (2)$$

Figure 12 suggests that [Na<sup>+</sup>] and [K<sup>+</sup>] strongly affect the reaction of phillipsite → analcime. As discussed

<sup>2</sup> See Taylor (1978) for a description of program.

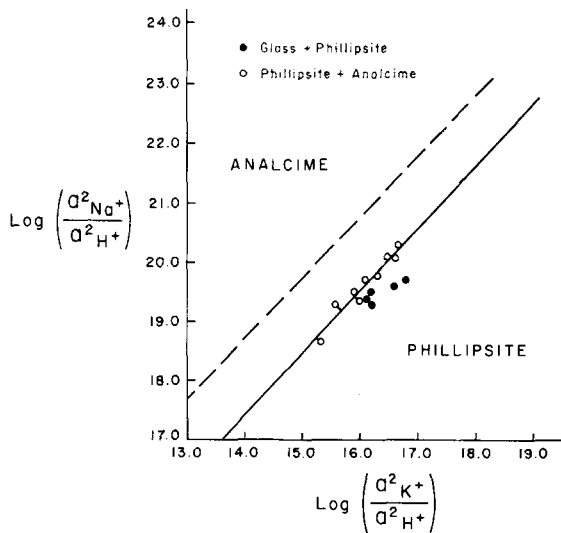


Figure 12. Stability diagram for analcime and phillipsite in system K<sub>2</sub>O-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O at 25°C and 1 atm pressure (Garrels and Mackenzie, 1971). The activity ratios of interstitial brines from Teels Marsh are plotted on diagram. The solid line was determined by linear regression. The dashed line is from Garrels and MacKenzie (1971) for the reaction analcime → K-feldspar. (The correlation coefficient for the linear regression is 0.979.)

above, the silica concentration of the brines is relatively constant with time.

Using Eq. (2) and assuming that the a<sub>H<sub>4</sub>SiO<sub>4</sub></sub> = constant = 2.94 × 10<sup>-4</sup> M, it follows that:

$$K' = (a_{\text{K}^+})^{0.43}/(a_{\text{Na}^+})^{0.43} \quad (3)$$

$$\text{or } \log K' = 0.43 \log a_{\text{K}^+} - 0.43 \log a_{\text{Na}^+} \quad (4)$$

$$\text{or } \log K' = 0.43 \log(a_{\text{K}^+}/a_{\text{H}^+}) - 0.43 \log(a_{\text{Na}^+}/a_{\text{H}^+}) \quad (5)$$

$$\text{Thus, } \log(a_{\text{Na}^+}/a_{\text{H}^+}) = \log(a_{\text{K}^+}/a_{\text{H}^+}) - \log K'/0.43 \quad (6)$$

To compute K' using the γ-intercept from Figure 12, the variables must be in the proper form. Thus, Eq. (6) must be multiplied by 2. It follows that:

Table 4. Chemical analyses of rhyolitic glass and phillipsite from Holocene tuffs at Teels Marsh.

Oxide	Chemical Analyses (wt. %)			Element	Barth Standard Cell	
	Rhyolitic glass <sup>1</sup>	Phillipsite <sup>1</sup>	Phillipsite <sup>2</sup>		Rhyolitic glass	Phillipsite <sup>3</sup>
SiO <sub>2</sub>	77.2	56.7	56.58	Si	66.6	41.6
Al <sub>2</sub> O <sub>3</sub>	12.6	15.3	15.15	Al	12.8	12.8
Fe <sub>2</sub> O <sub>3</sub>	1.2	1.2	1.25	Fe	0.7	0.7
CaO	1.2	0.1	0.40	Ca	1.1	0.1
Na <sub>2</sub> O	3.5	5.5	5.25	Na	5.7	7.6
K <sub>2</sub> O	4.2	6.2	6.13	K	4.7	5.6
Σ Oxides	99.2		99.95	Σ Oxygen	160	

<sup>1</sup> Microprobe analysis from Surdam and Sheppard (1978).

<sup>2</sup> Chemical analysis from Hay (1966).

<sup>3</sup> Calculated with respect to the Al content of rhyolite Barth Standard Cell, from Surdam and Sheppard (1978).

Table 5.  $a_{\text{Na}^+}/a_{\text{K}^+}$  ratios for interstitial brine.

Sample	$\gamma_{\text{Na}^+}$	$a_{\text{Na}^+}$	$a_{\text{K}^+}$	$a_{\text{Na}^+}/a_{\text{K}^+}$
2A	0.49	29,700	851	35
2B	0.54	42,800	1160	37
2C	0.48	33,800	879	38
2D	0.56	63,500	1770	36
2E	0.53	49,700	1480	34
2F	0.59	63,700	1790	36
2G	0.36	13,800	915	15
2H	0.49	54,700	3030	18
2I	0.43	40,500	1490	27
2J	0.42	40,700	1570	26
2N	0.28	18,700	900	21
2O	0.36	39,800	2320	17
2P	0.36	36,800	1150	32
2Q	0.38	44,400	1570	28
2V	0.41	42,300	1110	38
2W	0.41	42,300	1010	42
2X	0.39	43,200	1450	30

$$2 \log(a_{\text{Na}^+}/a_{\text{H}^+}) = 2 \log(a_{\text{K}^+}/a_{\text{H}^+}) - 2 \log K'/0.43, \quad (7)$$

$$\text{or } \log(a_{\text{Na}^+}/a_{\text{H}^+})^2 = \log(a_{\text{K}^+}/a_{\text{H}^+})^2 - 2 \log K'/0.43, \quad (8)$$

$$\text{then } y \text{ intercept} = -2 \log K'/0.43 = 2.94 \text{ and } (9)$$

$$\log K' = -6.63. \quad (10)$$

$$\text{Thus, } \log K' = -0.63, \text{ or } K' = 0.234. \quad (11)$$

$$\text{Thus, } K = 1.234(a_{\text{H}_4\text{SiO}_4})^{1.1} = 3.04 = 10^{-5}, \quad (12)$$

$$\text{and } \Delta G^0 \text{ of reaction (1)} = -(0.001987)(298)(2.303) \\ \cdot \log(3.04 \times 10^{-5}) \\ = +6.16 \text{ kcal/mole.} \quad (13)$$

The computation of  $\Delta G^0$  for phillipsite is as follows:

$$\Delta G^0_{\text{reaction (1)}} = (\Delta G^0_{\text{analcime}} + 1.1\Delta G^0_{\text{H}_4\text{SiO}_4} + 0.43\Delta G^0_{\text{K}^+}) \\ - (\Delta G^0_{\text{phillipsite}} + 0.43\Delta G^0_{\text{Na}^+}), \quad (14)$$

$$\text{then } \Delta G^0_{\text{phillipsite}} = \Delta G^0_{\text{analcime}} + 1.1\Delta G^0_{\text{H}_4\text{SiO}_4} + 0.43\Delta G^0_{\text{K}^+} \\ - 0.43\Delta G^0_{\text{Na}^+} - \Delta G^0 \text{ of reaction (1).} \quad (15)$$

Using the free energy values for  $\text{H}_4\text{SiO}_4$ ,  $\text{K}^+$ , and  $\text{Na}^+$  from Garrels and Christ (1965) and for analcime from Robie and Waldbaum (1968), it follows that:

$$\Delta G^0_{\text{phillipsite}} = (-734.26 - 330.33 - 29.01 + 26.91 - 6.16) \\ \text{kcal/mole,} \\ = -1072.85 \text{ kcal/mole (1 atm, } 25^\circ\text{C)} \quad (16)$$

Possible errors in the above calculations are: (1) the assumption that the activity coefficient of  $\text{K}^+$  is the same as for  $\text{Na}^+$  (the activity coefficient of  $\text{Na}^+$  was measured directly by specific-ion electrode); (2) the assumption that the activity of silica is constant; (3) the determination of best fitting line for the reaction boundary from Figure 12; (4) the assumption that analcime is

stoichiometric; (5) the experimental error related to sample collection and to measuring activity coefficients with specific-electrode equipment; (6) the unaccounted-for complexation; (7) the assumption that thermodynamic equilibrium was established between phases.

The above discussion leads to an important insight into the formation of zeolites in saline, alkaline-lake deposits. By using Eqs. (3) and (11) it is possible to compute the  $(a_{\text{Na}^+}/a_{\text{H}^+})$  ratio necessary to convert phillipsite to analcime at Teels Marsh. From Eqs. (3) and (11),

$$K' = (a_{\text{K}^+}/a_{\text{Na}^+})^{0.43} = 0.234, \text{ or } (17)$$

$$\log 0.23 = -0.63 = 0.43 \log(a_{\text{K}^+}/a_{\text{Na}^+}), \text{ or } (18)$$

$$\log(a_{\text{Na}^+}/a_{\text{K}^+}) = 1.47, \text{ and } (19)$$

$$a_{\text{Na}^+}/a_{\text{K}^+} = 10^{1.47}, \text{ or in mole ratio } (20)$$

$$\text{Na}^+/\text{K}^+ = 30. \quad (21)$$

The activity ratios listed in Table 5 suggest that many of the brines associated with the upper tuff are in equilibrium or oversaturated with respect to analcime. Furthermore, from Figure 12 there is some suggestion that the brines actually are in equilibrium with K-feldspar. In other words, what we may be observing presently at Teels Marsh are precursors to the ultimate reaction products suggesting that the reactions are controlled by kinetics rather than thermodynamic equilibrium.

#### SYNOPSIS OF ZEOLITIC REACTIONS

1. The principal zeolite-forming reaction at Teels Marsh is: rhyolitic glass + alkaline  $\text{H}_2\text{O} \rightarrow$  hydrous alkali aluminosilicate gel  $\rightarrow$  phillipsite.
2. The upper ash bed, particularly in those portions of the Marsh characterized by highly saline and alkaline waters, commonly is completely altered to phillipsite in 1000 years.
3. In some parts of the Marsh, analcime has begun to form as a result of the reaction of phillipsite with  $\text{Na}^+$ -rich brines. A stoichiometric equation for this reaction is:  $0.43\text{Na}^+ + \text{K}_{0.43}\text{Na}_{0.57}\text{AlSi}_{3.1}\text{O}_{8.2} \cdot 3.2\text{H}_2\text{O} \rightarrow \text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O} + 1.1\text{H}_4\text{SiO}_4 + 0.43\text{K}^+$ .
4. Using the above reaction, the estimated  $\Delta G^0$  of phillipsite forming at Teels Marsh, Nevada, is  $-1072.8$  kcal/mole at  $25^\circ\text{C}$  and 1 atm pressure.

#### ACKNOWLEDGMENTS

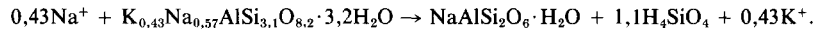
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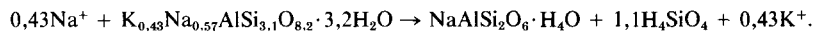
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**Резюме**—Наиболее рельефной аутигенной реакцией в голоценовых туфовых осадках в Тиилс Марш, Невада является гидратация риолитового стекла трещинной соленой водой и последующее образование филлипсита. Эта реакция протекает следующим образом: риолитовое стекло + H<sub>2</sub>O → воднощелочный алюмосиликатный гель → филлипсит. Филлипсит является наиболее распространенной аутигенной фазой в туфовых осадках (>95%), за ним идет анальцит, тогда как следы клиноптилолита появляются во фракции размером <2 мм. Анальцит образуется путем реакции филлипсита и Na<sup>+</sup>. Гейлюсит и сирлесит являются также популярными аутигенными фазами в Тиилс Марш. Концентрация кремнезема в трещинных соленых водах контролируется одной или более аутигенными реакциями при менее чем 100 миллионных. Стехиометрическое уравнение для реакции преобразования филлипсита в анальцит:



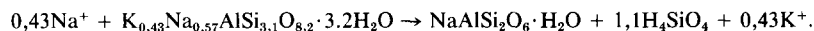
Натриевые и калиевые активности соленой воды, связанные с обоими, филлипситом и анальцитом, были использованы для определения константы равновесия для этой реакции, равной  $3,04 \times 10^{-5}$ . Величина  $\Delta G^0$  для реакции равна +6,2 ккал/моль при 25°C и давлении 1 атм. Величина  $\Delta G^0$  для филлипсита, определенная при использовании этой реакции, равна -1072,8 ккал/моль при 25°C и 1 атм. [E.C.]

**Resümee**—Die wichtigste authigene Reaktion in holozänen tuffhaltigen Sedimenten von Teels Marsh, Nevada, ist die Hydratation von Rhyolithglas durch Porenlösungen und die darauf folgende Bildung von Phillipsit. Diese Reaktion verläuft folgendermaßen: Rhyolithglas + H<sub>2</sub>O → wasserhaltiges Alkali-Alumosilikat-Gel → Phillipsit. Phillipsit ist die häufigste authigene Phase in den tuffhaltigen Sedimenten (>95%), Analcim ist die nächsthäufige Phase. Klinoptilolith kommt nur in Spuren in der Fraktion <2 mm vor. Analcim bildet sich durch die Reaktion von Phillipsit mit Na<sup>+</sup>. Gaylussit and Searlesit sind ebenfalls authigene Phasen in Teels Marsh. Die Konzentration an Siliziumdioxid in den Porenlösungen wird durch eine oder mehrere der authigenen Reaktionen kontrolliert und beträgt weniger als 100 ppm. Eine stöchiometrische Gleichung für die Reaktion von Phillipsit zu Analcim in Teels Marsh lautet:



Die Natrium- und Kaliumaktivitäten der Porenlösungen, die sowohl mit Phillipsit als auch mit Analcim im Gleichgewicht stehen, wurden verwendet, um die Gleichgewichtskonstante für diese Reaktion abzuschätzen. Sie beträgt  $3,04 \times 10^{-5}$ . Der  $\Delta G^0$ -Wert für die Reaktion beträgt +6,2 kcal/mol bei 25°C und 1 atm Druck. Der geschätzte  $\Delta G^0$ -Wert von Phillipsit beträgt, bei Verwendung dieser Reaktion, -1072,8 kcal/mol bei 25°C und 1 atm. [U.W.]

**Résumé**—La réaction authigénique la plus proéminente dans les sédiments holocènes tufacés à Teels Marsh, au Nevada, est l'hydratation du verre rhyolitique par des saumures interstitiales et la formation ultérieure de phillipsite. Cette réaction a la forme suivante: verre rhyolitique + H<sub>2</sub>O → gel alkali aluminosilicate hydré → phillipsite. La phillipsite est la phase authigénique la plus abondante dans les sédiments tufacés (>95%), suivie par la phase analcime, seconde en abondance, et la clinoptilolite apparaît comme trace minérale dans la fraction <2 mm. L'analcime est produite par la réaction de phillipsite et de Na<sup>+</sup>. La gaylussite et la searlesite sont aussi des phases authigéniques courantes à Teels Marsh. La concentration de silice dans les saumures interstitiales est contrôlée par une ou plusieurs réactions authigéniques à moins de 100 ppm. Une équation stœchiométrique pour la réaction de phillipsite en analcime à Teels Marsh est:



Les activités du sodium et du potassium des saumures avec à la fois la phillipsite et l'analcime ont été employées pour estimer comme constante d'équilibre pour cette réaction  $3,04 \times 10^{-5}$ . La valeur  $\Delta G^0$  pour la réaction est +6,2 kcal/mole à 25°C et à 1 atm de pression. La valeur estimée de  $\Delta G^0$  pour la phillipsite, utilisant cette réaction, est -1072 kcal/mole à 25°C et 1 atm. [D.J.]