

PHILLIPSITE OF SALINE LAKES AND SOILS

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ABSTRACT

Phillipsite has formed from volcanic glass in saline, alkaline lakes both saturated and undersaturated with respect to gaylussite and trona. It has also formed from volcanic glass in saline, alkaline soils of Olduvai Gorge, Tanganyika. Phillipsite occurs both as lath-shaped and as equant crystals, which are commonly zoned with refractive indices ranging between 1.438 and 1.490. Molecular $\text{SiO}_2/\text{R}_2\text{O}_3$ ratios are 5.1 for analyzed phillipsite of trachytic origin and 6.0 to 6.7 for rhyolitic phillipsite. All analyzed phillipsites are high in alkali ions and very low in alkaline-earth ions. Phillipsite occurs in seemingly compatible association with authigenic analcime, searlesite, K-feldspar, clinoptilolite, erionite, chabazite, natrolite, and dawsonite.

Phillipsite can form in a few hundred years, and a few thousand years are sufficient for complete zeolitic alteration of tuff beds. Optimum conditions for the rapid formation of phillipsite from volcanic glass appear to be a pH above 9 and a Na/K ratio between 10 and 50. Hydration and a large loss of silica are involved in forming phillipsite from rhyolitic glass. Phillipsite similar to that of saline lakes can be synthesized in the laboratory under conditions rather closely paralleling the saline-lake environment.

Dominance of phillipsite over clinoptilolite in saline, alkaline lakes may reflect a low activity of silica, and clinoptilolite appears to be favored over phillipsite where the activity of silica is high. Absence of heulandite in deposits of saline, alkaline lakes may reflect the very low activity of Ca^{2+} in this environment.

INTRODUCTION

Desert lakes and soils are ideal natural environments for studying low-temperature silicate equilibria in sodium-rich alkaline solutions. Volcanic glass, quartz, calcic plagioclase and nepheline are among the materials known to decompose in saline, alkaline solutions (Hay, 1963a; Hay and Moiola, 1963), and zeolites, borosilicates and K-feldspar are among the silicate minerals that form in this environment. The present study is largely concerned with the phillipsite formed from volcanic glass in the saline, alkaline environment. Virtually no published data are available on the relationship of zeolite mineralogy to water composition, hence several examples are presented here of phillipsite and associated zeolites that were formed in environments where the water composition is either known or can be inferred.

OCCURRENCE OF PHILLIPSITE

Lake Deposits with Saline Minerals.

(1) *Searles Lake, California* Authigenic phillipsite forms 80 to 90 per cent of the rhyolitic tuff laminae interbedded with gaylussitic clays of the late Pleistocene Parting Mud and Lower Salt. Phillipsite was earlier re-

ported at depths of 67 to 106 feet (Hay and Moiola, 1963), and two tuff laminae altered to phillipsite were later found near the top of the Parting Mud at a depth of 46.7 feet in the core of U. S. Geological Survey drill hole GS-27. Traces of analcime were noted in non-tuffaceous clays interbedded with salines of the Upper Salt, which overlies the Parting Mud. Authigenic K-feldspar and smaller amounts of analcime and searlesite occur in rhyolitic tuffs and clays of the Bottom Mud and Mixed Layer, from depths of 150 feet to the bottom of the hole at 875 feet. Saline minerals are common in clays of the Bottom Mud, and the Mixed Layer consists largely of pirssonite, gaylussite, trona and halite. Glass has been entirely altered in all of the ash layers of Searles Lake that were identified.

(2) *China Lake, California* Phillipsite is the principal authigenic silicate mineral in late Pleistocene tuffaceous layers throughout the entire 700-foot core length of U. S. Geological Survey core MD-1, taken from China Lake, California (Smith and Pratt, 1957). This core is nearly three-quarters clay and about one-quarter sand. Gaylussite is abundant in the core interval from 120 to 200 feet (Smith and Pratt, 1957), and crystals of gaylussite are sparsely disseminated in one-fourth of the samples from the underlying 500 feet of beds.

Fourteen zeolitized rhyolitic tuffs totalling 25.5 cm were identified by Moiola and the writer at various depths between 68 and 548 feet. Phillipsite occurs alone or predominates in 9 tuffs; clinoptilolite predominates in 3 tuffs and searlesite in two. Erionite and clinoptilolite are minor constituents in several samples of tuff. Analcime forms 5–10 per cent of most clays at depths of 0–155 feet and 550–700 feet; phillipsite, erionite and clinoptilolite are common in clays and sandstones from 266 to 550 feet. Analcime-bearing clays appear non-tuffaceous, except for those at depths of 70 and 101 feet, which contain pumice fragments altered to phillipsite.

(3) *Teels Marsh, Nevada* Phillipsite is abundant in rhyolitic tuffs and tuffaceous clays of Teels Marsh, a salt-crustated playa in western Nevada (Fig. 1). The sediments were sampled to depths of 10 to 20 feet in six places with a barrel-type soil auger, and in about 30 pits 1 to 2 feet deep. Reddish-brown playa clays constitute most of the upper 8 to 10 feet of the section, which is underlain by greenish-gray and black lacustrine muds rich in hydrogen sulfide. Gaylussite crystals are abundant in three quarters or more of the samples collected, and gaylussite molds are present in most of the remainder. A trona crust 2 mm to 1 cm thick covers most of the western half of the playa.

Eight or more vitric rhyolitic tuffs $\frac{1}{2}$ to 5 inches thick occur at various depths between 1 foot and 16 feet. These range from unconsolidated fresh ash to hard, completely zeolitized tuff. Phillipsite is the only authigenic

silicate mineral in most of the tuffs and clays, but a small number of tuff samples contain only searlesite. Searlesite, clinoptilolite and analcime are associated with phillipsite in a few samples. No difference in degree of mineralogy of alteration is apparent between tuffs of the playa sequence and those interbedded with black lacustrine clays.

Both the deep and the shallow tuffs vary laterally from fresh to completely zeolitized. The uppermost tuff, 6 to 15 inches below the surface, is partly or completely altered in the part of the playa that is thickly en-

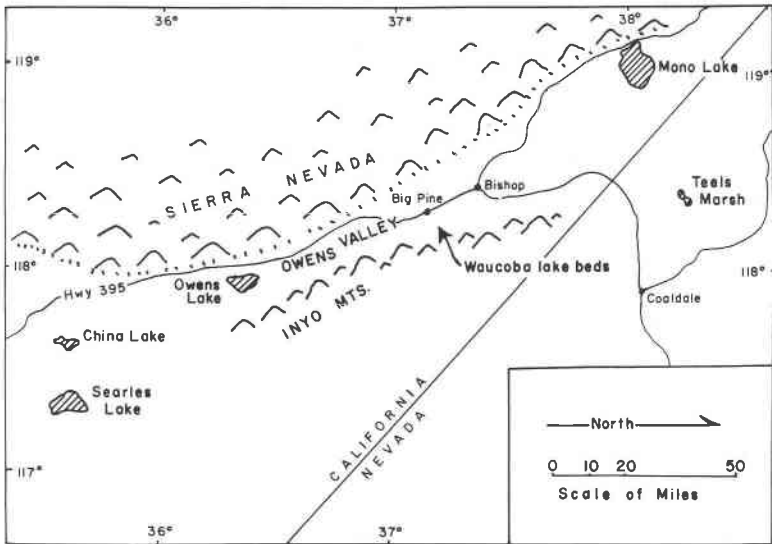


FIG. 1. Index map of east-central California and west-central Nevada.

crusted with trona and is fresh at the playa margin and in the eastern half of the playa, where salt efflorescences are either absent or thin. The uppermost tuff and another tuff two inches lower were sampled in detail over a trona-crust area of about three acres in the northwest corner of the playa. Here the thickness of the upper tuff is $\frac{3}{4}$ to $1\frac{1}{2}$ inches and of the lower tuff 2 to 5 inches. Over most of the three-acre area the upper tuff is slightly altered and the lower tuff is completely zeolitized; locally the upper tuff is totally altered and the lower tuff largely fresh. Transitions between fresh and zeolitized tuff commonly take place over distances of only a few millimeters.

(4) *Lake Magadi, Kenya* Zeolites are the principal constituents of reworked tuffaceous layers interbedded with trona in core samples from depths of 7 to 173 feet in the late Pleistocene and Recent sediments of

Lake Magadi, Kenya. Logs of the drill core are given by Baker (1958), and the zeolites are briefly mentioned by Hay (1963b). Erionite is the principal zeolite, and smaller amounts of clinoptilolite, phillipsite and chabazite are present in some of the 17 samples that were x-rayed. Sanidine, anorthoclase and aegirine-augite in the tuffaceous layers suggest that they were originally trachytic. Erionite and analcime have crystalline textures in the two coarsest of the zeolitic samples, and delicate pumice fragments replaced by erionite are visible in one of the two, thus indicating an authigenic origin for these zeolites. The zeolites in the other samples are probably authigenic although textural evidence is lacking.

Lake Deposits Lacking Saline Minerals.

(1) *Owens Lake, California* Zeolites occur in U. S. Geological Survey drill core No. 1 of Owens Lake, California, which is 920 feet long and consists largely of clay (Smith and Pratt, 1957). No saline minerals have been recognized in the core, although trona and gaylussite are present on the lake floor, where they were formed after diversion of the Owens River in 1913. This zeolite occurrence is rather similar to that of China Lake, 45 miles to the southeast, except for the fact that zeolites are apparently confined to depths of 366 to 650 feet, and unaltered rhyolite shards and pumice fragments are present in most of the sands and clays above and below the zeolitic interval. Phillipsite is the principal zeolite, which replaces the glass of a rhyolite tuff, weakly cements tuffaceous sandstones, and is disseminated in tuffaceous clays. Clinoptilolite and erionite are only slightly less common than phillipsite in the clays, and analcime is rare.

Formation of zeolites in the core interval from 366 to 650 feet probably reflects an episode when the lake contained saline, alkaline water much like that existing prior to the diversion of Owens River (Gale, 1915, p. 258). Glass is unaltered in the beds above and below the zeolitic interval probably because these sediments were deposited in essentially fresh water. Cyclic fluctuation from fresh to saline is in accord with the known pluvial-interpluvial Pleistocene history of Owens, China, and Searles lakes (Gale, 1915; Flint and Gale, 1958).

Zeolites should be expected near the surface of the core, in the post-Pleistocene sediments deposited after Owens Lake had again become saline and alkaline. Unfortunately, the U. S. Geological Survey recovered very little core from the uppermost 45 feet of sediments, and additional sampling is necessary to prove or disprove the occurrence of zeolites in the near-surface sediments.

(2) *Waucoba Lake beds, California* Rhyolite tuffs are replaced by phillipsite in the early Pleistocene (?) Waucoba Lake beds near Big Pine,

about 50 miles north of Owens Lake (Fig. 1). The exposed sequence, briefly described by Walcott (1897) and Knopf and Kirk (1918), is 250 to 300 feet thick and consists largely of siltstone and sandstone. Also included are about a dozen rhyolite tuffs half an inch to one-foot thick.

The Waucoba Lake beds are the deposits of a lake, and its influent streams, that lay in the Owens Valley east of the Sierra Nevada. This was prior to mid-Pleistocene (?) deformation that elevated the Inyo Moun-

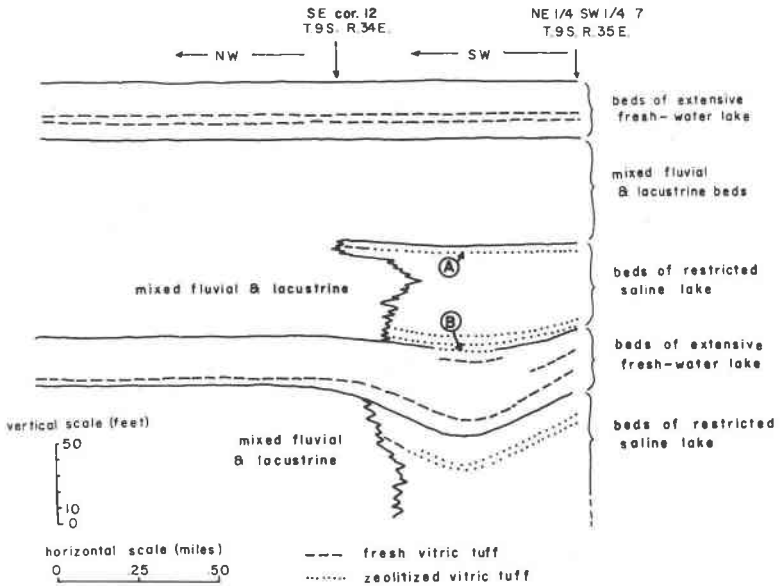


FIG. 2. Diagram showing relationship of zeolitic alteration to sedimentary facies in the Waucoba lake beds near Big Pine, California.

tains and tilted the lake beds, exposing them to erosion. While this lake existed, it fluctuated in size and salinity. Silt deposits of a large, shallow fresh-water lake can be recognized at two horizons (Fig. 2), and evenly bedded unaltered rhyolite tuffs, apparently undisturbed by waves and currents, can be traced widely in the silt sequences. Pelecypods and gastropods in the lower widespread unit of lacustrine silts are diagnostic of a fresh-water environment (J. Firby, 1963, pers. comm.).

Deposits of a small saline lake overlie and underlie the lower unit of fresh-water deposits. Here the lacustrine silts and tuffs were largely confined to a small closed basin at the foot of the Inyo Mountains. Molluscan fossils are generally absent, and rhyolite tuffs are almost entirely replaced

by zeolites. Phillipsite is the only zeolite in 9 of the 11 samples *x*-rayed, and clinoptilolite occurs together with phillipsite in the other two.

Slight discrepancies exist between the pattern of zeolitic alteration and the former limits of the saline lake as inferred on faunal and stratigraphic grounds. Two tuffs of the saline lacustrine facies are locally unaltered at the western margin of the basin (Fig. 2), possibly reflecting either a depositional site near the mouth of a fresh-water stream or the influx of fresh subsurface water after burial. Several species of fresh-water gastropods, identified by J. Firby, were found in a zeolitized tuff bed similar to those of the saline facies (Fig. 2; tuff bed of sample B). This tuff bed lies at the top of the fresh-water sequence, and relatively heavy saline water of the succeeding saline lake would only need to have displaced fresh water from a few feet of sediments in order to saturate the gastropod-bearing tuff.

Owens Lake and the pre-existing Waucoba Lake lie in the same structural trough, and they received most of their water from the Sierra Nevada to the west and the Inyo Mountains to the east. Source rocks for dissolved ions of the two lakes were almost the same, hence the waters of the two lakes should have been similar in their overall chemical character, and the water of Waucoba Lake during its saline phases was very likely alkaline and rich in dissolved sodium carbonate and bicarbonate, as Owens Lake is today.

(3) *Lacustrine facies of Bed II, Olduvai Gorge* Zeolitized trachyte tuffs occur throughout the extent of the lacustrine facies of Bed II, a mid-Pleistocene stratigraphic unit exposed in Olduvai Gorge, Tanganyika. The lacustrine sequence, about 100 feet thick, consists largely of unfossiliferous, locally pyritic clays but also contains trachyte tuffs, dolomites, limestones and chert nodules (Hay, 1963c). Vitric trachyte tuffs of the lacustrine facies of Bed II are totally altered, but nearby laterally equivalent land-laid and fluvial tuffs are fresh except where they have been weathered at the land surface (Hay, 1963a). Lacustrine tuffs are characteristically altered to phillipsite, K-feldspar, or to both. Searlesite, analcime and clinoptilolite were noted in a very few samples.

The lake of Bed II occupied a closed basin and was moderately or strongly saline for much of its history (Hay, 1963c). Sodium carbonate and bicarbonate were among the principal dissolved components, judging from the fact that these ions predominate in present-day lakes of the same region. Saline water rich in sodium carbonate now seeps from the lake beds into the sides of the gorge.

Saline Soils of Olduvai Gorge. Zeolites and dawsonite have formed at the land surface in the sides of the Olduvai Gorge and over the adjacent part

of the Serengeti Plain (Hay, 1963a). Phillipsite weakly cements a few feet of Recent nephelinite ash which lies in the gorge, and wind-worked nephelinite tuffs of Bed V, of very late Pleistocene or Recent in age, are thoroughly zeolitized. Phillipsite is the principal zeolite in the nephelinite tuffs and it is often accompanied by chabazite, analcime, natrolite and dawsonite. Natrolite and dawsonite have probably formed from the nepheline; the other zeolites are alteration products of nephelinite glass. Sodicy trachyte tuffs of Bed I are widely zeolitized to depths of 1 to 25 feet in the sides of the gorge. Phillipsite is the principal zeolite; erionite and chabazite are not uncommon, and locally they predominate.

Olduvai Gorge is hot and dry for most of the year. Sodium carbonate and bicarbonate have been extensively concentrated at the land surface by evapo-transpiration. Samples of soil and rock commonly give a pH of 9.5 to 10.6 when dispersed in water, and efflorescences of sodium carbonate and bicarbonate are common over outcrops of tuff.

Zeolites were formed twice at the land surface in the Olduvai region, during Pleistocene time before the gorge was eroded (Hay, 1963a). Both of these episodes of zeolitic alteration coincide with unusually dry periods, and they probably reflect saline, alkaline soils similar to those of the present. Except for a greater abundance of analcime and chabazite, these two earlier occurrences are mineralogically similar to the late Pleistocene and Recent zeolitic alteration.

DESCRIPTION OF PHILLIPSITE

Petrographic Relationships. Phillipsite characteristically occurs as a cement in tuffaceous sandstones and partly altered tuffs. Shards and pumice fragments in partly altered tuffs are usually much corroded, and the volume of zeolite in these beds appears to be of the same order of magnitude as the volume of dissolved glass. Totally altered tuffs consist of densely intergrown phillipsite crystals, and these rocks are usually hard, have a chalk-like texture, and are white, very pale orange or yellowish-gray. Vitroclastic textures are absent in most of the fine-grained zeolitized tuffs, but the coarser tuffs commonly contain molds of coarse shards that are either empty or lined with zeolite crystals (*cf.* Hay, 1963b, Pl. 2b). Phillipsite permeates non-tuffaceous clays and sandstones adjacent to ash layers, for distances of 0.5 to 3.0 mm.

Size, Shape, and Physical Properties. The phillipsite of saline lakes and soils occurs both as lath-shaped and as roughly equant crystals. The crystals of both habits are generally .005 to .015 mm long, and the largest crystals observed are about .05 mm long. Shapes of rhyolitic phillipsite

crystals have a curious distribution pattern. All of the phillipsite in Searles Lake is lath-shaped, whereas that of the Waucoba Lake beds is entirely equant. In Owens and China lakes, equant crystals characterize most of the tuffs, and lath-shaped crystals predominate in tuffaceous sandstones and in pumice fragments isolated in clays. Tuffs of Teels Marsh contain both lath-like and equant crystals. The phillipsite of trachyte and nephelinite tuffs is characteristically lath-shaped. Most of the phillipsite appears isotropic, but a little is weakly birefringent. The

TABLE 1. d-SPACINGS OF PHILLIPSITE FROM SALINE LAKES¹

(1)		(2)	
Å	Intensity	Å	Intensity
8.15	2	8.12	3
7.08	10	7.08	8
5.34	3	5.34	5
4.99	4	5.01	5
4.28	1	4.26	6
4.08	2.5	4.08	4
		3.24 } dblt.	7
3.65	1	3.23 }	
3.24	5		
3.17	10	3.17	10
2.93	2.5	2.93	4
2.73	2.5	2.72	3
2.54	1	2.67	3
		2.54	

¹ Quartz was used as an internal standard for calibration.

(1) Phillipsite from China Lake (Table 3, Anal. 2).

(2) Phillipsite from Waucoba lake beds (Table 3, Anal. 4).

d-spacings of saline-lake phillipsite (Table 1) differ somewhat from those of the coarse-grained phillipsite of basaltic rocks, but Taylor's ion-exchange experiments (1962) suggest that this difference may be due to different contents of exchangeable ions rather than to different Al-Si frameworks.

Refractive indices vary considerably, both between different habits and within single crystals. Most of the phillipsite crystals are zoned, with margins having the higher refractive index. Lath-shaped crystals have mean refractive indices of 1.472 to 1.484 (Table 2); equant crystals have mean indices of 1.462 to 1.470, with one exceptionally low value of 1.440. Crystals of equant habit are probably more siliceous than the lath-

shaped crystals, as they have lower refractive indices, are common in rhyolite ash deposits, scarce in trachyte tuffs, and absent in nephelinite ruffs.

Chemical Composition. Four chemical analyses (Table 3) were obtained of phillipsite separated from crystal-poor tuffs with heavy liquids. These

TABLE 2. HABIT AND REFRACTIVE INDICES OF SEDIMENTARY PHILLIPSITE

Sample location	Host rock	Habit	No. of samples	Refractive index		
				Inner zone	Outer zone	Mean
Searles Lake	rhyolitic tuff	lath-shaped	5	1.478-1.480±.002	1.484-1.490	1.480-1.482
China Lake	rhyolitic tuff	equant	4	1.458-1.470	1.470-1.474	1.466
	rhyolitic pumice in clay	lath-shaped	2	1.478	1.480-1.482	1.478-1.480
Teels Marsh	rhyolitic tuff	equant	1			1.438-1.442
		equant	1			1.464
		lath-shaped	1			1.475
Owens Lake	rhyolitic tuff	equant	1	1.466	1.472	1.470
Waucoba lake beds	rhyolitic tuff	equant	2	1.460	1.474-1.482	1.470
Olduvai Gorge (lacustrine facies, Bed II)	trachyte tuff	lath-shaped	2			1.478-1.480
Olduvai Gorge (non-lacustrine beds)	trachyte tuff	lath-shaped	6	1.466-1.474	1.474	1.472-1.474
		equant	1	1.460	1.482	1.470
	nephelinite tuff	lath-shaped	4	1.482	1.488	1.484
Total		lath-shaped	20			1.472-1.482
		equant	10			1.438-1.470

phillipsites are alkali-rich and more siliceous than the phillipsite of other origins (Fig. 3). Ferric iron may substitute for Al^{3+} in these phillipsites, judging from the fact that the molecular sum of MgO , CaO , Na_2O and K_2O slightly exceeds the mole fraction of Al_2O_3 in all four samples, but almost exactly equals the sum of Al_2O_3 and Fe_2O_3 in 3 of the 4 analyses. Part of the ferric iron in analysis No. 1 probably exists as free ferric oxide

TABLE 3. CHEMICAL ANALYSIS OF SEDIMENTARY PHILLIPSITE AND CHABAZITE FROM SALINE, ALKALINE ENVIRONMENTS

	Analysis 1			Analysis 2			Analysis 3			Analysis 4			Analysis 5		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
SiO ₂	54.56	54.16	.901	57.17	56.34	.938	60.44	58.95	.981	60.61	59.69	.993	50.6	.842	
Al ₂ O ₃	17.03	17.00	.167	14.92	15.22	.149	14.79	15.14	.148	14.54	14.70	.144	16.8	.165	
TiO ₂	.62	.66	(.008)	.10	(.001)	.157	.07	.07	(.001)	.05	.05	(.001)	.1	(.001)	.169
Fe ₂ O ₃	1.28	1.35	.008	1.22	1.28	.008	.88	.92	.006	.63	.67	.004	.6	.004	
FeO	.11	.12	(.002)	.24	.25	(.003)	.10	.11	(.002)	.10	.11	(.001)	0	—	
MgO	.55	.58	.014	.09	.09	.002	.59	.62	.015	.44	.47	.012	0	—	
CaO	.95	.70	.013	1.81	1.80	.032	1.42	1.37	.024	.82	.84	.015	1.35	.024	
Na ₂ O	5.18	4.92	.079	5.25	5.34	.086	3.69	3.72	.060	4.11	4.19	.067	8.88	.143	
K ₂ O	5.77	6.01	.064	3.49	3.53	.037	5.05	5.18	.055	5.34	5.25	.056	1.43	.015	
H ₂ O ⁺	5.90	6.25		7.04	7.37		6.35	6.68		6.43	6.85		19.43		1.080
H ₂ O ⁻	7.79	8.25		8.29	8.68		6.89	7.24		6.73	7.18				
CO ₂	.23			.07			.09			.02					
MnO	n.d.			n.d.			n.d.			n.d.			.5		
Total	99.97	100.00		99.69	100.00		100.36	100.00		99.82	100.00		99.68		
SiO ₂ /Al ₂ O ₃			5.4			6.3			6.8			6.9			2.6
SiO ₂ /Al ₂ O ₃ + Fe ₂ O ₃			5.1			6.0			6.4			6.7			2.5

Column (a) represents uncorrected analyses; (b) represents analyses corrected for contaminants; (c) represents mole ratios based upon corrected analyses (b).
 (1) Phillipsite from trachyte tuff of Bed II, Olduvai Gorge, Tanganyika, Y. Chiba, analyst. Analysis in column (b) is corrected for 5% feldspar (Al₂O₃) and .52% CaCO₃.
 (2) Phillipsite from rhyolite tuff at depth of 548.2 ft in the U. S. Geological Survey core of China Lake, California, Y. Chiba, analyst. In column (b), analysis is corrected for refractive index of phillipsite is 1.478 ± .002.
 (3) 2% quartz, 2% feldspar (average composition Ab₅₀Or₅₀) and 16% CaCO₃. Refractive index is 1.458 to 1.466.
 (4) Phillipsite of rhyolite tuff from Waucoba lake beds near Big Pine, California (Fig. 2, sample A; from C. SW 1 Sec. 7, T. 9 S., R. 35 E.), Y. Chiba, analyst. Analysis in column (b) is corrected for 3% quartz, 2% feldspar (Ab₅₀Or₅₀), and 21% CaCO₃. Refractive index ranges from 1.460 to 1.482.
 (5) Phillipsite of rhyolite tuff from Waucoba lake beds (Fig. 2, sample B; from same location as (3)), T. Mysson, analyst. Analysis in column (b) is corrected for 2% quartz, 4% feldspar (Ab₅₀Or₅₀), and .05% CaCO₃. Refractive index ranges from 1.460 to 1.474.
 (6) Chabazite of thin veins in non-lacustrine illite-montmorillonite clay of Bed II, Olduvai Gorge. Analyzed by R. N. Jack using x-ray emission spectrograph supplemented by flame photometer for K and Na. All iron shown as Fe₂O₃. Black iron-manganese oxides (?) stain a little of chabazite. Refractive index is 1.465.

which colors the tuff yellow. Molecular ratios of SiO_2 to R_2O_3 range from 5.1 for trachytic phillipsite to a maximum of 6.7 for rhyolitic phillipsite. This compares with the range of 2.6 to 4.4 accepted by Deer, Howie and Zussman (1963) for phillipsite.

Comparison with Marine Phillipsite. Phillipsite in sediments of the deep-sea floor characteristically forms elongate, prismatic crystals rather simi-

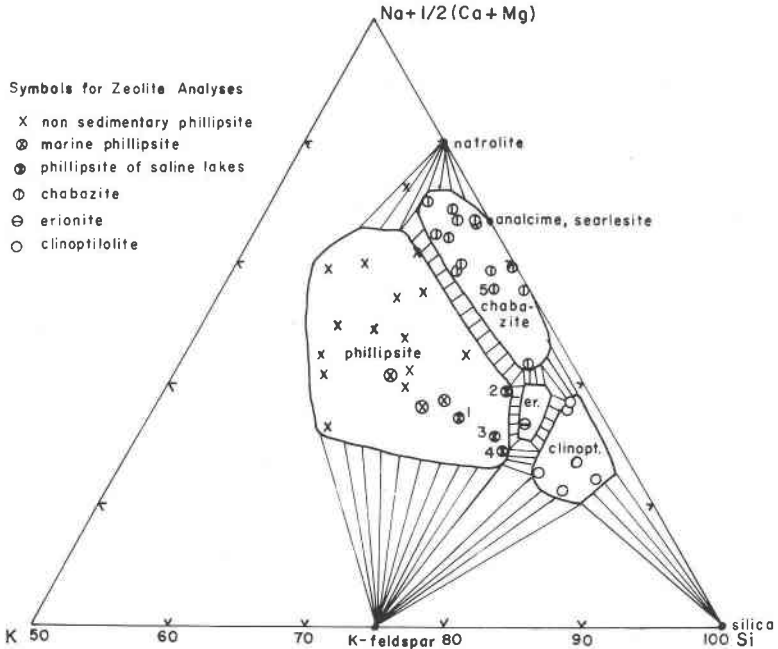


FIG. 3. Si-K- $\text{Na} + \frac{1}{2}(\text{Ca} + \text{Mg})$ compositional diagram for zeolites and associated silicate minerals known to form in saline, alkaline lakes and soils. Potentially co-existing minerals are connected by tie lines. Abbreviations are as follows: Er=erionite, and Clinopt.=clinoptilolite.

lar in shape to the lath-shaped crystals of saline lakes (Murray and Renard, 1891). Crystals of marine phillipsite average .03 mm in length, thus exceeding most crystals of saline lakes. Marine phillipsite crystals examined by the writer are zoned and have mean refractive indices of $1.484 \pm .003$.

The three published analyses of Murray and Renard seem to indicate a phillipsite richer in CaO and MgO and poorer in alkalis and silica than the phillipsite of saline lakes. Origin from basaltic glass may account for the lower silica content of the marine phillipsites.

Phase Relationships of Phillipsite. Phillipsite occurs in various associations with searlesite, K-feldspar, dawsonite, and five other zeolites (Table 4). In order to consider these associations from the standpoint of phase relationships, a ternary composition diagram (Fig. 3) has been pre-

TABLE 4. ZEOLITIC MINERAL ASSEMBLAGES OF TUFFS AND TUFFACEOUS CLAYS

Sample Location	Host Rock	Authigenic Minerals
Searles Lake	rhyolitic tuff	K*, P*, K+S*, K+A
China Lake	rhyolitic tuff	P*, P+C*, P+C+E, C+E, S+C+E
Teels Marsh	rhyolitic tuff	P*, P+S*, P+C, P+A, P+C+S, S
Owens Lake	rhyolitic tuff and tuffaceous clay	P*, P+C+E, P+E, C+E
Waucoba Lake beds	rhyolite tuff	P*, P+C
Olduvai Gorge (lacustrine facies of Bed II)	trachyte tuff	P*, K*, P+K*, P+K+S, K+A, C+A
Olduvai Gorge (non-lacustrine beds)	trachyte tuff and tuffaceous clay	P*, P+Ch*, P+E*, Ch+A*, P+Ch+E, Ch+E, P+C, C+A, P+Ch+A, Ch+N
	nephelinite tuff	P+N*, P+N+D*, P+N+A*, P+A+D, P, P+Ch+N, N+D, P+N+A+D

* Common occurrence.

P=phillipsite, A=analcime, K=K-feldspar, C=clinoptilolite, E=erionite, Ch=chabazite, S=searlesite, N=natrolite, D=dawsonite.

pared from chemical analyses of zeolites. Analyses of saline lake phillipsite and of chabazite from a zeolitic weathering profile are given in Table 3; other analyses are from published literature.

In the ternary diagram of Fig. 3, silicon and potassium were chosen as two of the end members, and the third end member comprises Na, Ca, and Mg. The third end member is given in the form $\text{Na} + \frac{1}{2}(\text{Ca} + \text{Mg})$ because two alkali ions can substitute for one alkaline-earth ion in many of the zeolites. Alumina is implicit in this diagram, as the number of Al^{3+}

ions (with substitution of Fe^{3+} or B^{3+} where appropriate) should equal the total of $\text{K}^+ + \text{Na}^+ + \frac{1}{2}(\text{Ca}^{2+} + \text{Mg}^{2+})$, disregarding the small amount of hydrogen ion which may occupy exchangeable-ion sites. Compositional fields were drawn to enclose analyzed clinoptilolites, chabazites, phillipsites and an analyzed erionite. Ideal formulas were assumed for analcime, searlesite, and K-feldspar. Shapes of the zeolite compositional fields are

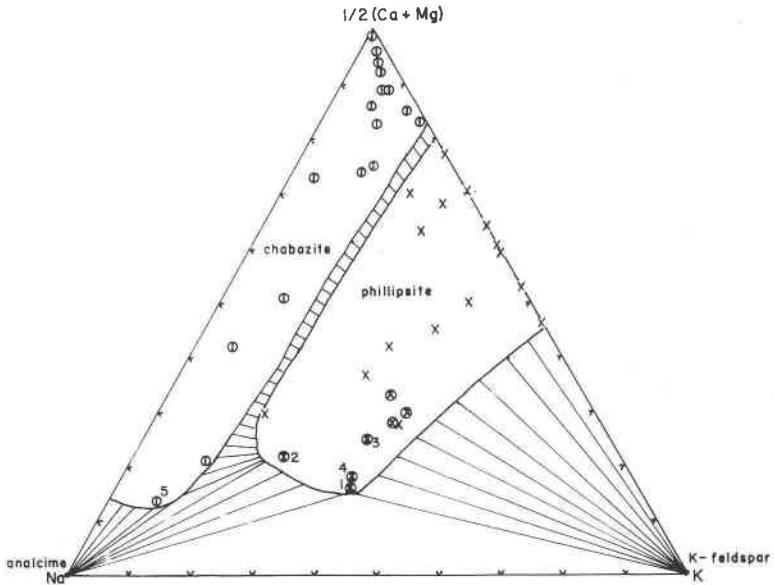


FIG. 4. $\text{K-Na}-\frac{1}{2}(\text{Ca}+\text{Mg})$ composition diagram for zeolites between the compositional points for analcime and K-feldspar on Fig. 3. Tie lines connect potentially co-existing minerals. Symbols for zeolite analyses as in Fig. 3. All compositional points for chabazite and phillipsite are plotted, regardless of whether or not the silica content places them in the plane of the cross-section.

highly uncertain, as are positions of the lines between adjacent zeolite fields.

A tetrahedron having the four end members Si, K, Na and $\frac{1}{2}(\text{Ca}+\text{Mg})$ is obviously required to represent the compositional relationships of lime-bearing zeolites, and Fig. 4 represents a cross-section through this tetrahedron between the compositional points for analcime and K-feldspar. All compositional points for chabazite and phillipsite are plotted, regardless of whether or not the silica content would place them in the plane of the cross-section.

The zeolitic mineral assemblages of saline lakes and soils seem to be compatible in terms of the Phase Rule. With a very few exceptions, all

of the associations predicted from Figs. 3 and 4 have been found. Predicted but not found is the association of clinoptilolite with chabazite, K-feldspar, and silica. Coexisting chabazite and clinoptilolite may be lacking because the erionite field is actually larger than shown and completely separates the fields of clinoptilolite and chabazite. Clinoptilolite is commonly associated with K-feldspar and opal in zeolitic tuffs outside the saline-lake environment (*e.g.*, Hay, 1936b); probably additional sampling would reveal it in saline-lake deposits. The common association of K-feldspar with analcime and searlesite appears incompatible on Fig. 3 but is compatible on a ternary diagram having Na shown separately from Ca and Mg (Fig. 4). The association of analcime with clinoptilolite may well be compatible on a diagram such as Fig. 4 where Na and $\frac{1}{2}(\text{Ca} + \text{Mg})$ are shown separately.

Compositional relations of Fig. 3 seem to explain why most of the zeolitized tuffs contain a single zeolite and relatively few contain as many as three zeolites. Phillipsite, clinoptilolite, chabazite and probably erionite have wide compositional ranges, and any one of these zeolites could crystallize from a chemical system varying between moderate limits. Compositional fields for two coexisting zeolites appear to be rather small, and fields for three zeolites are much smaller.

Microscopic textural evidence in several of the coarser-grained rhyolitic and trachytic tuffs indicate that the different authigenic silicate phases were co-precipitated. In some of the nephelinite tuffs, however, phillipsite formed first, as an alteration of glass, and was succeeded by dawsonite and natrolite formed from slowly altering nepheline.

ORIGIN OF PHILLIPSITE

Rate of Zeolitic Alteration. Phillipsite can form rapidly from volcanic glass in saline, alkaline lakes and soils. Zeolitic alteration of the shallowest ash layer in Teels Marsh was probably accomplished over a few hundred to perhaps as much as a few thousand years. This tuff lies at a depth of about a foot, and the transition from lacustrine muds to playa clays at a depth of 8 to 10 feet probably reflects the recent period of desiccation that began about 10,000 years ago (*cf.* Smith, 1962)¹. Zeolites formed in Olduvai Gorge at about the same rate as in Teels Marsh, for phillipsite weakly cements nephelinite ash probably between a few hundred and a few thousand years old, and eolian nephelinite tuffs of

¹ A C-14 date of $10,760 \pm 400$ years B.P. was recently obtained on gaylussite from a depth of 18 feet near the center of Teels Marsh (1964, H. R. Crane, pers. comm.). The dated gaylussite, which appears to be primary, lies 4 feet below the lowest of the tuffs that was studied, thus suggesting that even the lowermost tuff has been zeolitized in appreciably less than 10,000 years.

Bed V, as much as 15 feet thick, have been completely zeolitized within the past 8,000 to 20,000 years (Hay, 1963a). Another example is provided by rhyolitic tuff laminae altered to phillipsite at various levels in the Parting Mud of Searles Lake, which ranges in age from 10,000 to 20,000 years (Smith, 1962).

Phillipsite evidently forms much more slowly in the sea floor than in alkaline lakes and soils. Marine phillipsite is most abundant in areas of slow sediment accumulation (Murray and Renard, 1891), and the larger crystals are restricted to sediments of Tertiary age (Goldberg and Arrhenius, 1958).

Water Composition. Phillipsite associated with trona or gaylussite was formed in a sodium carbonate-bicarbonate brine probably having a pH between 9.1 and 10.0. The dilute sodium carbonate-bicarbonate solutions of Pleistocene Owens Lake, Waucoba Lake, and the lake of Bed II in Olduvai Gorge may have been as alkaline as the trona-bearing lakes, for the pH of a solution of sodium carbonate and bicarbonate depends largely upon the $\text{CO}_3^{2-}/\text{HCO}_3^-$ ratio and is independent of salt concentration between wide limits. Alkaline soils of Olduvai Gorge have a pH between 9.5 and 10.6 when they are moistened. The rapid rate at which glass alters to zeolites in alkaline lakes and soils probably reflects, at least in part, a relatively high solubility and rate of solution of glass at a pH greater than 9. Reaction rates are also favored by high salinity, judging from the association of zeolitized tuffs with trona crusts in Teels Marsh. In Teels Marsh the formation of phillipsite seems to be independent of Eh, as phillipsite occurs equally within oxidized reddish-brown playa clays and black lacustrine muds rich in hydrogen sulfide.

Phillipsite in marine sediments may seem to prove that it can form in normal sea water, which has a pH of about 8.0. The characteristic association of montmorillonite and phillipsite in palagonitic muds of the sea floor suggests, however, that hydrolysis of palagonitic glass to montmorillonite may be essential in creating the marine environment in which phillipsite is formed. Elevation of the pH should be one of the principal effects of this hydrolysis (*cf.* Hay, 1963b, p. 239-240).

The Na/K ratio should influence the formation of minerals that differ in their contents of Na and K (see Fig. 3). The ratio of Na to K varies over a wide range in environments where phillipsite has formed (Table 5), but the optimum Na/K ratio for phillipsite seems to lie between 10 and 50. Average Na/K ratios are between 28 and 34 in Olduvai Gorge, Teels Marsh, and the ocean, where phillipsite is the principal zeolite. Dominance of erionite over phillipsite in Lake Magadi may reflect the high Na/K ratio of its brines. Abundant analcime in the upper 155 feet of

beds in the China Lake core may reflect the high Na/K ratio of shallow subsurface water.

Using Searles Lake as an example, K-feldspar seems to be favored over phillipsite at low Na/K ratios. Analyzed brines of Searles Lake are extraordinarily rich in K, having Na/K ratios of 5.5 to 6.0 (Gale, 1915

TABLE 5. Na/K RATIOS IN WATERS OF ZEOLITIC ENVIRONMENTS

Locality	Na/K Ratio	Dominant Authigenic Silicates	Subordinate Authigenic Silicates
Lake Magadi	greater than 100 (lake water and interstitial water of cores)	erionite	analcime, phillipsite, clinoptilolite, chabazite
China Lake	54-244; 145 = ave. of 5 (water of shallow wells)	phillipsite, analcime	clinoptilolite, erionite, searlesite
Teels Marsh	21-46; 31 = ave. of 5 (water of core holes)	phillipsite	searlesite, clinoptilolite, analcime
Olduvai Gorge	30-42; 34 = ave. of 6 (anal. of salt crusts)	phillipsite	analcime, natrolite, chabazite, erionite
Searles Lake	5.5-6.0 (brine of Upper and Lower Salt)	K-feldspar	phillipsite, analcime, searlesite
Ocean	28 (sea water)	glauconite, phillipsite, montmorillonite, illite(?)	

References: Baker, 1958 and 1963 (pers. comm.); Moyle (1963); Teels Marsh (new data); Olduvai Gorge (Hay, 1963a); Searles Lake (Gale, 1915; Garrett, 1961); Ocean (Clarke, 1934).

and Garrett, 1961), and K-feldspar is the dominant authigenic silicate mineral in the sediments of Searles Lake. This example is not entirely satisfactory however, as analyzed brine samples were taken only from salines of the upper 150 feet of the sediments, and authigenic K-feldspar was recognized only at depths of more than 150 feet. Nevertheless, relatively low Na/K ratios of perhaps 6 to 10 seem likely for the original brine of the layers with K-feldspar, as crystallization of the vast quan-

tities of sodium salts in these beds should have enriched the brine in K. Authigenic K-feldspar is probably absent in salines of the upper 150 feet of beds because volcanic glass was lacking and because clay minerals have not yet reacted with the brine to form K-feldspar. Original Na/K ratios in water of the phillipsite-bearing Parting Mud may have differed vastly from those of the Searles Lake brines, as the Parting Mud was deposited during a pluvial episode of the late Pleistocene when Searles

TABLE 6. CHEMICAL COMPARISON OF CALC-ALKALI RHYOLITE
OBSIDIAN WITH PHILLIPSITE FROM SALINE LAKES

	(1)	(2)	(2a)	(3)
SiO ₂	73.66	58.33	52.23	-21.43
Al ₂ O ₃	13.45	15.02	13.45	—
TiO ₂	.22	.07	.06	- .16
Fe ₂ O ₃	1.25	.96	.86	- .39
FeO	.75	.16	.14	- .61
MgO	.32	.39	.35	+ .03
CaO	1.13	1.34	1.20	+ .07
Na ₂ O	2.99	4.42	3.96	+ .97
K ₂ O	5.35	4.65	4.16	- 1.19
H ₂ O	.78	14.67	13.14	+12.36
Other	.10	—	—	—
TOTAL	100.00	100.01	89.55	-10.35

- (1) Chemical composition of average calc-alkali rhyolite obsidian (Nockolds, 1954).
- (2) Average of phillipsite analyses 2, 3, and 4 from Table 3; (2a) was obtained from (2) by assuming Al₂O₃ content of analysis (1).
- (3) Gains (+) and losses (-) in zeolitic alteration which represent differences in amounts between columns (1) and (2a).

Lake was connected with China Lake to form a single large lake as much as 600 feet deep.

This discussion of water composition has assumed that zeolites crystallize from water having the same composition as analyzed samples obtained from wells and open bodies of water. Water in an altering tuff must, however, differ at least slightly in composition from water saturating non-tuffaceous beds, as zeolites precipitate adjacent to shards and pumice fragments where the activities of silica and alumina are elevated by solution of glass. In tuffs sealed off by relatively impervious clays, solution of glass can probably change significantly the amounts and proportions of even the more mobile ions such as Na and K. Phillipsite tuffs and pumice fragments in analcime-bearing clays of China Lake may indeed have been partly closed systems in which the Na/K ratio was

reduced by solution of glass to a level where phillipsite rather than analcime was formed. None of the phillipsite tuffs described in this paper can have been completely closed to their environment, however, as all of them have lost a large proportion of their original silica (see below).

Chemical Changes in Zeolitic Alteration.

(1) *Trachyte glass* Relatively little chemical change other than hydration and oxidation of ferrous iron is indicated by chemical analyses of essentially fresh vitric trachyte tuff and vitric tuff largely replaced by phillipsite in Olduvai Gorge (Hay, 1963a, p. 1285). Small amounts of K and Na appear to have been added, and some Ca and Mg lost.

(2) *Rhyolite glass* Hydration and a large loss of silica are the principal changes involved in forming phillipsite from rhyolite glass (Table 6). Assuming constant alumina and a parent glass of average calc-alkali rhyolite composition (Nockolds, 1954, p. 1012), then about 29 per cent of the silica originally present in the glass, equal to 21 per cent of the glass, has been lost in forming the analyzed phillipsites of Table 3. Probably Na has been gained, K has been lost, and some FeO has been oxidized. Gains and losses in TiO_2 , MgO, and CaO indicated by this comparison are not large enough to be accepted as valid.

The loss of silica in alteration of rhyolitic tuffs poses a mineralogic problem, as authigenic silica in the form of opal, chalcedony, or quartz has not been identified in either the tuffs or the associated sediments.

Laboratory Synthesis. Hydrothermal experiments with alkaline gels give results that are comparable in several respects to the alteration of vitric tuffs in saline, alkaline lakes. Phases closely related to natural phillipsite—the P-zeolite Group of Taylor (1962)—are among the commonest reaction products of NaOH and KOH gels at temperatures of 60 to 250° C. The orthorhombic K-Na phillipsite (= KM^3) of Barrer, *et al.* (1959) and the $\text{Na}_{28}\text{K}_{72}\text{-P}_0$ of Taylor (1962) have nearly the same d-spacings as the phillipsite of saline lakes. Optimum yields of synthetic phillipsite were obtained with a large excess of alkali, a condition which also prevails in saline lakes where phillipsite is formed. Phillipsites synthesized from the more siliceous gels characteristically have a much lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio than the initial gel, resembling in this respect the phillipsite formed from rhyolite glass in alkaline lakes.

Phillipsite was synthesized from volcanic glass by Di Piazza, *et al.* (1959) in solutions of NaOH and Na_2CO_3 at 100° C. Additional experiments with rhyolite glass in Na_2CO_3 solutions were made in the course of the present study (Table 7). Powdered rhyolite glass and sodium carbonate solutions were sealed in stainless-steel bombs held at 95 to

100° C. Phillipsite is the dominant reaction product, as it is in most of the sodium-carbonate lakes. Reaction rates seem to vary with the concentration Na_2CO_3 in these few experiments, as in Teels Marsh.

PROBLEM OF CLINOPTILOLITE-PHILLIPSITE OCCURRENCES

Statement of Problem. Clinoptilolite and heulandite appear to be the commonest low-temperature zeolitic alteration products of silicic glass in sedimentary rocks of environments less saline and probably less alkaline than the lakes in which phillipsite forms (*e.g.*, Deffeyes, 1959). By contrast, phillipsite appears to be rare in rhyolitic tuffs deposited outside the saline, alkaline environment. The very low activity of Ca^{2+} in sodium-carbonate lakes seems adequate to account for the absence of

TABLE 7. HYDROTHERMAL EXPERIMENTS WITH RHYOLITIC OBSIDIAN AT 95–100° C

Exp. No.	Wt. Glass	Vol. Solution	% Na_2CO_3	Time	Reaction Products	% Glass Remaining
1	.052 mg	.8 cc	20	64 days	P>>A	0
2	.055 mg	.8 cc	10	100 days	P>>Ch(?)	10–20
3	.055 mg	.6 cc	5	100 days	P	50

P=phillipsite, A=analcime, Ch=chabazite.

heulandite, which seems to require calcium as the dominant large cation (Mason and Sand, 1960). Clinoptilolite, like the phillipsite described here, is alkali-rich, and the principal difference between the two is in the content of silica. The molecular $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in analyzed clinoptilolites is 8.3 to 10.5 (Mumpton, 1960 and Hay, 1963b), whereas the $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio is 6.0 to 6.7 in analyzed phillipsites of rhyolitic origin.

Clinoptilolite not uncommonly accompanies phillipsite in deposits of saline lakes, thus proving that it does not require higher temperatures or pressures than phillipsite. Kinetic factors or different silica activities must therefore be responsible for the different occurrences of the two minerals. Clinoptilolite crystals in saline-lake deposits are about the same size as those of the associated phillipsite, suggesting that growth rates of the two minerals are comparable. Relative nucleation rates are unknown.

Significance of Laboratory Experiments. In laboratory experiments the pH exerts a strong control on the silica content of zeolites, apparently by controlling the activity of silica in solution. These laboratory experiments provide a model which may be applicable to the formation of clinoptilo-

lite and phillipsite in nature. The roles of pH and silica activity are illustrated in Fyfe's experiments (Coombs *et al.*, 1959, Fig. 11 and Tables 9 and 10) with mixes of the composition Na_2O (or 2NaHCO_3)- Al_2O_3 - 6SiO_2 . Mordenite crystallizes over a wide range in temperature where NaHCO_3 is the source of sodium ions and where amorphous silica is used. The mordenite field is extensively replaced by that of analcime in experiments where Na_2O is substituted for NaHCO_3 as the source of Na. These two experiments differed in pH, with the NaHCO_3 solution having the lower initial pH—about 9. The mordenite field was completely replaced by that of analcime where Na_2O was the source of sodium, and quartz was supplied instead of amorphous silica.

On the basis of zeolite composition, the activity of silica seems to have been highest in the NaHCO_3 solution, where the pH was lowest, and where amorphous silica was used. The activity of silica was apparently lowest where quartz was used. Low activities of silica are to be expected with quartz, as its solubility is much less than that of amorphous silica or cristobalite. Of the two experiments with amorphous silica, that with NaOH had the smaller mordenite field and presumably lower silica activity probably because the hydroxyl ion catalyzed the crystallization of amorphous silica to quartz (Campbell and Fyfe, 1960), so that the ultimate activity of silica in this solution was largely determined by equilibrium with quartz. Silica activity was probably higher in the mordenite-forming NaHCO_3 mixes because it was determined by equilibrium with cristobalite, which is much more soluble than quartz. These inferences are supported by the fact that cristobalite was identified in all runs where mordenite is the dominant zeolite, and only quartz is present in runs where analcime predominates.

The silica content of zeolites varies inversely with pH in many experiments too short for a crystalline silica phase to appear, as well as in those where quartz and cristobalite are formed (*e.g.* Ames, 1963). Fyfe has suggested (1963, pers. comm.) that in the more alkaline solutions the hydroxyl ion may reduce the activity of silica by catalyzing the polymerization of silica either to crystalline units too small to diffract x -rays or to a semi-crystalline phase structurally intermediate between silica gel and crystalline forms such as cristobalite. Semi-crystalline phases would presumably yield lower silica activities than would amorphous silica.

Zeolitic alteration of rhyolite glass in saline, alkaline lakes seems to parallel the laboratory experiments where no crystalline silica phase was produced. Except for Searles Lake, quartz grains of saline lakes show neither overgrowths nor solution etching, and cristobalite has not been identified in diffractometer patterns. Presumably, then, the silica ac-

tivity was determined either by metastable equilibrium with glass or with a semi-crystalline phase as inferred above. Using the laboratory experiments as a model, the hydroxyl ion is assumed to catalyze the polymerization of $\text{Si}(\text{OH})_4$, and if the rate of polymerization exceeds the rate of solution of glass, then the inferred semi-crystalline silica phase would largely determine the activity of $\text{Si}(\text{OH})_4$ in solution. A zeolite formed in this environment might be expected to have a lower content of silica than a zeolite formed at a lower pH where the activity of silica is determined entirely by equilibrium with glass.

Much of the detrital quartz is highly corroded in sediments of Searles Lake below a depth of 150 feet (Hay and Moiola, 1963), thus indicating that the activity of silica in the deeper layers is presently determined by equilibrium with quartz. Solution of quartz is not unexpected, as Searles Lake originally contained only a small amount of volcanic glass, which probably altered long ago, thus allowing the chemical system to equilibrate with quartz.

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