DIAGENETIC ALTERATION OF SILICIC ASH IN SEARLES LAKE, CALIFORNIA

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Abstract—Ash layers from Searles Lake, California, were sampled in core of drill hole KM-3, which penetrated 693 m of lacustrine sediment deposited in a playa-lake complex over the past 3.2 my. Lake water changed from moderately saline and slightly alkaline (pH ~7.5) to highly saline 2.04 my ago and to highly saline and alkaline (pH ~9.5) 1.28 my ago. As a result of brines flushing downward, the upper 291 m of sediment, spanning the past 1.28 my, contain highly saline, alkaline pore fluid. Silicic ash layers in contact with highly saline, alkaline pore fluid were first altered to phillipsite and merlinoite and then to K-feldspar and searlesite. The transformation of phillipsite and/or merlinoite to K-feldspar required more than 45,000 years and was largely completed in 140,000 years. Tephra layers in contact with moderately saline, slightly alkaline pore fluid vary from uncemented vitric ash containing minor smectite to bentonites in which glass is wholly altered to smectite, clinoptilolite, analcime, and opal. Layers with much fine tephra are more altered than the coarser, better-sorted layers. Alteration is attributed to hydrolysis in essentially a closed hydrologic system, in which the alteration of glass to smectite raised the pH, a_{SiO_2}, and $(Na^+ + K^+)/H^+$ activity ratio to the level where clinoptilolite formed. Some diffusion and/ or fluid flow is, however, indicated by the loss of SiO_2 during the alteration of ash layers to smectite and by anhydrite deposited during and after clinoptilolite in some tuffaceous sandstones.

Key Words—Alkaline, Saline lake, Anacime, Clinoptilolite, Diagenesis, K-feldspar, Merlinoite, Phillipsite, Volcanic ash, Zeolite.

INTRODUCTION

Searles Lake, a dry lake or playa, occupies a structural basin in the desert area to the east of the Sierra Nevada in eastern California (Figure 1). It is noted for its variety of saline minerals and for its alkaline brines that are ultilized for the commercial extraction of K, B, Li, and Na_2CO_3. Earlier work on drill cores from the upper 267 m of sediments showed that silicic tephra is altered to phillipsite at higher levels and to K-feldspar and searlesite ($NaBSi_2O_6 \cdot H_2O$) at lower levels (Hay and Moiola, 1963). The K-feldspar was believed to have formed from a phillipsite precursor (Hay, 1966), a reaction which Sheppard and Gude (1968) demonstrated elsewhere. Drill hole KM-3, by the Kerr-McGee Corporation, penetrated the entire 915 m thickness of basin fill, the upper 693 m of which are playa and lacustrine sediments spanning the past 3.2 my (Smith et al., 1983). These sediments record a progressive change in the chemistry of lake water from relatively dilute and slightly alkaline (pH ~7.5) to highly saline and alkaline (pH ~9.5). Silicic ash layers are interbedded at many horizons; thus, the core of drill hole KM-3 provides an opportunity to study the alteration of silicic ash in contact with pore waters of different chemical composition. Smith et al. (1983) reported heulandite and analcime in tephra layers of the lower part of the core, but Guldman (1984) identified the heulandite-type mineral as clinoptilolite and found

morillonite to be the principal alteration product of glass in the lower part of the core. The zeolite merlinoite, which is easily mistaken for phillipsite, was identified by Donahoe et al. (1984) in two of the uppermost tephra layers. This is the only reported occurrence of merlinoite in saline, alkaline lake deposits.

METHODS AND TERMINOLOGY

This study is based on 21 samples of relatively pure tephra layers and 7 samples of tuffaceous sandstone. Samples were studied in thin section, with immersion oils, and by X-ray powder diffraction (XRD). Bulk samples were analyzed by XRD using $CuK\alpha$ radiation to determine the species of zeolite and the structural type and amount of K-feldspar. Clay-mineral analyses were made on oriented preparations of the <2-μm, <0.2-μm, and <0.1-μm fractions mounted on glass slides and/or ceramic tile.

Mud samples from core KM-3 were analyzed by XRD as part of a study, still in progress, of the diagenetic alteration of detrital clay in Searles Lake. Data on non-silicate minerals from units G, H, and I of the Mixed Layer are included here to aid in interpreting the pore-water chemistry.

Mud is used here as defined by Smith et al. (1983) as a textural term for all fine-grained sediments except saline minerals and includes authigenic carbonate minerals as well as detrital silt and clay. Ash refers to
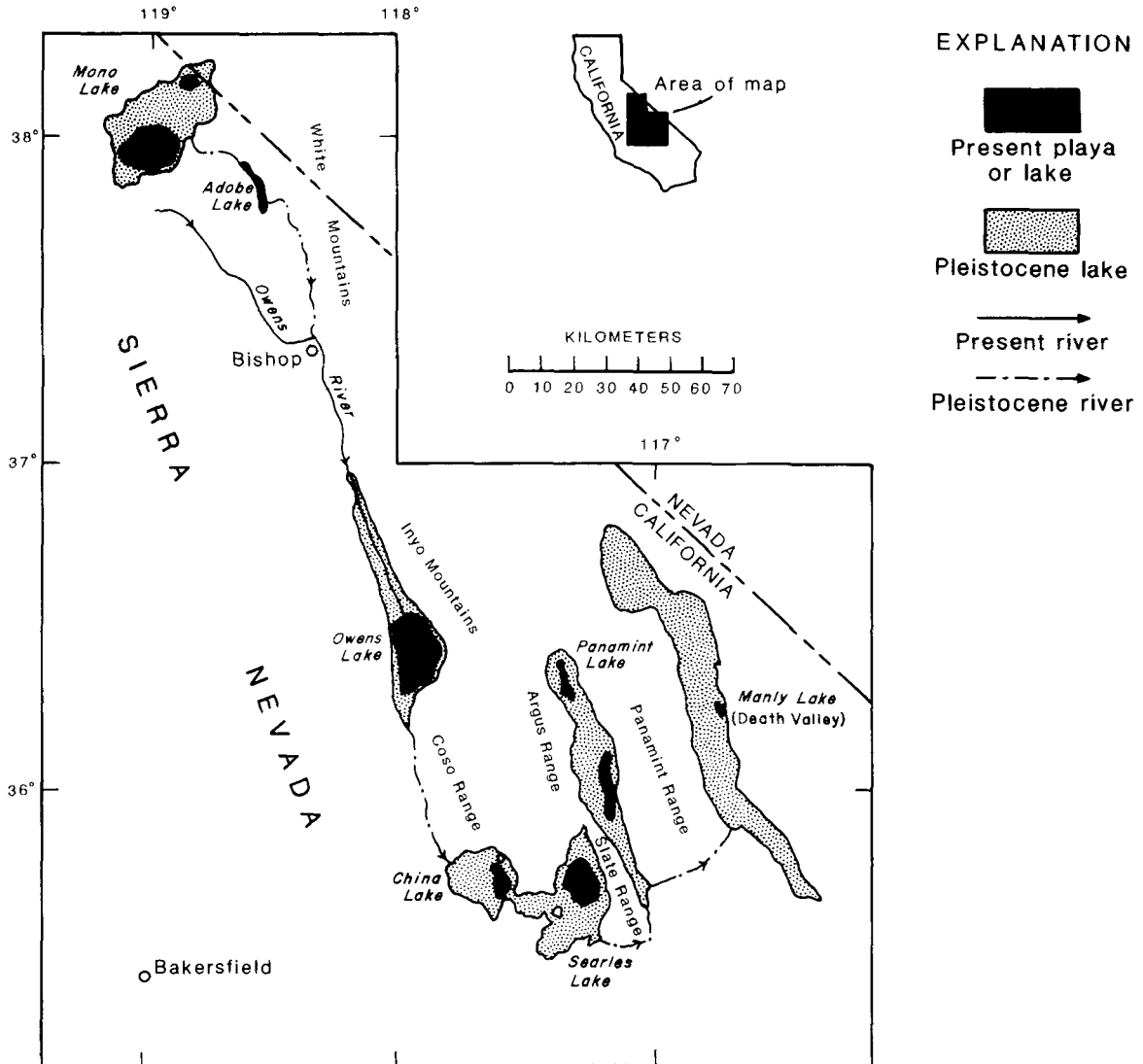
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Figure 1.   Map showing the location of Searles Lake, California, and lakes with which it was connected during wetter periods of the Pliocene and Pleistocene.

relatively unaltered and uncemented tephra less than 1 mm in grain size, and tuff refers to indurated volcanic ash, most of which is cemented by smectite. Bentonite is volcanic ash that is largely or wholly altered to smectite. The core of drill hole KM-3 is referred to as core KM-3, following the usage of Smith *et al.* (1983).

STRATIGRAPHY AND CHEMICAL EVOLUTION OF SEARLES LAKE

The upper 69 m of core KM-3 comprises five formal stratigraphic units, which are, from youngest to oldest, the Overburden Mud, Upper Salt, Parting Mud, Lower Salt, and Bottom Mud (Table 1). The 624-m thick Mixed Layer underlies the Bottom Mud and is subdivided into informal units A to I, from youngest to

oldest. Sediments of core KM-3 consist almost entirely of muds and evaporites. Searles Lake fluctuated from a perennial lake to a playa many times, and the hydrologic regime roughly fits a 400,000-year periodicity, on which shorter-term fluctuations are superimposed (Smith, 1984). Dominantly perennial lakes are represented by the Parting Mud, Bottom Mud, and units F and I of the Mixed Layer.

The chemistry of the lake water changed during deposition in Searles Lake, and the content of chemical sediment increased, reflecting increased aridity as a result of uplift of the Sierra Nevada (Smith *et al.,* 1983). The chemical evolution of the lake waters was discussed by Smith (1979) and Smith *et al.* (1983), and the following discussion also considers the probable

pore-water chemistry, emphasizing stratigraphic units containing tephra layers. Stratigraphic units are described from oldest to youngest, tracing the chemical evolution of Searles Lake.

Unit I, the lowest lacustrine unit, consists almost entirely of muds deposited in a perennial lake of relatively low salinity, which may have been briefly desiccated. Authigenic minerals in 18 samples of mud analyzed by XRD are halite (18 samples), calcite (11), anhydrite (7), and dolomite (1). Some of the halite is from the brine used in the drilling mud, but the remainder is from evaporation of pore water in the dried samples. The anhydrite is diagenetic (Smith *et al.,* 1983) and occurs as nodules in muds and as a cement in some sandstones and tephra layers. It may have been deposited as gypsum, which was dehydrated and to some extent remobilized after burial. The acid-soluble fraction from 23 samples was chemically analyzed by the Kerr-McGee Corporation. Most of the results were represented graphically by Smith *et al.* (1983) in the form of ion and normative mineral percentages. The following data are taken from the original chemical analyses and normative mineral percentages, which were made available by G. I. Smith (U.S. Geological Survey, Menlo Park, California). The acid-soluble fraction averages 14% of the core samples and comprises chiefly Ca, CO_3, lesser Na, Mg, SO_4, Cl, and very small amounts of K, Li, Br, and B_4O_7. The average normative mineral content is dolomite, 6.6%; halite, 3.9%; anhydrite, 1.8%; and minor glauberite and thenardite. Calcite is the principal carbonate mineral, hence, most of the normative dolomite may represent exchangeable Mg in smectite clays. The pH of pore water in unit I is determined largely by equilibrium between $CaCO_3$ and H_2CO_3 and is probably in the range of 7.3–7.8, as in marine sediments saturated with respect to calcite (Siever *et al.,* 1965).

Contamination of the acid-soluble fraction of core samples from unit I can be estimated to some extent inasmuch as brine of distinctive composition from the Upper and Lower Salt was the fluid used in the drilling mud (G. I. Smith, personal communication, 1987). This brine has about 35% total dissolved solids (TDS) and is enriched in B, K, Li, SO_4, and some other constituents as a consequence of hydrothermal activity in Long Valley caldera over the past 0.31 my (Smith, 1976). The Cl/B_4O_7 wt.-% ratio is generally 8–12 and averages about 10 in these brines in the vicinity of drill hole KM-3 (Smith, 1979). In the acid-soluble fraction of unit I, the ratio is generally 15–25 and averages 21. If all of the B_4O_7 in the analyzed samples is a result of contamination by a fluid with a Cl/B_4O_7 ratio of 10, roughly half of the analyzed Cl and normative NaCl of unit I is from pore water and half from the drilling fluid. If only half of the analyzed B_4O_7 is from the drilling fluid, only about one quarter of the Cl was acquired as a result of contamination by a fluid with

a Cl/B_4O_7 ratio of 10. The Cl/K ratio suggests even less contamination than the Cl/B_4O_7 ratio. This ratio averages about 6 in brine of the Upper and Lower Salt (Smith, 1979) and about 21 in the acid-soluble fraction of unit I. The possibility of K-fixation by illite or by illitization of smectite in unit I makes the Cl/K ratio seem less reliable than the Cl/B_4O_7 ratio.

If no more than half of the normative halite content (3.9%) is a result of contamination, the pore water of unit I is probably somewhat more saline than sea water (~3.5% TDS). To calculate the dissolved NaCl, half of the normative halite was assumed to be connate, and the porosity of the muds was taken as 30%, the average of marine muds buried to the same depths (Perrier and Quiblier, 1974), giving 5.6% halite in the pore water of unit I. If more than half of the halite is from pore water, then the content of NaCl is greater than 5.6%. Solutes in equilibrium with calcite and anhydrite would increase the salinity only slightly. In view of the various uncertainties, such as porosity, the salinity may be in the range 4–8%.

Unit H is chiefly playa muds, which are mineralogically similar to muds of unit I. The 40 samples analyzed by XRD contain halite (40 samples), calcite (38), anhydrite (15), glauberite (6), and dolomite (3). The acid-soluble fraction constitutes about 25% of the unit and is chemically similar to that of unit I, suggesting similar pore-water chemistry.

Unit G contains mud with interbeds of halite and was deposited in a lake of fluctuating level. Muds contain halite, calcite, and dolomite and, near the base, anhydrite and glauberite. The lake was highly saline and dominated by Na and Cl. The presence of calcite and the absence of normative or observed sodium carbonate or sodium borate minerals suggest that the present-day pore water is a slightly alkaline brine.

Unit F consists largely of muds deposited in a stable perennial lake in which water was relatively dilute (Smith *et al.,* 1983); however, the muds contain large amounts of pirssonite and dolomite, both modal and normative.

Pirssonite indicates that the pore water is now highly saline and alkaline, having a pH in the range 9–10. The pirssonite was attributed by Friedman *et al.* (1982) to reaction of calcium carbonate precipitated from the lake water with sodium-rich alkaline brines that flushed downward through unit F from younger and more saline phases of Searles Lake.

Units A to E of the Mixed Layer consist of muds and salines deposited in playas and deep to shallow lakes. The muds contained disseminated gaylussite and pirssonite; bedded salines include halite and trona. The pore water is a highly alkaline brine.

The Bottom Mud and overlying deposits consist of muds and bedded salines. The muds and salines contain a wide variety of saline minerals, including gaylussite, borax, and trona. Pore waters are saline and

unusually rich in K, as shown by K-bearing saline minerals in the Upper and Lower Salt and by a relatively high content of acid-soluble K in muds (Smith *et al.,* 1983). The measured pH is 9.2–9.4 in brine of the Lower Salt and 9.1–9.9 in brine of the Upper Salt (Smith, 1979).

RESULTS

Tephra layers

Fourteen tephra layers having a total thickness of about 5–6 m were identified in core KM-3 (Table 1). All but one are in deposits of perennial lakes (Table 2). The thickest was logged as 2.4 m (Smith *et al.,* 1983), but core samples of ash and tuff were distributed over a length of 3.6 m in core boxes when sampled for the present study. Measurements given in Table 1 are based on marked positions in the core boxes.

The tephra layers originally consisted chiefly of vitric ash. Glass is now altered to zeolites and/or K-feldspar in unit F and all stratigraphically higher units (Figure 2). These tephra layers are relatively hard, chalky, and pale orange. Vitroclastic textures generally are not preserved, although shard-shaped cavities were noted in one tuff altered to K-feldspar (Table 2, 233 m). An altered ash, about 1.2 m thick at a depth of 168.6 m, is tentatively correlated with the Lava Creek B ash (0.61 my) on the basis of its stratigraphic position relative to the Brunhes-Matuyama boundary (0.73 my), at 180 m (Liddicoat *et al.,* 1980) and on the scarcity of biotite (see Izett, 1981), which is common in nearly all of the other tuffs in core KM-3. Ash layers in unit I, between 640.2 and 690.7 m, either contain unaltered shards and pumice fragments or preserved vitroclastic textures. Bubble-wall and pumice shards 0.1–0.5 mm long are most common.

The ash layers were probably silicic. The Lava Creek B ash is rhyolitic, and nearly all of the widespread Pliocene and Pleistocene ash layers of the southwestern United States are dacitic to rhyolitic (Izett, 1981). Tephra layers of unit I are rhyolitic, as indicated by crystals of quartz, biotite, sodic plagioclase, and sanidine and by a refractive index of 1.495 for glass of the thickest bed (Smith *et al.,* 1983). Glass from this bed, analyzed by microprobe, contains 78.52% SiO_2, 12.99% Al_2O_3, 0.82% Fe_2O_3, 0.03% MgO, 0.50% CaO, 5.27% Na_2O, and 1.70% K_2O, on a water-free basis (A. Sarna-Wojcicki, U.S. Geological Survey, Menlo Park, California, personal communication, 1983). The atomic Na:K ratio is 4.6, which is anomalously high for rhyolite glass and presumably reflects ion exchange during hydration.

Volcanic ash of at least several eruptions must either have been lost in coring or was dispersed in muds, judging from the many Pliocene and Pleistocene ash layers known to occur within 100 km of Searles Lake (Izett, 1981). The Bishop Ash (0.72 my) must have

Table 1.   Lacustrine stratigraphic units in Searles Lake, California.[1]

Name of unit	Depth to base (m)	Age of base
Overburden Mud	7	3500 yr
Upper Salt	22	10,500 yr
Parting Mud	26	24,000 yr
Lower Salt	38	32,500 yr
Bottom Mud	69	0.13 my
Mixed Layer		
Units A + B	114.0	0.31 my
Unit C	166.4	0.57 my
Units D + E	227.7	1.00 my
Unit F	291.1	1.28 my
Unit G	425.5	2.04 my
Unit H	541.6	2.56 my
Unit I	693.4	3.18 my

[1] Data for the Mixed Layer are taken from Smith *et al.* (1983); Smith (1979) was used for the overlying units.

been deposited in units D and E of Searles Lake in view of its widespread occurrence in southeast California. Ash reworked and dispersed in muds with saline, alkaline pore water is difficult, if not impossible, to recognize after the glass has dissolved, especially because alteration products such as K-feldspar generally do not preserve vitroclastic textures. Several mud samples in units A to G are probably tuffaceous on the basis of a pale orange color and abundant unaltered biotite. These muds are not considered in the present study because reactions of vitric ash cannot readily be distinguished from those of detrital clay minerals.

Authigenic silicate minerals

Zeolites in core of KM-3 are phillipsite, merlinoite, clinoptilolite, and analcime. The phillipsite is similar to that in other cores from Searles Lake described by Hay and Moiola (1963). Merlinoite was identified by Donahoe *et al.* (1984) in two tuff samples of core KM-3. Merlinoite is structurally related to phillipsite, but is more potassic. Its XRD pattern is rather similar to that of phillipsite, but rechecking of the XRD patterns of tuffs described by Hay and Moiola (1963) confirmed their original identification as phillipsite. Clinoptilolite occurs as low birefringent crystals, generally 5–20 μm long. Its identification as clinoptilolite rather than heulandite was demonstrated by thermal stability and a refractive index of 1.476–1.478 (Boles, 1972). Analcime was found in a single tuff, at 690.7 m, where it occurs as pseudomorphs after shards (Figure 3D).

Searlesite was found in two tuffs altered principally to K-feldspar (Table 2). In one, at a depth of 169.8 m, it occurs as spherulites 0.10 mm in diameter and is similar to those in tuffs of core LWD from Searles Lake (Hay and Moiola, 1963). In the other tuff, at 233 m, it was identified only by XRD.

K-feldspar is the dominant authigenic silicate in tuffs of unit F and overlying deposits. Crystals are subhedral

Table 2. Silicate mineral composition of ash layers and tuffaceous sediments in core KM-3 of Searles Lake, California.

Depth (m)	Age (my)	Lithology	Thickness	Stratigraphic (unit)	FG	Ph	Mrl	Ksp	Sr	Sm	Op	Cp	An
19.9	0.009	Tuff	1–2 mm	Upper Salt	—	xxx	—	—	—	—	—	—	—
41.0	0.042	Tuff	1–2 mm	Bottom Mud	—	xxx	xx	—	—	—	—	—	—
42.1	0.045	Tuff	1–2 mm	Bottom Mud	—	xx	xxx	—	—	—	—	—	—
168.6	0.61	Tuff	1.2 m	Lava Creek B ash	—	—	—	xxx	—	—	—	—	—
169.8	0.61	Tuff		in units D and E	—	—	—	xxx	x	—	—	—	—
190.1	0.76	Tuff	18 cm	units D and E of Mixed Layer	—	—	—	xxx	—	—	—	—	—
233.3	0.97	Tuff	5 cm	unit F	—	—	—	xxx	x	—	—	—	—
245.7	1.08	Tuff	5 cm	unit F	—	—	—	xxx	—	—	—	—	—
640.2a	2.96	Bentonite	2 cm	unit I	—	—	—	—	—	xxx	x	x	—
640.2b	2.96	Tuffaceous sandstone	~1 cm?	unit I	—	—	—	—	—	x	—	x	—
642.1	2.97	Tuffaceous sandstone	~1 cm?	unit I	—	—	—	—	—	xx	—	x	—
649.4	3.00	Bentonite	8 cm	unit I	+	—	—	—	—	xxx	x	x	—
655.5	3.02	Bentonite	2 cm	unit I	—	—	—	—	—	xxx	+	x	—
656.0	3.02	Tuffaceous sandstone	2 cm	unit I	—	—	—	—	—	x	—	x	—
656.6	3.03	Tuffaceous sandstone	≥4 cm	unit I	—	—	—	—	—	x	—	x	—
658.7	3.04	Sandy bentonite	few cm?	unit I	—	—	—	—	—	xxx	+	x	—
664.3	3.06	Tuffaceous sandstone	few cm?	unit I	—	—	—	—	—	x	—	x	—
669.4	3.08	Tuff + bentonite	few cm?	unit I	xxx–xx	—	—	—	—	xx–xxx	—	—	—
669.5	3.08	Ash	9 cm	unit I	xxx	—	—	—	—	x	—	—	—
680.0	3.12	Sandy bentonite	12 cm	unit I	—	—	—	—	—	xxx	x	x	—
680.2	3.13	Ash	25 cm	unit I	xxx	—	—	—	—	xx	x	+	—
680.5	3.13	Ash			xxx	—	—	—	—	x	+	—	—
681.7	3.13	Tuff			xxx	—	—	—	—	xx	+	—	—
682.6	3.13	Ash			xxx	—	—	—	—	x	+	—	—
683.2	3.13	Ash and tuff	3.6 m	unit I	xxx	—	—	—	—	xx	+	—	—
683.8a	3.13	Tuff			xxx	—	—	—	—	xx	—	—	—
683.8b	3.13	Bentonite			—	—	—	—	—	xxx	x	x	—
690.7	3.17	Bentonite	50 cm	unit I	—	—	—	—	—	xxx	x	—	xx

Abbreviations are: FG, fresh glass; Ph, phillipsite; Mrl, merlinoite; Ksp, K-feldspar; Sr, searlesite; Sm, smectite; Op, opal; Cp, clinoptilolite; and An, analcime. Symbols for amount are as follows: —, absent; +, trace; x, trace to 10%; xx, 10–50%, and xxx, >50%.

[1] Refers to samples used in Figure 2.

to euhedral and average about 2.5 and 0.5 μm in size in samples from depths 168.6 and 169.8 m, respectively (Guldman, 1984). The feldspar is monoclinic on the basis of its XRD pattern.

Dioctahedral smectite is a common alteration product of glass in unit I. It is fully expandable on glycolation and has rational 00*l* spacings through 006, showing an absence of mixed layering. Inasmuch as the smectite is an alteration product of silicic glass, it is almost certainly montmorillonite in composition. Khoury and Eberl (1981) describe the montmorillonite of a bentonite 100 km northeast of Searles Lake, which is probably correlative with tephra between 680.2 and 683.8 m in core of KM-3 (Hay *et al.*, 1986). A small amount of smectite, illite, or both is present in all of the altered tuffs of unit F and stratigraphically higher units. Whether these clay minerals are authigenic, detrital, or both is unknown.

Material identified as opal occurs in unit I. It is isotropic and has a refractive index considerably less than 1.470. It is most common as patchy concentrations in a smectite matrix. The concentrations are aggregates of rounded to irregular particles 2–5 μm in diameter. Some aggregates contain short fibers with lobes, 1–2 μm in diameter. Opal also coats vitric shards and occupies pore space such as vesicles in pumice and commonly occurs together with smectite replacing pumice fragments. Opal is also disseminated in massive smectite. Opal is not sufficiently abundant for identification in any XRD patterns, either as a shoulder for noncrystalline silica or as a peak for opal-CT.

ASH DIAGENESIS

Diagenetic environments differ greatly between the upper and lower parts of the stratigraphic section. The upper part of the section, including unit F, contains highly saline pore water having a pH of about 9.5. Unit I, the lowermost lacustrine unit, contains moderately saline pore water having a pH of about 7.5.

Because of the geothermal gradient, temperatures of unit I are higher than those of unit F and overlying deposits. The mean annual temperature at Searles Lake is 20°C, and the measured geothermal gradient in the upper 80 m of sediments is 95°C/km (Smith, 1979). This gradient extrapolates to temperatures of 48°C at the base of unit F and 85°C at the base of unit I. Because porosity decreases with depth, however, conductivity should increase and the geothermal gradient should decrease downward (A. H. Lachenbruch, U.S. Geological Survey, Menlo Park, California, personal communication, 1986). A temperature of 45°C was measured at the base of unit I during drilling (G. I. Smith, personal communication, 1986), which is a minimum for unit I inasmuch as drilling was not stopped long enough for the drilling fluid to equilibrate with the sediments. Hence, the temperature at the base of unit
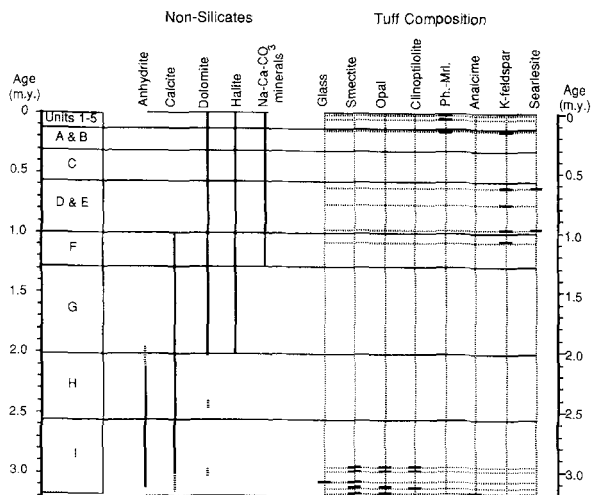

Figure 2. Columnar section showing stratigraphic units of core KM-3, major authigenic nonsilicate minerals, and mineral composition of tephra layers. Units 1–5 are, in descending order, Overburden Mud, Upper Salt, Parting Mud, Lower Salt, and Bottom Mud. The lettered units are in the Mixed Layer. Tephra composition is indicated by short horizontal bars on vertical lines representing different constituents. Tuff compositions for unit I are based on representative samples and do not include all of the data given in Table 2. Abbreviations are Ph., phillipsite and Mrl., merlinoite. Data are from core KM-3, except for tuff having an age of 0.14 my, which is explained in text. Non-silicate mineralogy is taken from Smith *et al.* (1983) supplemented by present study. Time scale is based on paleomagnetic stratigraphy of Liddicoat *et al.* (1980).

I presumably lies between 45° and 85°C, and that at the base of unit F is probably less than 48°C.

Diagenesis in saline, alkaline environments

The uppermost ash layers in core KM-3, 9000 to 45,000 yr in age, are altered to phillipsite, merlinoite, or both (Table 2). The potassic zeolite merlinoite in Searles Lake may reflect the relatively potassic pore waters in the Bottom Mud and overlying deposits. Tuffs ranging from 0.61 to 1.08 my in core KM-3 are altered to K-feldspar, with or without searlesite. Phillipsite is the zeolite in tuffs of other cores of the Parting Mud and Bottom Mud from Searles Lake that have been described. These range in depth from 20.4 to 32.6 m and in age from about 12,000 to 40,000 yr B.P. (Hay and Moiola, 1963). Tuff a few meters below the top of the Mixed Layer at a depth of 80.7 m in core LDW-8 is altered to K-feldspar and lesser phillipsite and/or merlinoite (Hay, 1970, p. 242). This tuff is about 0.14 my in age and is believed to represent the incomplete alteration of phillipsite and/or merlinoite to K-feldspar. Reaction of these zeolites to form K-feldspar in sediments of Searles Lake is attributed to the transformation of a metastable phase to a stable one (Hay, 1970).
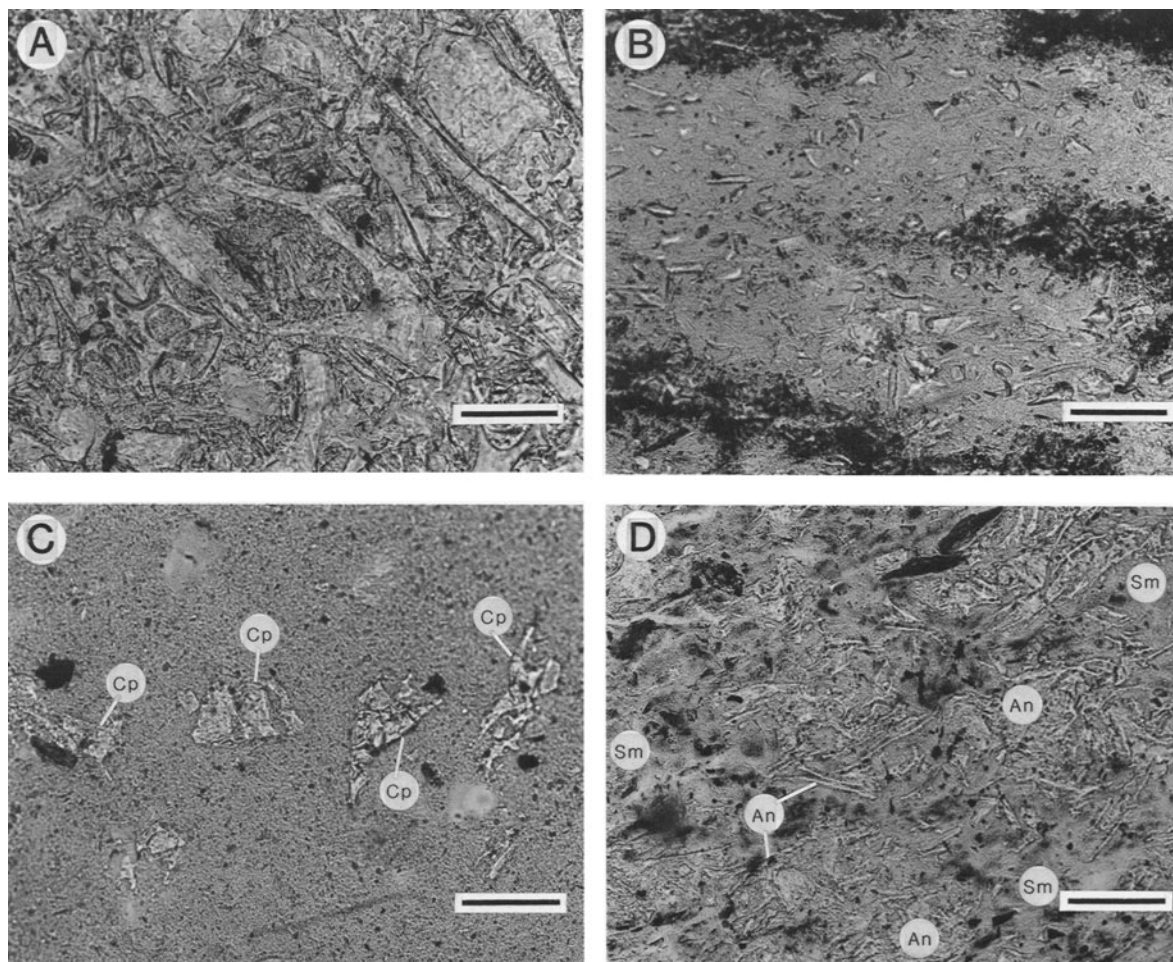
Figure 3. Photomicrographs of ash layers from unit I of core KM-3. All bar scales are 0.10 mm. A. Relatively coarse ash from depth of 662.6 m consisting of unaltered glass shards containing minor interstitial smectite. B. Fine-grained ash from depth of 683.2 m consisting or 5–10% small shards in matrix of smectite. Most of the smectite is translucent, but some is opaque and appears black. C. Bentonite from depth of 649.4 m containing relatively large shards replaced by clinoptilolite (Cp). D. Bentonite from depth of 690.7 m containing about 30% analcime (An), most of which has a vitroclastic texture. Smectite is indicated by Sm.

On the basis of tuffs in core KM-3, K-feldspar crystals large enough to diffract X-rays require between 45,000 and 140,000 years to form from phillipsite and/or merlinoite. K-feldspar has also formed from detrital smectite in contact with saline, alkaline pore fluid in Searles Lake (Hay and Moiola, 1963; Hay, 1966), and ages of the youngest muds with identifiable K-feldspar show that it can form in substantially less than 100,000 years at low temperatures in saline, alkaline environments. The youngest sediments with K-feldspar are in the Bottom Mud at depths of 37.6 m in core 254, with an age of about 48,000 years, and at depths of 46.0 m in core LWD, with an age of about 62,500 years (Smith, 1979). The youngest sediments found to contain K-feldspar in core KM-3 are at a depth of 55.8 m, which has an age of about 88,000 years.

Saline, alkaline playa-lake complexes have been con-sidered by some as closed hydrologic systems (e.g., Surdam, 1977), but Friedman *et al.* (1982) showed, by isotopic evidence, that brine periodically flushed downward through the sediments of Searles Lake to a brine-escape zone at a depth of about 290 m, the base of unit F. This movement of brine would have sub-jected the sediments to a more uniform pore fluid than if the system had been truly closed. Brine movements account for much of the gaylussite and pirssonite down through unit F, as noted above, and may account for alteration of tuffs to K-feldspar in unit F, which was deposited in a relatively dilute lake having open drain-age.

Diagenesis in saline, slightly alkaline environments

Ash layers in the lower 53 m of unit I are altered to widely varying degrees (Figure 3). They include unce-

mented vitric ash containing minor smectite, ash layers cemented by smectite to form friable tuff, and bentonites in which the glass is wholly altered, principally to smectite. The degree of alteration, as described below, appears to be primarily related to sorting and grain size of the ash. The coarser, better-sorted ash layers are least altered (Figure 3A), but fine-grained and poorly sorted layers with much fine ash are most altered (Figure 3B).

Zeolite and opal are present in some of the tuffs and all of the bentonites. Clinoptilolite is the zeolite in all but the lowermost bentonite, which contains analcime. Clinoptilolite and opal each constitute a trace to 5% of the bentonites, as estimated microscopically, except for the lowermost bentonite, which consists of about 70% smectite, 30% analcime, and a small amount of opal. The stages of alteration leading to the formation of bentonite are shown by comparing samples altered to different degrees.

1. In the first stage, smectite was deposited as a thin coating over shards (e.g., at 669.5 and 683.2 m).

2. Next, glass dissolved, as evidenced by corrosion of shards and pumice fragments, and smectite and minor opal filled much of the pore space. Thin-walled tubular pumice fragments were replaced by smectite and opal.

3. Continued solution of glass was accompanied by precipitation of clinoptilolite, the end product being a massive bentonite containing shard cavities lined or filled by clinoptilolite (Figure 3C). Clinoptilolite also crystallized as patchy aggregates, 50–150 μm in diameter, probably from shards and pumice fragments, but it did not preserve their shape.

4. The lowermost, analcimic tuff (Figure 3D) probably involved an additional stage of replacement of an early-formed zeolite such as clinoptilolite by analcime (see, e.g., Sheppard and Gude, 1969).

Alteration in some samples varies considerably over the area of a thin section. In a bentonite from a depth of 649.4 m, for example, shards are unaltered in one small area but elsewhere are replaced by clinoptilolite. In a thin section of tuff from 680.2 m, clinoptilolite is concentrated in areas 0.5–1.0 mm across where shard dissolution was greater than elsewhere in the slide.

Tuffaceous sandstones of unit I contain clinoptilolite, which coats sand grains and replaces shards and some pumice. It also forms small, subequant to irregular aggregates that probably formed from shards without preserving their shapes. Clinoptilolite generally makes up 3–5% of the sandstones, but may comprise 10–20% of some thin sandstone laminae in bentonitic claystone. Thin-walled tubular pumice fragments are altered to smectite, with or without clinoptilolite. Some of the sandstones are cemented by anhydrite, which forms as much as 40% of the rock by volume. Clinoptilolite in anhydrite-rich sandstones, at depths of 640.2, 642.1, and 656.6 m, occurs both as a grain-coating

cement and throughout the anhydrite, suggesting that clinoptilolite crystallization both preceded and accompanied precipitation of the anhydrite.

Alteration of ash layers in unit I is attributed to hydrolysis in a relatively closed system. Here, the alteration of glass to smectite raised the pH, a_{SiO_2}, and $(Na^+ + K^+)/H^+$ activity ratio to levels where clinoptilolite formed. As evidence, clinoptilolite occurs only in ash layers extensively altered to smectite. The ash layers did not act as perfectly closed systems, however, because alteration of rhyolitic glass to smectite and minor clinoptilolite should yield far more than the observed trace to 5% of opal. The lack of diagnostic peaks for opal in XRD patterns indicates that submicroscopic opal, if present, is not abundant. Considering only the balance of SiO_2 and Al, 100 g of rhyolitic obsidian having the composition of the analyzed shards should yield about 64 g of bentonitic montmorillonite of the type formed from rhyolitic glass (e.g., Khoury and Eberl, 1981), 5 g of clinoptilolite having a Si:Al ratio of 4.25, and 40 g of opal. Diffusion, fluid flow, or both can account for the inferred loss of SiO_2 and for the substantial addition of Na required to form analcime in the lowermost tuff. Flow or diffusion is also indicated by the large amount of diagenetic anhydrite cement and by the relatively uniform dispersal of grain-coating clinoptilolite in the sandstones. Nevertheless, diffusion or flow was not rapid enough to create a uniform chemical environment and, thus, uniform alteration in the ash layers, judging from the variable degree of alteration over the area of a thin section.

The alteration of ash layers in unit I is similar to that in deep-sea sediments, which constitute a relatively closed hydrologic system except where localized heat sources cause convective flow. Sea level constitutes base level for deep-sea sediments, hence gravity-driven flow does not exist in sea-floor sediments, and pore fluids move only as a result of compaction except where localized heat sources cause convective flow. Diffusion is slow enough for pore waters to attain significant chemical differences from sea water. As an example, SiO_2 commonly reaches concentrations of 50 ppm in the uppermost 15 cm of sediment, whereas overlying sea water averages 1 ppm SiO_2 (Siever *et al.,* 1965). Ash layers of silicic to intermediate composition in deep-sea sediments alter to bentonites with minor zeolite (Hein and Scholl, 1978); the rate of alteration is comparable to that in unit I. In cores from leg 19 of the Deep Sea Drilling project, in the Bering Sea, a few ash beds as young as late Pliocene are altered to bentonite, and the ratio of bentonite to relatively unaltered ash layers increases with age into the Miocene (Hein and Scholl, 1978).

SUMMARY AND CONCLUSIONS

In highly saline, alkaline environments of Searles Lake, silicic ash was altered initially to phillipsite and

merlinoite. K-feldspar was formed from phillipsite and merlinoite, and the transformation was largely completed in 140,000 years. Ash layers containing moderately saline, slightly alkaline pore fluid vary from uncemented vitric ash with minor smectite to bentonite in which the glass is altered to smectite and lesser zeolite and opal. The zeolite is clinoptilolite in all except one bentonite, which contains analcime. The degree of alteration seems primarily related to sorting and grain size; layers with much fine ash are more altered than the coarser, better-sorted layers. Alteration of ash layers containing saline, slightly alkaline pore fluid is attributed to hydrolysis in a relatively closed system, in which alteration of glass to smectite raised the pH, a_{SiO_2}, and $(Na^+ + K^+)/H^+$ activity ratio to levels where clinoptilolite formed. Diffusion of ions, fluid flow, or both is required to account for the inferred loss of silica in bentonites, for the addition of Na to form analcime, for the abundant anhydrite, and for the distribution of clinoptilolite in tuffaceous sandstones.

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REFERENCES

Boles, J. R. (1972) Composition, optical properties, cell dimensions, and thermal stability of some heulandite-group zeolites: *Amer. Mineral.* **57**, 1463–1493.

Donahoe, R. J., Liou, J. G., and Guldman. S. (1984) Synthesis and characterization of zeolites in the system Na_2O-K_2O-Al_2O_3-SiO_2-H_2O: *Clays & Clay Minerals* **32**, 433–443.

Friedman, I., Smith, G. I., and Matsuo, S. (1982) Economic implications of the deuterium anomaly in the brine and salts in Searles Lake, California: *Econ. Geol.* **77**, 694–702.

Guldman, S. G. (1984) Silicate diagenesis in core KM-3 from Searles (dry) Lake, California: M.S. thesis, University of California, Berkeley, California, 61 pp.

Hay, R. L. (1966) Zeolites and zeolitic reactions in sedimentary rocks: *Geol. Soc. Amer. Spec. Paper* **85**, 130 pp.

Hay, R. L. (1970) Silicate reactions in three lithofacies of a semiarid basin, Olduvai Gorge, Tanzania: *Mineral. Soc. Amer. Spec. Pap.* **3**, 237–255.

Hay, R. L. and Moiola, R. J. (1963) Authigenic silicate minerals in Searles Lake, California: *Sedimentology* **2**, 312–332.

Hay, R. L., Pexton, R. E., Teague, T. T., and Kyser, T. K. (1986) Spring-related carbonate rocks, Mg clays, and associated minerals in Pliocene deposits of the Amargosa Desert, Nevada and California: *Geol. Soc. Amer. Bull.* **97**, 1488–1503.

Hein, J. R. and Scholl, D. W. (1978) Diagenesis and distribution of late Cenozoic volcanic sediment in the southern Bering Sea: *Geol. Soc. Amer. Bull.* **89**, 197–210.

Izett, G. A. (1981) Volcanic ash beds: Recorders of upper Cenozoic silicic pyroclastic volcanism in the western United States: *J. Geophys. Res.* **86**, 10200–10222.

Khoury, H. N. and Eberl, D. D. (1981) Montmorillonite from the Amargosa Desert, southern Nevada, U.S.A.: *Neues Jb. Mineral. Abh.* **141**, 134–141.

Liddicoat, J. C., Opdyke, N. D., and Smith, G. I. (1980) Palaeomagnetic polarity in a 930 m core from Searles Valley, California: *Nature* **286**, 22–25.

Perrier, R. and Quiblier, J. (1974) Thickness changes in sediment layers during compaction history; methods for quantitative evaluation: *Amer. Assoc. Petrol. Geol. Bull.* **58**, 507–520.

Sheppard, R. A. and Gude, A. J., 3rd (1968) Distribution and genesis of authigenic silicate minerals in tuffs of Pleistocene Lake Tecopa, Inyo County, California: *U.S. Geol. Surv. Prof. Pap.* **597**, 38 pp.

Sheppard, R. A. and Gude, A. J., 3rd (1969) Diagenesis of tuffs in the Barstow Formation, Mud Hills, San Bernardino County, California: *U.S. Geol. Surv. Prof. Pap.* **634**, 35 pp.

Siever, R., Beck, K. C., and Berner, R. A. (1965) Composition of interstitial waters of modern sediments: *J. Geol.* **73**, 39–73.

Smith, G. I. (1976) Origin of lithium and other components in the Searles Lake evaporites, California: *U.S. Geol. Surv. Prof. Pap.* **1005**, 92–103.

Smith, G. I. (1979) Subsurface stratigraphy and geochemistry of Searles Lake late Quaternary evaporites, Searles Lake, California: *U.S. Geol. Surv. Prof. Pap.* **1043**, 130 pp.

Smith, G. I. (1984) Paleohydrologic regimes in the southwestern Great Basin, 0–3.2 my ago, compared with other long records of "global" climate: *Quat. Res.* **22**, 1–17.

Smith, G. I., Barczak, V. J., Moulton, G. F., and Liddicoat, J. C. (1983) Core KM-3, a surface-to-bedrock record of late Cenozoic sedimentation in Searles Valley, California: *U.S. Geol. Surv. Prof. Pap.* **1256**, 24 pp.

Surdam, R. C. (1977) Zeolites in closed hydrologic systems: in *Mineralogy and Geology of Natural Zeolites,* F. A. Mumpton, ed., Reviews in Mineralogy **4**, Mineralogical Society of America, Washington, D.C., 65–79.