CLAY MINERAL DIAGENESIS IN CORE KM-3 OF SEARLES LAKE, CALIFORNIA

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Abstract—Core KM-3 at Searles Lake, California, comprises 693.4 m of lacustrine sediments deposited over the past 3.2 m.y. The lake water evolved from moderately saline, slightly alkaline, and dominated by Na, Ca, Cl, SO_4, and $HCO_3 + CO_3$ to a highly alkaline brine dominated by Na and CO_3 ions. Sediments are chiefly muds and evaporites. Montmorillonite and illite are the principal detrital clay minerals supplied to Searles Lake at present and probably during the late Pliocene and Pleistocene.

The drill core is divided into three diagenetic zones on the basis of clay-mineral reactions. The upper zone (0–291.1 m) contains authigenic Fe-illite, Mg-smectite, K-feldspar, and analcime, which average 60–70% of the <2-μm silicate fraction of mud samples. The principal silicate reactants are detrital montmorillonite and kaolinite, which have been largely consumed. The middle zone (291.1–541.6 m) also contains authigenic Fe-illite, Mg-smectite, K-feldspar, and analcime, but they form only 20 to 30% of the <2-μm silicate fraction, and considerable detrital montmorillonite and kaolinite remain unaltered. In muds of the lower zone (541.6–693.4 m), a small amount of clinoptilolite is the only authigenic silicate mineral identified, although authigenic montmorillonite probably coexists here as well. Vitric ash is the silicate reactant, and detrital clay minerals apparently remain unaltered in the lower zone.

Diagenetic zoning reflects the pore-water chemistry, in which pH may have been the most important parameter. Sediments of the upper zone were deposited in highly alkaline lakes of variable salinity, and sinking brines with a pH of 9.0–10.0 have saturated all sediments. Sediments of the middle zone were deposited in lakes of moderate to high salinity. The pH was overall lower than in the upper zone, although it probably exceeded 9.0, at least locally, during silicate diagenesis. Moderate salinity and a slightly alkaline pH (~7.5–8.0) are inferred for both the lake and pore water of the lower zone.

Oxygen-isotope values of authigenic Fe-illite, Mg-smectite, and K-feldspar, and phillipsite in the upper diagenetic zone reflect a high degree of evaporative concentration and presumably of salinity. Equilibrium water values calculated for 22°C from the oxygen-isotopic composition of authigenic phyllosilicates range from −3.5 to +1.9‰, averaging −1.2‰ (SMOW). Higher salinities are suggested for K-feldspar, for which water values range from +1.8 to +4.8‰, averaging +3.4‰. The water value for phillipsite is +0.3‰. By comparison, rainfall at Searles Lake has an average $\delta^{18}O$ value of about −9.8‰, and a brine sample has a value of +4.0‰.

Mud samples of the middle and upper diagenetic zones tend to be rich in Fe-illite or Mg-smectite, but not in both, indicating that the two minerals are favored to some extent by different environments. Fe-illite seems to be generally favored by oxidizing conditions and probably by a playa environment, and Mg-smectite seems to be favored by reducing conditions and an open-water environment. One stratigraphic unit of the upper zone does not fit this pattern and contains abundant Fe-illite in sediments of a deep perennial lake.

Key Words—Analcime, Diagenesis, Fe-illite, K-feldspar, Mg-smectite, Montmorillonite, Oxygen isotopes, Phillipsite, Searles Lake.

INTRODUCTION

Temperature-related controls on reactions involving smectite and illite have been intensively studied for many years, but little is known about the role of solution composition on reactions involving these minerals. Sediments of Searles Lake, California, offer an excellent opportunity to gauge the control of solution composition on mineral reactions at low temperatures because of the generally similar composition of detrital clay minerals and the widely variable solution composition through time. In this study, the silicate min-

eralogy of muds from a 693-m core of playa and lacustrine sediment taken from drill hole KM-3 (hereafter referred to as core KM-3) in Searles Lake has been examined. Sediments of this core span the past 3.2 m.y. and consist almost wholly of muds and saline layers, which record the evolution of lake and playa water from moderately saline and nonalkaline or slightly alkaline to highly saline and highly alkaline. One goal of the present study was to distinguish diagenesis in slightly alkaline saline environments from that in highly alkaline saline environments.

The nature of clay mineral reactions in these sedi-

ments has been inferred principally by the associations of detrital and authigenic silicate minerals with saline minerals. The oxygen-isotopic composition of authigenic minerals has also been determined for a better understanding of the nature and chemical environments of silicate reactions in desert lakes.

Core KM-3 was studied by Smith *et al.* (1983) and Smith (1984) with regard to paleochemistry, hydrology, and paleoclimate. Other reports on core KM-3 have been largely concerned with alteration of ash layers (Guldman, 1984; Donahoe *et al.*, 1984; Hay and Guldman, 1987), although Guldman's mineralogic work on mud composition (1984) laid the foundation for the present study.

Silicate diagenesis in Searles Lake has also been discussed in reports based on other cores. Droste (1961a) reported on the clay-mineral composition of several cores. Hay and Moiola (1963) characterized the silicate diagenesis in three cores, the deepest of which extends into unit F. Smith (1979) provided drill-core data from which he inferred a relation between saline layers and the distribution of K-feldspar and analcime in the Bottom Mud.

METHODS AND TERMINOLOGY

This study is based largely on laboratory study of 84 samples of mud from core KM-3. 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 carbonate minerals as well as silt and clay. Samples for this study were selected for a high content of silicate material. Some of the samples were provided by J. C. Liddicoat following his use for paleomagnetic measurements. Bulk powders of most muds were analyzed by XRD without pretreatment. Saline minerals, where abundant, were removed with 5% acetic acid before XRD analysis. Dispersion and centrifuging were used to obtain the <2-, <0.2-, and <0.1-μm fractions. Oriented mounts of the <2-μm fraction were analyzed for all samples. Mounts for the <0.1-μm fraction were analyzed for 26 samples in the first phase of the work, at Berkeley, and mounts of the <0.2-μm fraction were analyzed for 11 samples in the final phase, at Champaign-Urbana. Most of the oriented mounts were prepared by suction through Millipore filters and transferred to glass slides (Drever, 1973); the remainder were prepared by suction through ceramic tile. All oriented mounts were run air-dry; most were run after glycolation; and about one-third were run after heating to 375°C for 1 hr.

Proportions of kaolinite-chlorite, illite, and smectite were estimated from areas under the low-angle peaks, using multiplier factors of 1 for the 12.6–17.7-Å peak of smectite, 2 for the 7-Å peak of kaolinite and chlorite, and 3 for the 10-Å peak of illite (Hallberg *et al.*, 1978). Peak areas from air-dry mounts were used in the Berkeley diffractograms because of problems in measuring

the low-angle base line of glycolated samples. Peak areas from glycolated samples were used in Champaign-Urbana. These slightly different methods yielded nearly the same results for samples analyzed at both labs. The clay mineral estimates are probably ±30% of the amount present (Bayliss, 1986), which is sufficient for the present study, in which the most important distinction is between samples that are wholly or almost wholly illite and those that contain substantial amounts of smectite.

Compositional varieties of illite and smectite were distinguished on the basis of 060 reflections of randomly oriented powders. These were made on <2-μm clay fractions of 31 samples and <0.1- and <0.2-μm clay fractions of 11 samples. Random mounts were made using Al sample holders, except for a few in which the amount of clay was insufficient. For these samples, random mounts were made on the surface of glass slides. Slow scans ($0.05°2\theta/min$) yielded well-defined 060 reflections (see, e.g., Figure 3). As discussed below, the 060 reflections were interpreted on the basis of the following d-values: aluminous illite (1.497–1.503 Å), iron-rich illite, here termed Fe-illite (1.506–1.514 Å), montmorillonite (1.497–1.503 Å), Mg-rich smectite, here termed Mg-smectite (1.514–1.521 Å), and chlorite (1.530–1.537 Å). Broad 060 peaks such as the asymmetrical peak of Mg-smectite clay from a depth of 19.9 m (Figure 3b) can be attributed either to varying degrees of mixed-layering or to compositional heterogeneity. A d(060) value of 1.530–1.535 Å, presumably from chlorite, was noted in several samples for which a 7-Å spacing was lacking in the patterns from oriented mounts. Apparently, smaller amounts of chlorite in core KM-3 could be identified by the 060 peak from random mounts than could be identified from the 002 peak of oriented mounts.

Samples for chemical analysis were Na-exchanged three times with a 1 N NaCl solution, then centrifuged, and finally dialyzed for 4 days at room temperature to remove excess Na. Fe-illite from surface exposures was treated with a pH-buffered Na dithionate solution to remove free ferric oxide before chemical analysis.

Amounts of K-feldspar and analcime were estimated from XRD patterns of both bulk powders and oriented mounts of the primary 84 samples. XRD patterns from K-feldspar in oriented mounts showed no preferred orientation, and amounts estimated from oriented mounts were the same as estimates from random mounts of the same material. XRD analyses were made of 18 additional bulk samples in the search for K-feldspar and analcime in units H and I below 455.8 m, the deepest of the 84 samples in which K-feldspar was identified.

Oxygen-isotope analyses were made by the method of Clayton and Mayeda (1963). The samples corresponding to analyses 2, 5, 6, 7, 8, 10, and 13 in Table 4 were heated overnight at 110°C to remove H_2O+;

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

Name of unit	Depth to base (m)	Nature of lake[2]
Overburden Mud	7	Shallow
Upper Salt	22	Salt flat; salines
Parting Mud	26	Deep, perennial
Lower Salt	38	Fluctuating level; salines
Bottom Mud	69	Deep, perennial; salines rare
Mixed Layer		
Units A + B	114.0	Shallow, fluctuating; salines
Unit C	166.4	Salt flat; salines
Units D + E	227.7	Moderately deep, fluctuating; salines
Unit F	291.1	Deep, perennial
Unit G	425.5	Moderately deep, fluctuating; salines
Unit H	541.6	Playa
Unit I	693.4	Deep, perennial

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

[2] Salines refers to saline layers and not to dispersed saline crystals.

the remaining clays were heated to 500°C except for sample 1, which was mistakenly run after dehydration in a vacuum at room temperature. Values are relative to standard mean ocean water (SMOW).

STRATIGRAPHY AND CHEMICAL EVOLUTION OF SEARLES LAKE

The upper 69 m of core KM-3 consists of five stratigraphic units, which are, from youngest to oldest, the Overburden Mud, Upper Salt, Parting Mud, Lower Salt, and Bottom Mud (Table 1). The Mixed Layer, 624 m thick, underlies the Bottom Mud and is divided into nine informal units, only seven of which were recognizable in core KM-3. These were designated units A to I, from youngest to oldest. Sediments of core KM-3 consist almost wholly of muds and evaporites, and the known thickness of ash layers is about 4.6 m (Hay and Guldman, 1987). Searles Lake fluctuated from a perennial lake to a playa or salt pan many times (Table 1), and the several hydrologic regimes fit a 400,000-year periodicity on which shorter-term fluctuations are superimposed (Smith, 1984). The deep perennial lakes were supplied chiefly by runoff from the Sierra Nevada via Owens and China Lakes (Figure 1).

The chemistry of the lake water changed during lacustrine deposition, and the content of chemical sediment increased overall upward, reflecting increased aridity as a result of the uplift of the Sierra Nevada (Smith *et al.*, 1983). Lake and playa waters of units G, H, and I were dominated by Na, Ca, Cl, SO_4, and HCO_3 + CO_3. The lake of unit I and the playa of unit H were
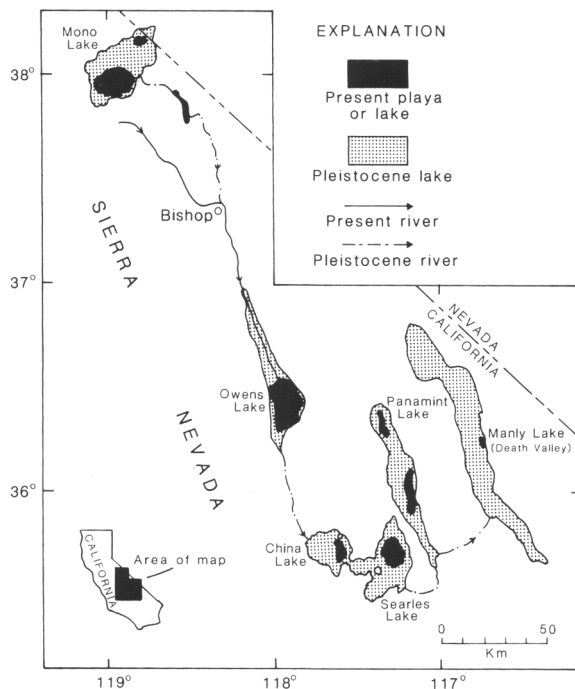

Figure 1. Map showing the location of Searles Lake, California, and lakes with which it was connected during wetter periods of the Pliocene and Pleistocene.

moderately saline, and both units contain small amounts of anhydrite that may be recrystallized gypsum. Salinities reached higher levels in the lake of unit G, resulting in layers of halite and thenardite (Na_2SO_4). The proportion of Na and CO_3 ions increased with time, and these ions became dominant in the lake of units A + B, where trona and nahcolite are the principal evaporites.

The pH of pore water is of particular concern to the present study. Saline minerals, both observed and normative, seem to indicate non-alkaline saline water for units G, H, and I and highly alkaline brine in unit F and overlying sediments (Smith, 1979; Smith *et al.,* 1983). Authigenic silicate minerals, however, indicate that pore waters of units G and H are in some important aspect(s) closer to that of the overlying deposits rather than to pore waters of unit I. Pore fluid in muds of unit I very likely has a pH of ~7.5 to 8.0, comparable to that in sea water buffered by calcium carbonate, and the only authigenic silicate minerals identified were montmorillonite and zeolite formed from rhyolitic glass (Hay and Guldman, 1987). By contrast, units G and H contain authigenic Fe-illite, Mg-smectite, K-feldspar, and analcime, of which larger amounts are found in unit F and overlying deposits. As discussed below, high pH is a chemical parameter that favors these authigenic silicates, which are commonly if not generally associated with a pH of 9 or above. The trend toward highly alkaline lake water probably began with unit H,

and the content of Na and CO_3 was sufficient to raise the lake-water pH, possibly to 9 or above, but not in sufficient quantity to precipitate trona or another sodium-carbonate mineral. In support of a high pH for unit G, at least locally, are dolomite and magnesite (Smith *et al.*, 1983).

Brine with a pH of 9 to 10 constitutes the pore fluid of unit F and all younger deposits. The measured pH is 9.2–9.4 in brine of the Lower Salt and 9.1 to 9.9 in brine of the Upper Salt (Smith, 1979), and primary sodium carbonate minerals (e.g., trona or nahcolite) point to saline and highly alkaline lake water for all deposits above unit G except for unit F and the Parting Mud. Diagenetic gaylussite ($CaCO_3 \cdot Na_2CO_3 \cdot 5H_2O$), pirssonite ($CaCO_3 \cdot Na_2CO_3 \cdot 2H_2O$), or both, are abundant in all deposits above unit G, showing that the pore-water pH is 9–10 in unit F as well as in younger deposits. The gaylussite and pirssonite are attributed to reaction of earlier-deposited calcite with Na-rich brine that descended to an escape zone to the east that occurs at the base of unit F (Friedman *et al.*, 1982).

Thus, core KM-3 can be subdivided into three diagenetic zones on the basis of silicate diagenesis, which reflect differences in pore-water chemistry. Unit I constitutes a lower zone with minimal silicate diagenesis in which the pore water is moderately saline and slightly alkaline pH (~7.5–8.0). Units G and H constitute a middle zone of increased silicate diagenesis with pore fluid that is moderately to highly saline and may have had a pH as high as 9 or above, at least locally, during silicate diagenesis. Deposits above unit G constitute an upper zone of maximum silicate diagenesis, in which the pore fluid is an alkaline brine with a pH of 9.0–10.0.

An outcrop of upper-zone deposits containing green authigenic Fe-illite will be considered in this report. The illite occurs in the upper 30–60 cm of a paleosol with caliche nodules developed on magnetite-rich sandstones that are the outcropping equivalent of the uppermost part of the Mixed Layer 6 km southeast of the present playa in SE ¼ Sec. 32, T.26S., R.43E. It is overlain by carbonate-rich sediments, which are the outcropping equivalent of the Bottom Mud. The paleosol lies about 33 m above the present playa and about 102 m above the base of the Bottom Mud in the center of the lake.

RESULTS AND DISCUSSION

Silicate minerals

Illite. Illite is present in all mud samples; it constitutes at least 90% of both the <2-μm fraction in 20 of the 84 samples (Figure 2) and the fine clay fraction of 11 of 30 fine clay fractions analyzed. Two types of illite are indicated by the d(060) value. One variety has a d-value of 1.497–1.503 Å; the other has a d-value of 1.506–1.514 Å (Figures 3d, 3e, and 3g). Illite having

the smaller d-values is aluminous, and a detrital origin is inferred because it is the only type of illite in Unit I, in which the clay minerals are largely detrital. The illite having a d(060) value of 1.506–1.514 Å is rich in iron and is termed Fe-illite. It is considered to be authigenic because of its Fe-rich composition and because it is most abundant and may be the only illite in the fine clay fractions (see, e.g., Hower *et al.*, 1963). It contains a small amount, possibly 5%, of interstratified illite/smectite (I/S) as indicated by a broadening of the 002 peak and an increase in the intensity of the 003 peak relative to the 001 peak in glycolated mounts compared to the air-dry mounts (Šrodoń and Eberl, 1984). The chemically analyzed sample from core KM-3 (Table 2, sample 3) contains 10.36% Fe as Fe_2O_3. This Fe-Illite can be considered celadonitic, as most of the charge is in the octahedral sheet (Table 3, sample 3), and its 060 d-value is 1.509 Å (Bailey, 1980). Authigenic green illite from the outcropping paleosol contains 18.3% Fe as Fe_2O_3 (Table 3, sample 4), and the d(060) value is 1.511 Å, which falls in the range accepted for glauconite (Bailey, 1980). Chemically similar authigenic green illite has been termed glauconitic illite by Parry and Reeves (1966). No green illitic clays were noted in core KM-3, although the Fe-illite in two samples has a d(060) value of 1.514 Å, in the range for glauconite.

Illite-rich muds above unit F are generally pale yellow and brown and are commonly mottled gray and brown. Common colors of dry muds are 10YR 6/4, 10YR 7/3, and 5Y 7/3 in the Munsell system. Illite-rich muds of unit F are generally pale olive (e.g., Munsell color 10Y 6/2).

Smectite. Smectite has been identified in most muds of Searles Lake. The coexistence of two types is indicated by the d(060) values. One type is dioctahedral and has a d(060) value of 1.497–1.503 Å. The d(060) value of the other type is 1.514–1.521 Å, suggesting a trioctahedral smectite, nontronite, or a smectite intermediate in composition. The 001 peak of the dioctahedral smectite expands to 17–18 Å on glycolation and collapses to 10 Å on heating to 375° for 1 hr. The intensity of the 002 and 003 peaks is highly variable relative to the 001 peak, suggesting differences in particle size, shape, or composition, and possibly mixed layering in some samples. Weak superlattice peaks at 33–35 Å are present in the XRD patterns of a few glycolated samples from units G and H. Montmorillonite has formed in bentonitic ash layers of unit I (Hay and Guldman, 1987), and authigenic montmorillonite may well be present in tuffaceous muds of unit I.

The smectite having a d(060) value of 1.514–1.521 Å is Mg-rich trioctahedral smectite. The 060 peaks are generally sharp and rather narrow (Figure 3c), but a few are broad and asymmetric (Figure 3b). Broad peaks can be due either to interstratification of dioctahedral
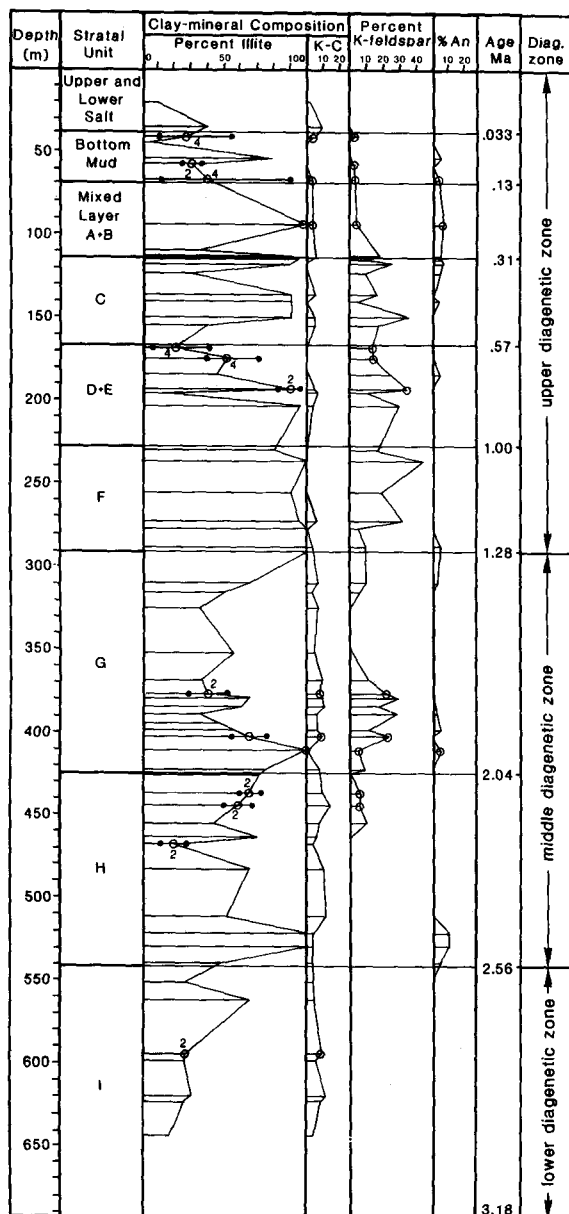
Figure 2. Columnar section showing sampled stratigraphic units of core KM-3 and clay mineral composition and content of authigenic K-feldspar in the <2-μm fraction. Clay mineral composition is given in terms of percentage of illite and percentage of kaolinite and/or chlorite (K-C). The amount of smectite is the difference between 100% and the sum of illite and K-C. The percentage of analcime (% An) is based on bulk samples, which indicate the content of analcime in the muds more accurately than the amount in the <2-μm fraction. Small numbered circles represent the average of two or more samples, and numbers indicate the number of samples that were averaged. Small black circles represent the range of illite content in the averaged samples.
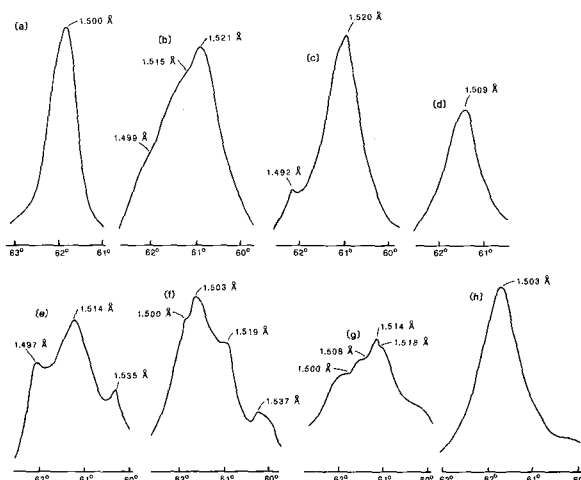

Figure 3. 060 patterns of clay mineral samples from core KM-3. (a) <0.2-μm fraction of montmorillonite with no mixed layering from bentonite at a depth of 683.8 m in unit I (Hay and Guldman, 1987). (b) <1-μm fraction of Mg-smectite with 5% illite from a depth of 19.9 m in the Upper Salt. Broad peak may indicate interstratification or a physical mixture of dioctahedral and trioctahedral smectite. Significance of faint shoulders at 1.499 Å and 1.515 Å is uncertain. (c) <2-μm fraction consisting of Mg-smectite (90%) and illite (10%) from a depth of 167.5 m in unit D + E. Shoulder at 62° may represent detrital illite. (d) <0.2-μm fraction of Fe-illite from a depth of 96.0 m in unit A + B; its chemical analysis is no. 3 in Table 5. (e) <2-μm fraction consisting of illite (90%) and Mg-smectite (10%) from a depth of 54.5 m in the Bottom Mud. Peak at 1.514 Å represents Fe-illite and possibly Mg-smectite; peak at 1.497 Å probably represents detrital illite; peak at 1.535 Å probably represents chlorite. (f) <2-μm fraction consisting of illite (45%), smectite (50%), and kaolinite and/or chlorite (5%) from a depth of 455.8 m in unit H. Peak at 1.503 Å and shoulder at 1.500 Å represent detrital illite and montmorillonite; shoulder at 1.519 Å represents Mg-smectite; peak at 1.537 Å is attributed to chlorite. (g) <2-μm fraction of illitic clay from a depth of 411.3 m in unit G. Peak at 1.514 Å and shoulder at 1.508 Å represent authigenic illite, shoulder at 1.500 Å probably represents detrital illite, and shoulder at 1.518 Å may represent Mg-smectite. (h) <2-μm fraction consisting of detrital illite (25%), montmorillonite (72%) and kaolinite and/or chlorite (3%) from a depth of 550.6 m in unit I.

and trioctahedral smectite, or to a physical mixture of the two. The 001 peak expands to 17.8 Å on glycolation and collapses only partly to 10 Å on heating to 375°C. Both samples from Searles Lake that were chemically analyzed (Table 2, samples 1 and 2) contain considerable non-exchangeable K (3.97 and 3.34% K_2O). The reason for the high content of nonexchangeable K in the Mg smectite is not known. Structural formulae give octahedral occupancies of 2.41 and 2.28, respectively.

Montmorillonite-rich muds are brown, gray, or green, but muds rich in Mg-smectite are generally greenish. Pale olive (10Y 5/2) is a common color of muds rich in Mg-smectite. These colors suggest that montmorillonite-rich muds were deposited in both oxidizing and

Table 2. Chemical analyses[1] of Na-exchanged clays from Searles Lake, California.

	(1)	(2)	(3)	(4)
SiO_2	54.2	51.6	51.4	54.1
TiO_2	0.23	0.29	0.57	0.30
Al_2O_3	6.81	9.56	12.5	7.18
Fe_2O_3	3.15	3.70	9.21	16.83
FeO	n.d.	n.d.	1.05	1.33
MnO	0.04	0.08	0.04	0.04
MgO	15.4	13.6	6.95	4.84
CaO	0.28	0.93	0.32	0.26
Na_2O	0.46	2.30	1.03	0.88
K_2O	3.97	3.34	5.90	6.11
P_2O_5	0.04	0.12	0.06	0.03
L.O.I.	16.2	n.d.	10.3	8.05
Total	100.8	85.5	99.3	100.0

(1) <0.2-μm fraction of mud consisting of Mg-smectite and a trace of illite from units D + E at depth of 167.5 m.

(2) <1-μm fraction of mud from Upper Salt at a depth of 19.9 m, consisting of Mg-smectite and a trace of illite.

(3) <0.2-μm fraction of Fe-illite from unit A + B at depth of 96.0 m.

(4) <2-μm fraction of green Fe-illite with a trace of montmorillonite from paleosol beneath outcrop equivalent of Bottom Mud.

[1] Analyses are by X-ray Assay Laboratories, Don Mills, Ontario. All Fe is calculated as Fe_2O_3 except in (5) and (6), for which FeO and Fe_2O_3 were determined by J. W. Stucki.

Table 3. Unit formulae set to 22 charges for Na-saturated fractions of clay minerals from Searles Lake.[1]

		(1)	(2)	(3)	(4)
Tetrahedral	Si	3.96	3.78	3.71	3.87
	Al	0.04	0.22	0.29	0.13
	Σ	4.00	4.00	4.00	4.00
Octahedral	Al	0.55	0.58	0.77	0.48
	Ti	0.01	0.02	0.03	0.02
	Fe^{3+}	0.17	0.20	0.50	0.91
	Fe^{2+}	n.d.	n.d.	0.07	0.08
	Mg	1.68	1.48	0.75	0.52
	Σ	2.41	2.28	2.12	2.01
Interlayer	Ca	0.02	0.07	0.03	0.02
	Na	0.07	0.33	0.14	0.12
	K	0.37	0.31	0.54	0.55
Charge	Tet	0.04	0.22	0.29	0.19
	Oct	0.45	0.56	0.43	0.49
	Σ	0.49	0.78	0.72	0.68
	Int	0.48	0.78	0.74	0.71

[1] Sample numbers are the same as in Table 2; samples (1) and (2) are Mg-smectite, (3) is non-green Fe-illite, and (4) is green Fe-illite.

reducing environments, but Mg-smectite seems to have been favored by a reducing environment.

Kaolinite and chlorite. Kaolinite and chlorite are minor constituents of many muds. They were distinguished in some samples on the basis of the 002 peak of kaolinite at 3.58 Å and the 004 peak of chlorite at 3.54 Å.

K-feldspar, analcime, searlesite, and clinoptilolite. Authigenic K-feldspar is a minor to major constituent of many Searles Lake muds. The K-feldspar is monoclinic on the basis of its XRD pattern, which is similar to that of the authigenic K-feldspar in tuffs of Searles Lake (Hay and Moiola, 1963). K-feldspar is present in the <2-μm fraction, but it is generally absent in the <0.2-μm fraction, suggesting that the crystals may be about the same size as in the tuffs, i.e., about 0.5 to 5 μm in diameter.

Analcime is a minor constituent of some muds. Crystals are generally 4 to 20 μm in diameter, and, consequently, XRD peaks are commonly more intense from bulk samples than from the <2-μm fraction. Clinoptilolite was identified by XRD in one sample of tuffaceous mud from unit I, and it is relatively common in bentonitic ash layers of unit I. Searlesite ($NaBSi_2O_6 \cdot H_2O$) was identified by XRD in one mud sample from unit D + E.

Detrital silt and sand. The more common detrital sand- and silt-size minerals are quartz, microcline, orthoclase, and plagioclase; less common are biotite, horn-

blende, augite, and magnetite. Etched quartz was noted in a few samples from unit A + B through unit D + E, but no systematic observations were made of the etching.

Oxygen-isotope composition of silicate minerals

Several factors must be considered in interpreting the oxygen-isotopic composition of authigenic silicate minerals of Searles Lake. The isotopic composition of meteoric water supplied to Searles Lake is different for interpluvial times like the present, when water is from the local drainage basin, and pluvial times when the Sierra Nevada was the principal source of water. Rainfall at Searles Lake had an average δD value of $-68‰$ in 1982–1988 (George I. Smith, U. S. Geological Survey, Menlo Park, California, personal communication, 1989). Water in the Owens River in 1969–1970 had an average δD value of $-120‰$ (Friedman *et al.*, 1976). Using the meteoric water line of Craig (1961), these deuterium measurements correspond to $\delta^{18}O$ values of $-16.3‰$ for the Owens River and $-9.8‰$ for rainfall at Searles Lake. The only $\delta^{18}O$ measurement of brine is $+4.0‰$, for a sample from the upper Salt in drill hole L-31 at a depth of 15.2 m (I. Friedman, U.S. Geological Survey, Denver, Colorado, personal communication, 1990). Deuterium values can range widely within brine and hydrous minerals of individual stratigraphic units (Friedman *et al.*, 1982). Much of this variation is attributable to brine flushing, i.e., the sinking of dense brines toward the outlet at the base of unit F.

Progressive deuterium depletion of 40‰ has been recorded in fluid inclusions in travertine of Death Valley over the past 3 m.y. (Winograd *et al.*, 1985). The decrease is attributed to uplift of the Sierra Nevada

Table 4. Oxygen-isotope composition of silicate minerals from core KM-3.

Sample and stratigraphic unit	Depth (m)	Size fraction	Composition	% Detrital	$\delta^{18}O$ ‰ (SMOW)	Water[2] value $\delta^{18}O$
Upper Salt						
1	19.9	$<1~\mu m$	95% Mg-S, 5% I	5	+22.4	−3.5
2	19.9	bulk	phillipsite	0	+30.3	+0.3
Bottom Mud						
3	43.6	$<2~\mu m$	50% Mg-S, 50% mt	50	+21.2	
4	54.4	$<2~\mu m$	90% I, 10% Mg-S	30–40	+24.6	
5	54.4	$<0.2~\mu m$	75% I, 25% Mg-S	20	+22.2	
Mixed Layer						
6 unit A + B?[1]	0	$<2~\mu m$	green Fe-I	5	+20.4	−2.7
7 unit A + B	96.0	$<0.2~\mu m$	non-green Fe-I	0	+20.8	−2.3
8 unit D + E	167.5	$<0.2~\mu m$	Mg-S, 5% I	5?	+27.8	+1.9
9 unit D + E	168.6	bulk	K-feldspar	0	+31.9	+1.8
10 unit D + E	169.1	bulk	K-feldspar	0	+35.9	+4.8
11 unit D + E	169.8	bulk	K-feldspar	0	+33.8	+3.7
12 unit G	375.5	$<2~\mu m$	63% mt + Mg-S, 33% I, 4% K-C	50–75	+21.7	
13 unit I	622.8	$<2~\mu m$	75% mt, 20% I, 5% K-C	100	+19.3	−7.9
14 unit I	684.0	$<2~\mu m$	mt	0	+20.1	+2.7

Abbreviations are I, illite; Fe-I, Fe-illite; mt, montmorillonite; Mg-S, Mg-smectite; and K-C, kaolinite-chlorite.

[1] Surface exposure of paleosol developed over the Mixed Layer.

[2] Water values were calculated for 22°C except for analyses 13 and 14 for which water values were calculated at 15° and 73°C, respectively.

and Transverse ranges with attendant orographic depletion of D from inland-bound Pacific storms. This decrease in deuterium corresponds to a decrease of ~5‰ in $\delta^{18}O$. Searles Lake lies 50 km southwest of Death Valley, and its meteoric water should have been affected to about the same extent.

The temperature is 21°C near the surface of sediments in Searles Lake and 27°C at a depth of 75 m (Smith, 1979). The geothermal gradient should decrease with depth because of lower porosity and increased thermal conductivity. The calculated temperature at the base of unit I is about 73°C, if the compaction of sediments in Searles Lake is about the same as that of marine muds (T. Corbett, Department of Geology, University of Illinois, Urbana, Illinois, personal communication, 1989).

Illite. The $\delta^{18}O$ values of green and non-green Fe-illite from the upper zone are +20.4 and +20.8‰, respectively (Table 4, samples 6 and 7), which give water values of −2.7 and −2.3‰ using a temperature of 22°C and $\Delta_{\text{illite-water}} = 2.43~(10^6/T^2) - 4.8$ (Eslinger and Savin, 1973). The Eslinger-Savin relationship was developed for aluminous illites, and some evidence exists that the clay-H_2O fractionation decreases with increasing Fe content because the Fe–O bond is weaker than the Al–O bond (see, e.g., Savin and Lee, 1988). Thus, water values may have been slightly greater than calculated above, and the water value for the green illite may have been greater than that for non-green illite. The nearly similar $\delta^{18}O$ values are surprising inasmuch as the non-green Fe-illite is from mud between saline layers in the center of the lake basin and the green Fe-illite is from

a paleosol 6 km southwest of the present playa in which the overlying calcite-rich lacustrine sediments were deposited by presumably dilute waters of an expanding lake. As discussed below, the green Fe-illite was very likely formed by reaction of detrital materials with descending brine.

Coarse and fine illitic clay from the Bottom Mud give $\delta^{18}O$ values of +24.6 and +22.2‰, respectively (Table 4, samples 4 and 5). The coarse clay is about 90% illite that is dominantly authigenic, 10% Mg-smectite, and a trace of analcime. The fine clay fraction is about 75% illite that is dominantly authigenic and 25% Mg-smectite. The isotope values for these mixtures suggest that the authigenic illite has a higher $\delta^{18}O$ value than the associated Mg-smectite. Probably, the $\delta^{18}O$ value of the authigenic Fe-illite is about +23 or +24‰. A value of +23.5‰ would correspond to a water value of +0.4‰ at 22°C.

Smectite. Oxygen-isotope results were obtained from authigenic smectites and from clay-mineral separates containing varying amounts of detrital and authigenic smectite. Samples of Mg-smectite from the Upper Salt and unit D + E yielded $\delta^{18}O$ values of +22.4 and +27.8‰, respectively (Table 4, samples 1 and 8). Using $\Delta_{\text{montmorillonite-water}} = 2.67~(10^6/T^2) - 4.8$ (Yeh and Savin, 1977) for the two Mg-smectite samples gives $\delta^{18}O$ water values of −3.5‰ and +1.9‰ at 22°C. The $\delta^{18}O$ value of +22.4‰ for the younger of the two smectite samples very likely reflects framework oxygen either inherited from a montmorillonite precursor or as an admixture of detrital montmorillonite, or both. This interpretation is supported by the broad 060 XRD peak

of the sample (Figure 3b). Moreover, as noted below, a water value of +0.3‰ is indicated for phillipsite of the same core sample as the Mg-smectite giving a $\delta^{18}O$ water value of −3.5‰.

A $\delta^{18}O$ value of +20.1‰ was obtained from authigenic montmorillonite (Table 4, sample 14) of a bentonite near the base of unit I, where the temperature is estimated to be about 73°C. The smectite-water equation of Yeh and Savin (1977) gives a $\delta^{18}O$ value of +2.7‰ for water at this temperature. This $\delta^{18}O$ value is unreasonably high for a perennial lake with external drainage, and the bentonite may have been formed at depths substantially shallower and cooler that at present. At a temperature of 40°C, for example, the water value is −2.3‰, which nevertheless implies considerable evaporative concentration.

A $\delta^{18}O$ value of +19.3‰ was obtained from montmorillonitic clay of unit I that is interpreted here as wholly detrital (Table 4, sample 13). Using a temperature of 15°C for a hypothetical origin by weathering gives a $\delta^{18}O$ value of −7.9‰ for the water, using the montmorillonite-water fractionation factor given above. This value is not unreasonable for rainfall about 3 m.y.B.P., when the Sierra Nevada was much lower.

Samples containing both detrital montmorillonite and authigenic Mg-smectite give $\delta^{18}O$ values of +21.2 and +21.7‰ (Table 4, samples 3 and 12). These values are reasonable for mixtures of authigenic and detrital smectite.

Phillipsite. A $\delta^{18}O$ value of +30.3‰ was obtained for phillipsite from an altered ash layer in the Upper Salt (Table 4, sample 2). By comparison, low-temperature marine phillipsite has $\delta^{18}O$ values of +33.6 to +34.9‰ (Savin and Epstein, 1970; Bohlke *et al.,* 1984). The phillipsite-water fractionation factor may be close to that for K-feldspar-water inasmuch as both minerals are alkali tectosilicates, and the phillipsite formed from silicic glass in saline alkaline lakes has about the same Si:Al ratio as K-feldspar (Sheppard and Fitzpatrick, 1989). The O'Neil and Taylor (1967) equation for $\Delta_{\text{alkali feldspar-water}} = 2.91(10^6/T^2) − 3.41$ gives a $\delta^{18}O$ value of +34.3‰ for phillipsite formed in sea water at 5°C and +30.0‰ for phillipsite formed in sea water at 22°C, the temperature of the Upper Salt. Using this equation, the phillipsite in the Upper Salt crystallized in a fluid with a $\delta^{18}O$ value of +0.3‰.

K-feldspar. Samples of K-feldspar from different levels of altered Lava Creek B ash (0.62 Ma) give very high values of +31.9 to +35.9‰ (Table 4, samples 9–11). The large amount of variation may be due to brine movements over a lengthy period required for growth of the K-feldspar crystals. The crystals range in average size from ~0.5 to 4 μm, and the sample with the largest crystals has the highest $\delta^{18}O$ value. Using the equation of O'Neil and Taylor (1967), water values for K-feldspar range from +1.8 to +4.8‰ at a temperature of 22°C. As noted below, the K-feldspar probably crystallized over a lengthy time span at average temperatures a few degrees higher than 22°C. Higher temperatures would require higher oxygen-isotopic values for water in order to give the measured $\delta^{18}O$ values for K-feldspar.

Oxygen-isotope summary. Oxygen-isotope values calculated for waters of authigenic silicates in the upper diagenetic zone reflect a high degree of evaporative concentration and presumably salinity. Higher salinities are suggested for K-feldspar than for phyllosilicates, using the fractionation factors accepted here. Calculated water values for K-feldspar at 22°C range from +1.8 to +4.8, averaging +3.4‰, compared to water values of −3.5 to +1.9, averaging −1.2‰ for phyllosilicates. The water value for phillipsite is +0.3‰. For the lower diagenetic zone, a water value +2.7‰ is calculated for montmorillonite formed from volcanic glass at the present temperature of about 73°C. This $\delta^{18}O$ value is unreasonably high for water of a lake with external drainage, suggesting that the montmorillonite was formed at a depth and temperature substantially less than at present.

Distribution of authigenic silicates

Upper diagenetic zone. Authigenic silicates constitute about half or more, averaging 60–70%, of the <2-μm silicate fraction of muds from the upper diagenetic zone, which comprises the Upper Salt down through unit F (Figure 4). The principal authigenic silicates are Mg-smectite, Fe-illite, and K-feldspar; minor constituents are analcime and searlesite. Mg-smectite is the only smectite identified except in the <2-μm fraction of a sample from a depth of 42.1 m in the Bottom Mud, which shows 060 peaks of both trioctahedral and dioctahedral smectite (Table 5). The fine clay fraction of this sample contains only Mg-smectite. The nature of the smectite in unit F of core KM-3 has not been determined, but Mg-smectite has been identified recently as the smectite in a sample from a depth of 260.4 m in unit F of core L-W-D (see Hay and Moiola, 1963). Authigenic Fe-illite very likely predominates over detrital illite in the illite-rich samples, because its 060 peak is more intense than that of detrital illite in four of the five illite-rich coarse clay fractions on which 060 measurements were made (Table 5; Figure 3e). The fine clay fraction of three highly illitic samples is largely or wholly Fe-illite. No general correlation exists between the illite-rich horizons and salt layers, as logged by Smith *et al.* (1983).

Muds tend to have high contents of Mg-smectite or Fe-illite, but not subequal amounts of both. This distribution pattern is illustrated by the proportions of smectite and illite in the <2-μm fraction of the upper diagenetic zone (Figure 5A). The samples cluster in two groups, one with ≥90% illite, and the other with
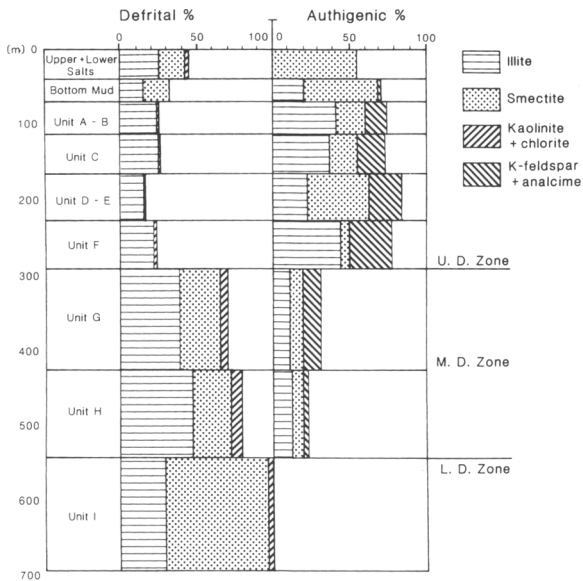
Figure 4. Estimated amounts of detrital and authigenic silicate minerals in the <2-μm fraction of muds from core KM-3. L. D., M. D., and U. D. Zone refer to the lower, middle, and upper diagenetic zones, respectively. Percentage estimates are based on the sizes of 001 and 060 peaks. Data are least reliable in the middle diagenetic zone, as discussed in text.

>50% smectite. The smectite is nearly all Mg-smectite, but the illite includes both authigenic and detrital varieties. If detrital illite were excluded, the distribution of muds into Mg-smectite-rich and Fe-illite-rich populations would still be bimodal. Such a bimodal distribution indicates that Mg-smectite and Fe-illite were favored to some extent by different environments, either depositional or post-depositional. No obvious relation exists between species of authigenic clay mineral and salinity, but different colors of Fe-illite-rich and Mg-smectite-rich muds above unit F suggest that the two minerals may have been favored by environments of different Eh and water depth. Yellow and brown colors of most of the illite-rich samples are compatible with an oxidizing (possibly a playa) environment, and the green and gray colors of samples rich in Mg smectite are compatible with a reducing lacustrine environment. Unit F is an exception in having abundant Fe-illite in olive-colored clays that were deposited in a deep perennial lake.

K-feldspar increases irregularly downward from the Bottom Mud, where it averages about 2% of the <2-μm fraction, to unit F, where it averages about 22% (Figure 4). It is present in all samples from unit A + B through unit F, and larger amounts are found in illite-rich than in Mg-smectite-rich muds. Small amounts of analcime occur in about 20% of the samples from middle and upper diagenetic zones and are most common in the illite-rich muds. Searlesite was identified in only one sample, from a depth of 193.0. Additional searles-
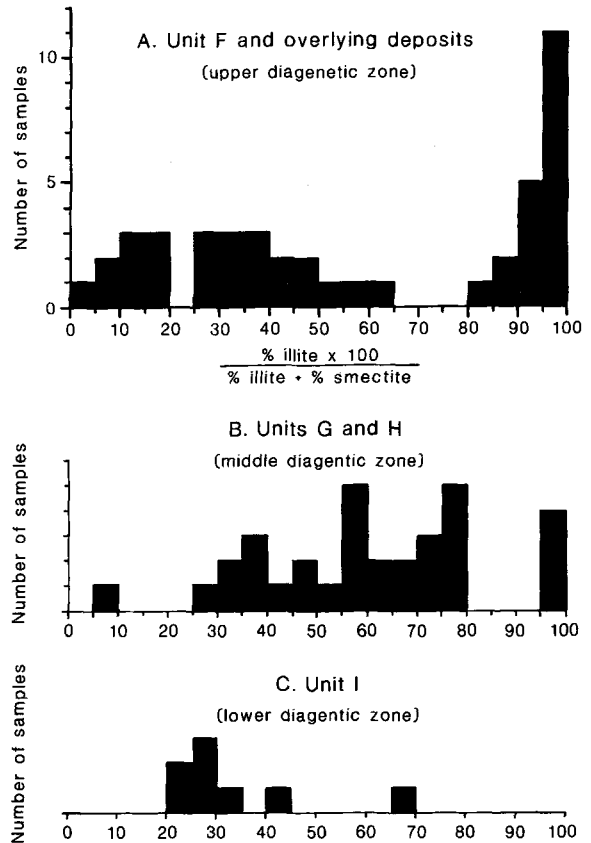

Figure 5. Histograms showing the relative percentages of illite and smectite in the <2-μm fractions of (A), the upper diagenetic zone; (B), the middle diagenetic zone; and (C), the lower diagenetic zone. In A, nearly all the smectite and probably most of the illite are authigenic; in B, most of the smectite and illite are detrital; and in C, all of the illite and smectite are considered detrital.

ite in muds of unit F was reported by Smith *et al.* (1983).

Middle diagenetic zone. In the middle zone, comprising units G and H, authigenic silicates are both less abundant and more unevenly distributed than in the upper zone. Mg-smectite was identified in 5 of the 10 smectitic samples from units G and H for which 060 measurements were made. It is the dominant smectite in only one sample, from a depth of 539.6 m (Table 5). Illite constitutes 90% or more of the <2-μm fraction of 4 out of the 27 samples from the middle zone, compared to 16 of 42 samples from the upper zone. Fe-illite predominates in the three illite-rich samples for which 060 patterns were made. As in the upper zone, illite-rich muds tend to be brown, and claystones richest in Mg-smectite tend to be olive or gray. K-feldspar was identified in 16 of the 27 samples and appears to be absent in the lower one-third of the zone, based on XRD analyses of 10 bulk samples below a depth of 455.8 m in addition to the 8 for which the <2-μm

Table 5. Clay-mineral composition of coarse clay fractions from core KM-3.[1]

Depth (m)	Strat. unit	(001) Results			(060) Results				
		ΣI	ΣS	K-C	dI	Fe-I	mt	Mg-S	C
19.9	Upper Salt	5	95	tr	?	?	0	xxx	0
42.1	Bottom Mud	15	85	tr	0	xx	0	xxx	0
43.6	Bottom Mud	5	95	tr	tr	?	?	0	xxx
54.4	Bottom Mud	85	15	tr	xx	xxx	0?	xx	x
68.9	Bottom Mud	90	10	0	xxx	xxx	0	xx	0
96.0	Unit A + B	100	0	tr	xx	xxx	0	0	x
167.5	Unit D + E	10	90	0	x?	0?	0	xxx	0
175.3	Unit D + E	55	45	0	xx	xx?	0?	xxx	x
183.7	Unit D + E	45	55	0	xxx	xx?	0	xxx	x
203.8	Unit D + E	100	0	tr	xx	xxx	0	0	x
289.3	Unit F	100	0	tr	xx	xxx	0	0	x
315.3	Unit G	50	50	tr	xxx	xx	xxx	0	0
325.0	Unit G	35	60	5	xx	x?	xxx	xx	x
352.4	Unit G	55	40	5	xxx	0?	xxx	xx	x
369.0	Unit G	35	55	10	xxx	xx	xxx	x?	x
375.5	Unit G	35	60	5	xx	xxx	xxx	xx	0
399.1	Unit G	15	80	5	x?	x	xxx	x?	x
411.3	Unit G	100	0	0	xx	xxx	0	x	x
438.0	Unit H	60	30	10	xxx	xx	xxx	0	0
455.8	Unit H	45	50	5	xxx	?	xxx	xx	x
466.5	Unit H	10	90	tr	xxx	0	xxx	0	x
521.8	Unit H	100	0	tr	x	xxx	0	0	x
529.6	Unit H	100	0	tr	x	xxx	0	0	tr
539.6	Unit H	45	55	tr	xxx	?	x?	xxx	0
550.6	Unit I	70	25	5	xxx	0	xxx	0	0
562.3	Unit I	30	65	5	xxx	0	xxx	0	x
596.0	Unit I	25	65	10	xxx	0	xxx	0	x
599.1	Unit I	25	75	10	xxx	0	xxx	0	0
623.0	Unit I	25	70	5	xxx	0	xxx	0	x

[1] Data are from <2-μm fraction, except for samples at 19.9 m (<1 μm) and 68.9 m (1–2 μm). Abbreviations are ΣI, all illite; dI, detrital illite; Fe-I, Fe-illite; ΣS, all smectite; mt, montmorillonite; Mg-S, Mg-smectite; K, kaolinite; C, chlorite. Abundance estimates are xxx, major constituent; xx, constituent in intermediate abundance; x, minor constituent; tr, trace; 0, absent; and ?, uncertain or questionable interpretation.

fraction was analyzed. Analcime is a minor constituent in units G and H, as in the overlying deposits, and it is present in all four illite-rich samples.

Montmorillonite and kaolinite of detrital origin are present in most samples, and chlorite is more common than in the upper zone. The presence of montmorillonite and kaolinite increases the uncertainty in interpreting 060 peaks, and in some samples the d(060) values serve only to distinguish authigenic Mg-smectite + Fe-illite (060 = 1.506–1.520 Å) from detrital illite + montmorillonite + kaolinite (060 = 1.490–1.503 Å).

Lower diagenetic zone. Unit I constitutes the lower diagenetic zone, in which a small amount of clinoptilolite was identified in one mud sample. This sample is from a depth of 649.4 m, within the interval in which ash layers are altered to smectite, opal, and clinoptilolite (Hay and Guldman, 1987). Hence, some of the montmorillonite in the sample is probably authigenic. The absence of K-feldspar and analcime in muds of the lower zone is supported by bulk XRD analyses of eight samples in addition to the eight for which the <2-μm fraction was analyzed.
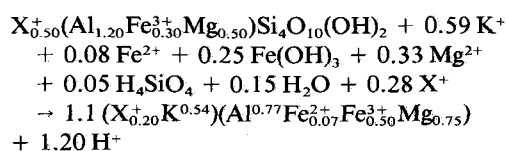
Origin of authigenic silicates

Mineral reactions. Detrital montmorillonite was probably the principal aluminosilicate reactant in forming Fe-illite, Mg-smectite, K-feldspar, and analcime. This conclusion is based on (1) the scarcity or lack of montmorillonite in the muds richest in authigenic silicates, and (2) the large proportion of detrital smectite, presumably montmorillonite, in source areas for Owens, China, and Searles Lakes (Droste, 1961b). Montmorillonite should also have been a major clay mineral supplied to Searles Lake during the Pleistocene and late Pliocene in view of the overall dry climate and stability of the Owens-China-Searles Lake drainage system during the past 3.2 m.y. (Smith, 1984). Kaolinite was very likely a common reactant in the upper diagenetic zone, where it was detected in only a few of the samples, and to a lesser extent in the middle zone, where it is absent or rare in samples richest in authigenic illite. Kaolinite may be unaltered in the middle zone except for the four illite-rich samples of the middle zone, in which kaolinite is absent or rare. Vitric ash is a reactant in the lower diagenetic zone and may have been a reactant in some muds of the middle and
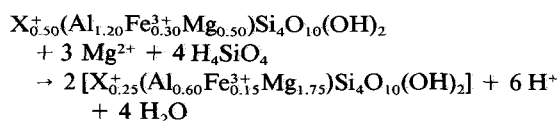
upper diagenetic zones. Known ash layers in the eastern part of the Mojave Desert (Izett, 1981), however, can account for only a small fraction of the authigenic silicates in the middle and upper diagenetic zones. Alteration of rhyolitic tephra to form montmorillonite and clinoptilolite in the lower zone has been discussed elsewhere (Hay and Guldman, 1987) and will not be considered further.

Hypothetical reactions are given below to illustrate the major chemical considerations in reaction of montmorillonite to form the three principal authigenic silicates. The montmorillonite is assumed to have a composition close to the average of pedogenic montmorillonites developed from volcanic rocks in the drainage basin of Lake Abert, Oregon (Jones and Weir, 1983), which is an arid environment not greatly different from the part of the Searles Lake drainage basin that lies to the east of the Sierra Nevada. Alumina is assumed constant in the reactions. Reaction (1) forms Fe-illite having the composition of the non-green analyzed sample (Table 2, sample 3). Reaction (2) forms Mg-smectite having a composition near that of sample 1 in Table 2. In reaction (3), K-feldspar is formed, and $MgCO_3$ is used to represent precipitation of Mg.
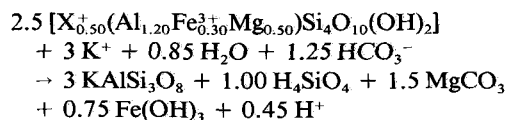
(1) Reaction to form Fe-illite

$X_{0.50}^+(Al_{1.20}Fe_{0.30}^{3+}Mg_{0.50})Si_4O_{10}(OH)_2 + 0.59\,K^+$
$\quad + 0.08\,Fe^{2+} + 0.25\,Fe(OH)_3 + 0.33\,Mg^{2+}$
$\quad + 0.05\,H_4SiO_4 + 0.15\,H_2O + 0.28\,X^+$
$\rightarrow 1.1\,(X_{0.20}^+K^{0.54})(Al^{0.77}Fe_{0.07}^{2+}Fe_{0.50}^{3+}Mg_{0.75})$
$+ 1.20\,H^+$

(2) Reaction to form Mg-smectite

$X_{0.50}^+(Al_{1.20}Fe_{0.30}^{3+}Mg_{0.50})Si_4O_{10}(OH)_2$
$\quad + 3\,Mg^{2+} + 4\,H_4SiO_4$
$\quad \rightarrow 2\,[X_{0.25}^+(Al_{0.60}Fe_{0.15}^{3+}Mg_{1.75})Si_4O_{10}(OH)_2] + 6\,H^+$
$\quad\quad + 4\,H_2O$

(3) Reaction to form K-feldspar

$2.5\,[X_{0.50}^+(Al_{1.20}Fe_{0.30}^{3+}Mg_{0.50})Si_4O_{10}(OH)_2]$
$\quad + 3\,K^+ + 0.85\,H_2O + 1.25\,HCO_3^-$
$\quad \rightarrow 3\,KAlSi_3O_8 + 1.00\,H_4SiO_4 + 1.5\,MgCO_3$
$\quad\quad + 0.75\,Fe(OH)_3 + 0.45\,H^+$

All three reactions can be considered "back-weathering," favored by high pH and yielding H^+. A high pH also favors reaction kinetics by increasing the solubility of both Al and SiO_2 (see, e.g., Eberl *et al.*, 1986). Possibly, a post-depositional lowering of the pore-water pH by diagenetic reactions may partly explain the incomplete reaction of montmorillonite in the middle diagenetic zone. The neoformation of Fe-illite, Mg-smectite, and K-feldspar is considered in more detail below.

Fe-illite. The reaction of montmorillonite to form Fe-illite was probably a solution-precipitation process in view of the high $\delta^{18}O$ values and content of Fe in the octahedral sheet of the two analyzed Fe-illites. Wetting and drying penecontemporaneous with deposition may have aided illitization in playa deposits (Eberl *et al.*, 1986). Some of the illites were formed after burial, probably by reaction with descending brine. The green Fe-illite of the outcropping paleosol, for example, has a $\delta^{18}O$ value of $+20.4\permil$, suggesting a brine, for which downward movement seems likely (Friedman *et al.*, 1982). The green illite is particularly rich in Fe, much of which was probably supplied by alteration of the associated magnetite, most of which is replaced by soft, porous hematite. The uppermost sample in which Fe-illite was identified is from a depth of 42.1 m, with a depositional age of about 45 ka.

Mg-smectite. The composition of the Searles Lake Mg-smectite can be obtained by addition of Mg-silicate to montmorillonite, either by interstratification (Jones, 1986) or by precipitation on a montmorillonite template. Mg-smectite appears to have been the principal chemical sink for SiO_2 in Searles Lake. The Mg-smectite appears to have formed more rapidly than Fe-illite and K-feldspar as it is the dominant clay mineral in the uppermost sample, with a depositional age of about 9000 years. Mg-smectite can probably form in less than 1000 years in view of its occurrence in surface sediments of Lake Chad (Tardy *et al.*, 1974; Gac *et al.*, 1977) and at depths of 20–40 cm in Lake Abert (Jones and Weir, 1983). Rapid reaction has also been inferred from the short residence time of Mg in water of Lake Turkana, a highly alkaline closed-basin lake in northern Kenya (Yuretich and Cerling, 1983). The Mg-smectite sample from a depth of 167.5 m has a substantially higher $\delta^{18}O$ value and content of Mg than the sample from a depth of 19.9 m. It is not clear whether compositional differences in the two analyzed Mg-smectites are original or a result of post-depositional recrystallization, analogous to the diagenetic evolution of glauconite (Odin, 1988).

K-feldspar. The highest contents of K-feldspar are in muds rich in Fe-illite; hence, the two minerals were favored at least to some extent by the same environments. Their formation may be coupled as the reaction of montmorillonite to form K-feldspar releases Mg and Fe, which are required for Fe-illite. The uppermost sample with K-feldspar identifiable by XRD is from the Bottom Mud at a depth of 41.0 m, a horizon with a depositional age of about 42 ka, and the content of K-feldspar in core KM-3 increases with depth into unit C. This suggest that K-feldspar continued to crystallize over a period of about 300,000 years or more, either from montmorillonite that escaped reaction to form Mg-smectite and Fe-illite, or by the diagenetic recrystallization of early-formed Mg-smectite with the release of Al.

Analcime and searlesite. Montmorillonite is the most likely reactant in forming analcime and has been shown elsewhere to yield analcime in highly alkaline saline environments (e.g., Baldar and Whittig, 1968). Analcime can form rapidly and has been identified in surface muds of Searles Lake (Hay and Moiola, 1963). Availability of silica may have been the controlling factor in crystallization of searlesite as the other constituents are present in brines. Possible sources of silica are clay-mineral reactions, detrital quartz, and silicic ash.

SUMMARY AND CONCLUSIONS

1. Core KM-3 can be divided into three diagenetic zones on the content of authigenic silicate minerals in muds. The upper zone (0–291.1 m) contains Fe-illite, Mg-smectite, K-feldspar, and analcime, which average 60–70% of the <2-μm silicate fraction. The middle zone (291.1–541.6 m) contains 20–25% of the same authigenic silicates found in the upper zone. In the lower zone (541.6–693.4 m), a small amount of clinoptilolite has been identified, and authigenic montmorillonite probably coexists.

2. Diagenetic zoning is a result of pore-water chemistry in which the pH may have been the most important chemical variable. Pore water of the upper zone is an alkaline brine with a pH of 9.0–10.0. Pore water of the middle zone is moderately to highly saline, and the pH is lower overall than in the upper zone, although it probably exceeded 9.0, at least locally, during silicate diagenesis. Pore water in the lower zone is moderately saline, and the pore-water pH is estimated to be generally in the range of 7.5 to 8.0.

3. Detrital montmorillonite was the principal aluminosilicate reactant and kaolinite a lesser reactant in forming Fe-illite, Mg-smectite, K-feldspar, and analcime. Montmorillonite and kaolinite were almost wholly consumed by silicate reactions in the upper zone, but a considerable amount of the two remains unaltered in the middle zone. Silicate reactions yielded H^+; hence, lowering of the pore-water pH by diagenetic reactions may partly explain the incomplete reaction of montmorillonite and kaolinite in the middle diagenetic zone. Vitric ash is the only silicate reactant identified in the lower zone, where detrital clay minerals apparently remain unaltered.

4. Oxygen-isotope values of authigenic Fe-illite, Mg-smectite, K-feldspar, and phillipsite in the upper diagenetic upper zone reflect a high degree of evaporative concentration and presumably of high salinity. Calculated equilibrium H_2O values suggest that K-feldspar crystallized from water more saline than the authigenic phyllosilicates.

5. Samples tend to be rich in Mg-smectite or Fe-illite but not in both, indicating that the two minerals are favored to some extent by different environments. Fe-illite seems to be generally favored by oxidizing conditions and probably by a playa environment, and Mg-smectite seems to be favored by reducing conditions and an open-water environment. Unit F is a major exception and has abundant Fe-illite in sediments of a deep perennial lake.

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