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MIXED-LAYER KEROLITE/STEVENSITE FROM THE AMARGOSA DESERT, NEVADA

DENNIS D. EBERL
U.S. Geological Survey, Denver Federal Center, Denver, Colorado 80225

BLAIR F. JONES
U.S. Geological Survey, National Center, Reston, Virginia 22092

HANI N. KHOURY
Department of Geology and Mineralogy, University of Jordan, Amman, Jordan

Abstract—Mixed-layer clays composed of randomly interstratified kerolite/stevensite occur as lake and/or spring deposits of probable Pliocene and Pleistocene age in the Amargosa Desert of southern Nevada, U.S.A. The percentage of expandable layers of these clays, determined from computer-simulated X-ray diffractograms, ranges from almost 0 to about 80%. This range in expandabilities most likely results from differences in solution chemistry and/or temperature at the time of formation. An average structural formula for the purest clay (sample P-7), a clay with about 70% expandable layers, is:

$$[(Mg_{2.72}Al_{0.07}Fe_{0.03}Li_{0.09})(Si_{3.96}Al_{0.04})O_{10}(OH)_2]^{-0.21}[X^{+}_{0.21}]^{+0.21}.$$

The data suggest that talc, kerolite, and stevensite form a continuous structural series based on layer charge.

Key Words—Hectorite, Kerolite, Layer charge, Mixed layer, Smectite, Stevensite, Talc.

INTRODUCTION

Kerolite is a trioctahedral phyllosilicate similar to talc in structure and composition, but it has a basal spacing of about 9.65 Å, compared to a spacing of 9.38 Å for talc. The enlarged spacing is thought to result from disordered layer stacking that leads to a misfit between 2:1 layers (Brindley *et al.*, 1977). Ideal stevensite is a trioctahedral smectite that derives its layer charge primarily from octahedral vacancies (Faust and Murata, 1953; Faust *et al.*, 1959). Brindley (1955) first showed that natural stevensite may be interstratified, possibly with non-expanding, talc-like layers.

Mixed-layer kerolite/stevensite has been identifed as an abundant mineral in lake and/or spring deposits of Pliocene and Pleistocene age in the Amargosa Desert, southern Nevada (Khoury *et al.*, 1982). The present paper describes the mineralogy and chemistry of this unusual clay.

LOCATION AND METHODS

Sampling locations are shown in Figure 2 of Khoury *et al.* (1982). Samples from the Amargosa Flat area include P-7 taken from an open pit mine labeled 7 in this figure, and D-2 and 12-14 taken from auger hole D. Samples of sepiolite and near end-member kerolite from the same area were supplied by R. L. Hay. Sample H-1 came from the Hectorite-Whiting pit (labeled HE) located nearby in California. The Amargosa Flat clays are associated with authigenic dolomite and calcite and form a major component of Pliocene and Pleistocene lake and spring deposits. Sample H-1 occurs with quartz as a crack filling in a travertine deposit that is located in and surrounded by two conglomerate layers.

Textures of freshly broken hand specimens were studied with a JSM U3 scanning electron microscope.[1] All other measurements were carried out on <0.1-μm size fractions separated by high-speed, angle-head centrifugation (Jackson, 1975). Samples were examined by X-ray powder diffraction (XRD) with a Siemens D-500 diffractometer using CuKα radiation, a graphite monochromater, and scanning speeds of 1°2θ/min. XRD patterns were simulated with a modified version of the computer program of Reynolds and Hower (1970), using the tri-mica-smectite mode, with a crystallite size of 1 to 8 layers, spacings of 9.65 Å and 16.9 Å for the kerolite and stevensite layers, and random interstratification.

The rapid rock-analysis method of Shapiro (1975), modified for use with samples as small as 20 to 40 mg (Rettig *et al.*, 1983), was used for chemical analysis. Major elements were determined by atomic absorption spectrometry according to techniques given by Skougstad *et al.* (1979). Cation-exchange capacity (CEC) was determined by analyzing the clays for calcium following calcium saturation. Clays were saturated by shaking in

[1] Use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

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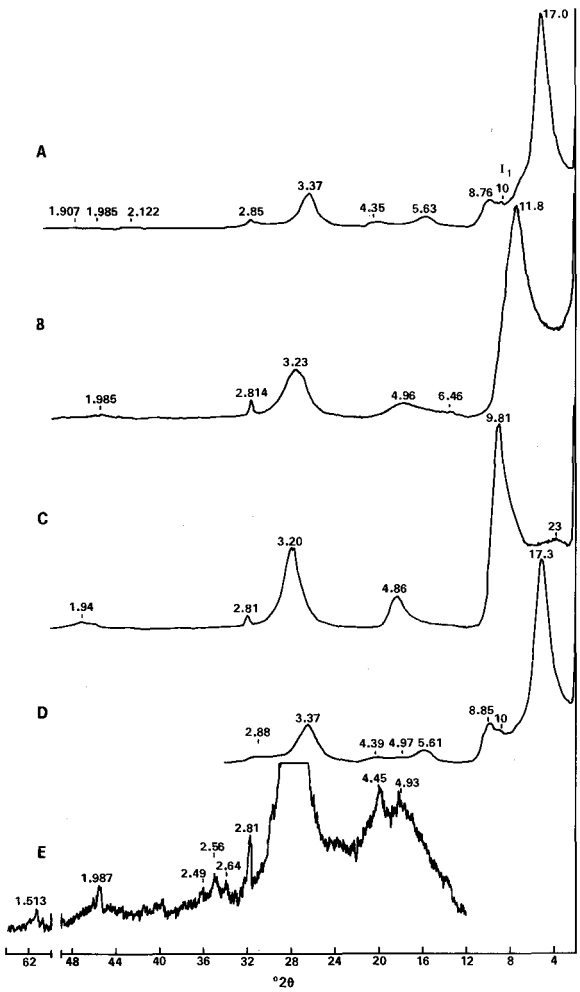


Figure 1. Diffractograms of <0.1-μm fraction of Amargosa clay sample H-1. A = oriented and treated with ethylene glycol. I_1 indicates a trace of illite. The shoulder at about 7°2θ may be due to a sepiolite alteration product (see Khoury *et al.*, 1982). B = oriented and air-dried. C = oriented, heat-treated at 550°C for 1 hr and then allowed to equilibrate with the atmosphere at room temperature. D = sample C treated with ethylene glycol. E = randomly oriented and air-dried; sharp peaks at 2.81 and 1.967 Å are due to halite impurity.

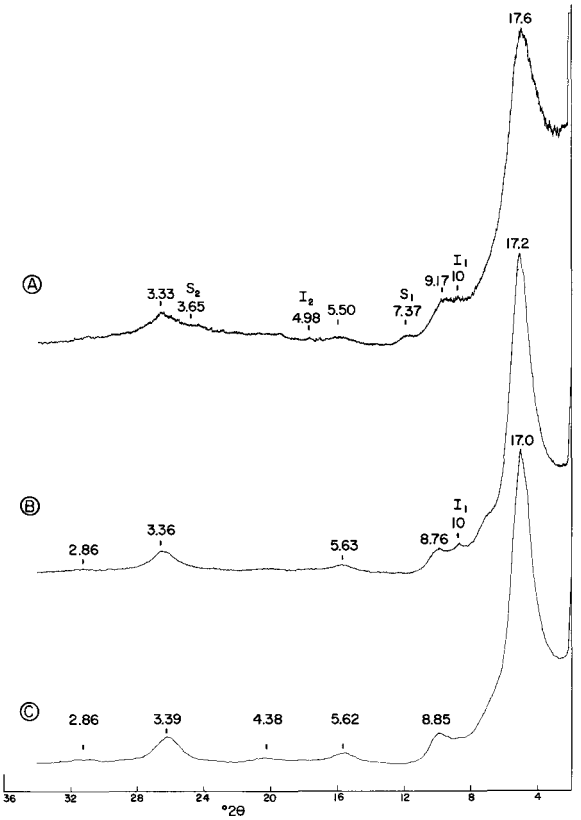


Figure 2. Diffractograms of <0.1-μm oriented, ethylene glycol-treated Amargosa clays. I_1 indicates illite. S suggests a 7-Å phase. A = sample D-2, B = sample 12-14, and C = sample P-7. The shoulder at about 7°2θ in B may be due to a sepiolite alteration product (see Khoury *et al.*, 1982).

0.1 M $Ca(NO_3)_2$ for several hours (process repeated three times; supernatant saved), and were washed by ultracentrifugation in distilled water until Ca^{2+} in the supernatant was below detection by atomic absorption spectrometry. Exchangeable Na^+, Mg^{2+}, and K^+ (hereafter termed leachable cations) were determined by analysis of the combined supernatant collected after the $Ca(NO_3)_2$ saturations. Efflorescent salt contamination was determined by analyzing these same solutions for chloride ions.

RESULTS

XRD patterns of sample H-1 after various treatments are shown in Figure 1. Smectite is indicated by expansion of the 001 reflection to about 17 Å on ethylene glycol solvation and collapse to 9.81 Å on heating to 550°C. An irrational sequence of basal reflections for the ethylene glycol-treated sample suggests mixed layering. A 001 spacing of 11.8 Å for air-dried clay suggests a monovalent interlayer cation, and reexpansion of the heated clay upon ethylene glycol treatment shows that the mineral resists irreversible collapse.[2] The 060 reflection at 1.513 Å indicates a trioctahedral structure. Samples P-7, 12-14, and D-2 behaved similarly to sample H-1 under the various treatments. Patterns of ethylene glycol-solvated, oriented samples are shown in Figure 2.

Chemical analyses, cation-exchange capacities (CEC), and leachable cations are presented in Table 1. The sodium analysis for sample P-7 has been reduced by 28.3%, and that for sample H-1 has been reduced by 24.3%, based on leachable chloride content, on the assumed presence of a halite impurity (see Figure 1E for XRD evidence for halite). Other possible salt contaminants (e.g., traces of sulfo-carbonate efflorescences such as those found on the surface of the Amargosa playa) could not be determined in the very small amounts of ultrafine material obtained by size separation.

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Table 1. Chemical data for magnesian clays from the Amargosa Desert, southern Nevada (<0.1-μm fractions).[1]

Sample number	Anhydrous oxide percent									CEC (meq/100 g)	Leachable cations (meq/100 g)		
	SiO_2	Al_2O_3	Fe_2O_3[2]	MgO	CaO	Na_2O[3]	K_2O	Li_2O	TiO_2		Na^+[3]	Mg	K
Kerolite/smectites													
P-7	63.15	1.44	0.69	29.23	0.01	3.86	1.18	0.38	0.05	54	87	43	9
12-14	62.64	3.76	1.76	28.92	0.05	0.85	1.68	0.27	0.08	46	19	55	4
D-2	59.64	2.66	1.05	31.46	3.22	0.31	1.27	0.32	0.08	53	7	50	2
H-1	62.71	2.83	1.21	27.47	0.05	4.05	1.00	0.60	0.08	67	110	32	4
Sepiolite[5]	67.17	1.10	0.61	30.88	0.00	0.76	0.52	0.03	0.04	n.d.[4]	n.d.	n.d.	n.d.
Kerolite[5]	64.45	0.48	0.20	33.55	0.40	0.61	0.30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[1] Fluoride, not included, is as follows: P-7 = 1.79%; 12-14 = 1.34%; D-2 = 0.42%; H-1 = 2.64%.
[2] Total iron is reported as Fe_2O_3.
[3] Sodium analyses have been corrected for an equivalent chloride content of 1.44% for sample P-7 and 1.22% for sample H-1.
[4] n.d. = not determined.
[5] Supplied by R. L. Hay.

The structural formulae presented in Table 2 were calculated from the data in Table 1, assuming an anion content of −22 equivalents. Leachable cation data in Table 1 indicate that all samples contain exchangeable cations in excess of the measured CEC. In addition to the traces of salts noted above, cations may be derived from other leachable material that was undetected by XRD. Hence, the structural formulae in Table 2 have been calculated by assuming an interlayer cation occupancy equivalent to the measured CEC.

The structural formulae are average values for the entire mixed-layer structure. They corroborate evidence from the 060 reflections that these clays are predominantly trioctahedral. The smectite component of the structure can be named according to the dominant mechanism for creating layer charge. If a majority of charge in a trioctahedral smectite is created in the tetrahedral sheet by Al^{3+} for Si^{4+} substitution, the smectite is termed saponite. If a majority of charge arises in the octahedral sheet, however, the trioctahedral smectite is termed either hectorite or stevensite, depending on whether the charge results from the substitution of Li^+ for Mg^{2+} or from octahedral vacancies, respectively. In the formula for sample P-7, the only sample with no detectable mica, sepiolite, or 7-Å impurity, the majority of layer charge develops from octahedral vacancies. Hence, the expanding component is termed stevensite. Based on structural formulae calculated for the less pure clays, the smectite component in samples 12-14 and D-2 is saponite, and that in sample H-1 is stevensite.

The nonswelling component of these clays is unlikely to be illite, because the XRD patterns do not fit calculated profiles for mixed-layer illite/smectite (Reynolds and Hower, 1970). In addition, the clays contain too little potassium and aluminum: for example, an illite/smectite (sample KB-B, listed in Hower and Mowatt, 1966) which has a percentage of expandable layers similar to that of sample D-2 (based on low-angle scattering) contains 22.99% Al_2O_3 and 2.78% K_2O vs. 2.66% and 1.27% for sample D-2.

Following the suggestion of Brindley (1955) that natural stevensite may be interstratified with talc-like layers, sets of computer-simulated XRD patterns of randomly interstratified, mixed-layer talc/smectite were calculated as a function of % expandable layers and compared to XRD patterns of the Amargosa samples. One set of patterns was calculated using a spacing for

[2] Eberl *et al.* (1978) showed that this type of clay also resists hydrothermal reaction.

Table 2. Average structural formulae[1] and % expandable layers[2] for mixed-layer kerolite/smectite.

Sample	Tetrahedral				Octahedral					Interlayer X^+	% expandable layers
	Si	Al	Fe^{3+}	Σ tet	Mg	Al	Fe^{3+}	Li	Σ oct		
P-7	3.96	0.04	0.00	4.00	2.72	0.07	0.03	0.09	2.91	0.21	70
12-14[3]	3.85	0.15	0.00	4.00	2.65	0.12	0.08	0.07	2.92	0.18	80
D-2[4]	3.77	0.20	0.03	4.00	2.96	0.00	0.02	0.02	3.00	0.21	50
H-1[3]	3.92	0.08	0.00	4.00	2.56	0.13	0.06	0.15	2.90	0.26	80

[1] Calculated, assuming an anion content of $O_{10}(OH)_2$, using cation-exchange capacity as a measure of interlayer occupancy.
[2] Calculated by comparing diffractograms of ethylene glycol-solvated clay with calculated profiles given in Figure 3.
[3] X-ray powder diffraction pattern shows a small amount of a mica impurity.
[4] X-ray powder diffraction pattern shows a small amount of a mica + a 7-Å phase impurity.

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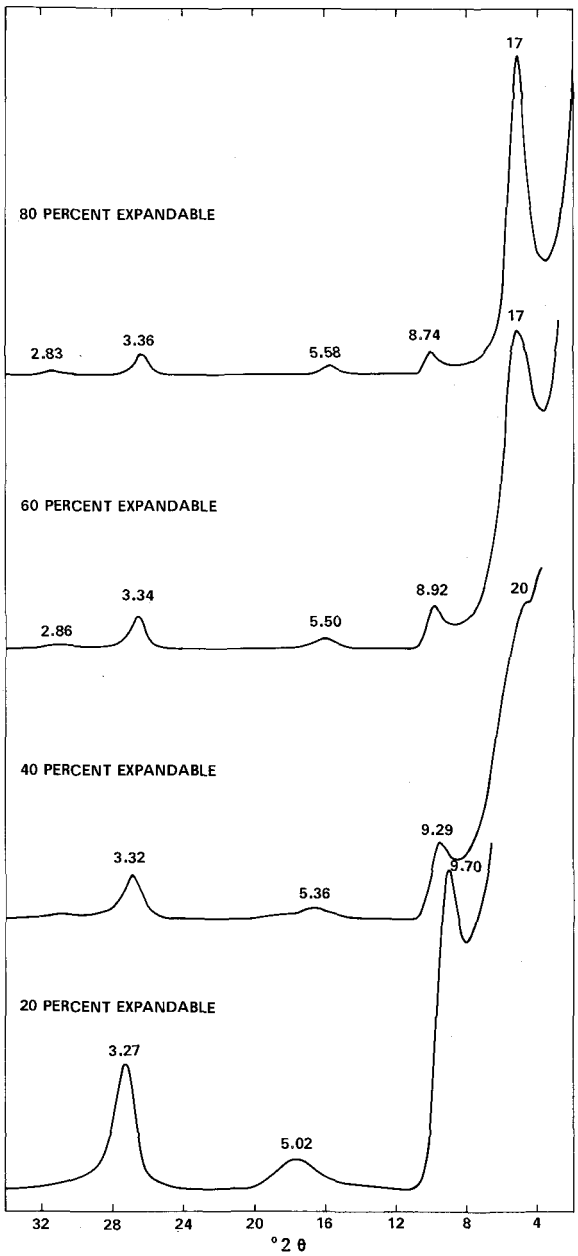


Figure 3. Computer-simulated diffractograms of randomly interstratified kerolite/smectite. Calculated for 16.9-Å expanding layers, 9.65-Å nonexpanding layers, and a crystalline thickness of 1 to 8 layers.

the nonexpanded layers (9.3 Å) similar to that of talc, whereas the other set used a kerolite spacing of 9.65 Å. A 16.9-Å spacing was used in both sets of calculations for the stevensite layers. The set of patterns calculated with the 9.65-Å spacing more closely resembled the XRD patterns of the Amargosa clays. Thus, the nonexpanded layers are probably kerolite, a conclusion that is supported by the recent collection of near end-member kerolite in the study area (analysis given in Table 1; this

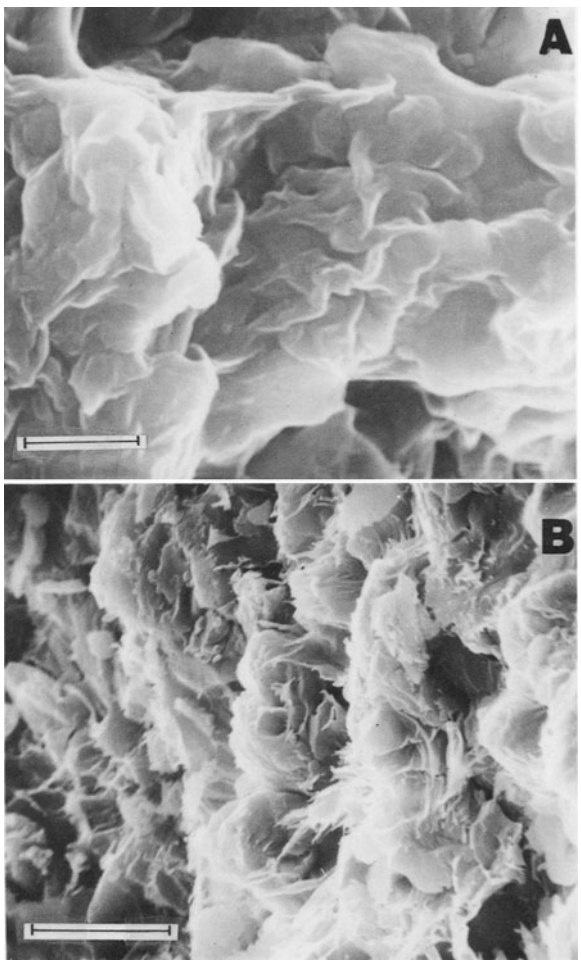


Figure 4. Scanning electron micrographs of kerolite/smectite from: (A) the Amargosa Flat area and (B) the Hectorite-Whiting travertine deposit. The bar in (A) = 2 μm; the bar in (B) = 8 μm.

kerolite has an XRD pattern similar to the patterns for kerolite given in Brindley *et al.*, 1977).

Calculated profiles for randomly interstratified kerolite/smectite are presented in Figure 3. This illustration was used to determine the % expandable layers for the natural samples listed in Table 2 by plotting the difference in 2θ between the second and third diffraction maxima as a function of expandability. Expandabilities for other mixed-layer kerolite/smectites that may be found in future studies can be determined similarly, but a precise fit between real and calculated patterns should not be expected. Differences in crystallite size, differences in spacings for expanded layers, and mineral heterogeneity will shift peak positions from those given in Figure 3.

The morphology of clays from the Amargosa Flat area (samples P-7, 12-14, and D-2) is typified by Figure 4A, in which the clay can be seen to form continuous sheets.

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Sample H-1 from the travertine deposit is more fibrous (Figure 4B), although its diffraction pattern is very similar to that of sample 12-14. Sample H-1 also differs from the other clays in that it has the lowest magnesium content and the highest content of lithium and fluorine.

REPORTS OF SIMILAR PHASES

Randomly interstratified mixed-layer kerolite/smectite containing interlayer magnesium was found to be a principal clay mineral in the sediments of saline, alkaline Lake Abert in south-central Oregon (Weir and Jones, 1978; Jones and Weir, 1983). Dyni (1976) and Tettenhorst and Moore (1978) described a similar material from lacustrine deposits of Eocene age from the Green River Formation in Utah. The mineral described by Dyni (1976) gives an XRD pattern for the glycolated sample that is similar to that of Amargosa Desert sample H-1. Chemically, however, it is higher in aluminum and iron, and lower in magnesium that sample H-1. A structural formula for the Green River clay, based on a chemical analysis presented by Dyni (1976, p. 9), and corrected for a celadonite impurity is:

$$[(Mg_{1.77}Fe^{3+}_{0.29}Li_{0.04}Al_{0.45})(Si_{3.82}Al_{0.18})O_{10}(OH)_2]^{-0.38}\ [Na_{0.37}Ca_{0.01}]^{+0.39}.$$

Its octahedral occupancy (2.55) is lower, and its layer charge (−0.39) is higher than the values reported here for the Amargosa clays. Chemically, it resembles the neoformed <0.1-μm clay from Lake Abert (Jones and Weir, 1983).

The stevensite ooids examined by Tettenhorst and Moore (1978) give an XRD pattern that has considerable low-angle scattering associated with a large 17.7-Å reflection, and a poorly developed reflection at 5.64 Å. The authors reported 20–30% nonexpanding layers based on comparison with computer-synthesized XRD patterns, and they calculated a structural formula with silica in excess of 4.0 atoms per half unit cell, despite an allowance for 3% quartz in the sample, as was determined by semi-quantitative XRD. Subtraction of another 4.78% SiO_2 (presumably noncrystalline) from their analysis, in order to give a formula with ideal tetrahedral occupancy, yields the following:

$$[(Mg_{2.67}Fe^{3+}_{0.03}Al_{0.07})(Si_{4.0})O_{10}(OH)_2]^{-0.36}\ [Na_{0.14}K_{0.02}Ca_{0.08}]^{+0.32}.$$

This formula, which is slightly off balance electrically, has a layer charge (about −0.34) and an octahedral occupany (2.77) that lie between the clay described by Dyni (1976) and the Amargosa samples.

DISCUSSION

The identification of mixed-layer kerolite/stevensite leads to speculation on the origin and geological significance of the mixed layering. A continuous series based on layer charge may exist between talc, kerolite, and stevensite. The enlarged basal spacing of kerolite compared to that of talc may result from the formation of a talc-like structure in which there is a small number of octahedral vacancies. The negatively charged 2:1 layers would tend to repel each other, leading to a disordered stacking in which (as suggested by Brindley *et al.*, 1977) basal oxygens in opposing 2:1 layers are no longer partially packed together, as in talc, but are juxtaposed. The layer charge could be balanced by cations sorbed on crystal edges, an idea consistent with the chemical data for kerolite presented by Brindley *et al.* (1977). An even greater layer charge would lead to increased repulsion and eventual expansion, with hydrated cations moving into the interlayer region. Mixed-layer kerolite/stevensite would thus be composed of layers that have insufficient layer charge for appreciable expansion (kerolite) and those that have enough octahedral vacancies to expand, to take in interlayer cations, and, thereby, to form stevensite.

The range in expandabilities found for the Amargosa clays is unlikely to result from differences in pressure or reaction time, because these clays occur in near-surface deposits that show no systematic variation in expandability with depth (Khoury, 1979; Khoury *et al.*, 1982). Differences in expandability could result from differences in temperature of formation (hot spring vs. cold spring or lake precipitation) or from differences in solution chemistry. A reaction for the conversion of an ideal stevensite layer into an ideal talc layer can be written:

$$Mg_{2.85}Si_4O_{10}(OH)_2X^+_{0.3}\cdot nH_2O + 0.15Mg^{2+} \rightleftarrows Mg_3Si_4O_{10}(OH)_2 + 0.30X^+ + nH_2O.$$

This reaction suggests that expandability may reflect the Mg^{2+}/alkali ratio of the solution from which the mineral precipitated and/or the activity of water. Availability of lithium and aluminum may also be a factor in determining expandability through their tendency to increase layer charge by hectorite-like or saponite-like substitutions.

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Резюме—Смешано-слойные глины, составленные из случайно внутринапластованного керолита/стевенсита залегают как озерные и/или источниковые осадки, вероятно, плиоценовой и плейстоценовой эпохи на пустыни Амаргоса в южной Неваде, С.Ш. Процентное отношение расширяющихся слоев в этих глинах, определенное путем компьютерномоделированных рентгеновских дифрактограммов, находится в диапазоне от 0 до 80%. Этот диапазон, вероятно, есть результатом различной химии растворов и/или разных температур во время формирования. Средняя структурная формула наиболее чистого образца глины (P-7) с около 70% расширающихся слоев есть:

$$[(Mg_{2,72}Al_{0,07}Fe_{0,03}Li_{0,09})(Si_{3,96}Al_{0,04})O_{10}(OH)_2]^{-0,21}[X^+_{0,21}]^{+0,21}.$$

Эти новые данные указывают на то, что тальк, керолит и стевенсит формируют непрерывные структурные серии на основе слойного заряда. [E.C.]

Resümee—Unregelmäßige Wechsellagerungen aus Kerolit/Stevensit treten als Ablagerungen von Seen und Quellen, wahrscheinlich aus dem Pliozän und Pleistozän, in der Amargosa Wüste, Südnevada, USA, auf. Der Anteil quellfähiger Lagen in diesen Tonen, der mittels Computer-simulierten Röntegendiffraktogrammen bestimmt wurde, reicht von nahezu 0 bis etwa 80%. Diese unterschiedliche Expandierbarkeit resultiert höchstwahrscheinlich aus der unterschiedlichen Lösungszusammensetzung und/oder Temperatur während der Bildung. Eine durchschnittliche Strukturformel für den reinsten Ton (Probe P-7), ein Ton mit 70% quellfähigen Schichten, lautet:

$$[(Mg_{2,72}Al_{0,07}Fe_{0,03}Li_{0,09})(Si_{3,96}Al_{0,04})O_{10}(OH)_2]^{-0,21}[X^+_{0,21}]^{+0,21}.$$

Aus diesen neuen Ergebnisse geht hervor, daß Talk, Kerolit, und Stevensit eine kontinuierliche strukturelle Serie darstellen, die auf unterschiedlichen Schichtladungen beruht. [U.W.]

Résumé—Des argiles à couches melangées composées de kerolite/stévensite interstratifiées au hasard sont trouvées comme dépôts de lacs et/ou de sources, probablement d'âge pliocène et pléistocène dans le Desert Amargosa du Névada du sud, U.S.A. Le pourcentage de couches expansibles de ces argiles, determiné par des diffractogrammes aux rayons-X simulés par l'ordinateur, varie de zero à à peu près 80%. Cette étendue d'expansions est sans doute le résultat de différences dans la chimie et/ou la température lors de la formation. Une formule structurale moyenne pour l'échantillon d'argile le plus pur (P-7), une argile ayant des couches approximativement 70% expansibles, est:

$$[(Mg_{2,72}Al_{0,07}Fe_{0,03}Li_{0,09})(Si_{3,96}Al_{0,04})O_{10}(OH)_2]^{-0,21}[X^+_{0,21}]^{+0,21}.$$

A partir de ces nouvelles données, on suggère que le talc, la kérolite, et la stévensite forment une série structurale continue basée sur la charge de couche. [D.J.]

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