

MAGNESIUM-RICH CLAYS OF THE MEERSCHAUM MINES IN THE AMBOSELI BASIN, TANZANIA AND KENYA

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Abstract—The Sinya Beds of the Amboseli Basin in Tanzania and Kenya consist largely of carbonate rocks and Mg-rich clays that are intensely deformed where exposed in and near former meerschaum mines. The carbonate rocks consist of limestone and dolomite in Tanzania, but only dolomite has been identified in Kenya. Sepiolite and mixed-layered kerolite/stevensite (Ke/St) are subordinate constituents of the carbonate rocks. The carbonate rocks and overlying bedded sepiolite were deposited in a semiarid lake basin at the foot of the large volcano Kilimanjaro. Calcite and dolomite of the carbonate rocks have $\delta^{18}\text{O}$ values 4–6‰ lower than calcite and dolomite of the late Pleistocene Amboseli Clays, suggesting that the Sinya Beds were deposited in the middle or early Pleistocene under a different climatic regime when meteoric water had lower $\delta^{18}\text{O}$ values than at present.

Mg-rich clay minerals form veins and fill cavities in the Sinya Beds. The principal clay minerals are sepiolite and Ke/St, some of which contains substantial Al and Fe (Al-Ke/St). NEWMOD® modeling and other X-ray diffraction (XRD) data suggest that most of the Ke/St contains 25–50 percent kerolite layers, but minor amounts of kerolite-rich Ke/St are present in some samples. Illite with an inferred high content of Fe or Mg is a minor constituent of the samples with Al-Ke/St. The cavity-filling clays were chemically precipitated, as shown by field relationships and SEM study. The early-deposited clays of veins and cavities are principally Ke/St with minor sepiolite, and the latest clay is sepiolite (meerschaum), generally with minor Ke/St.

The $\delta^{18}\text{O}$ values of cavity-filling Ke/St range from 22.5–25.6‰ and correlate with mineral composition, with the highest values associated with the highest content of stevensite and the lowest values with the highest content of kerolite. This relation suggests that high salinities favored stevensite and low salinities favored kerolite. $\delta^{18}\text{O}$ values of sepiolite (meerschaum) fall in the middle of the range for Ke/St, suggesting that salinity was not the main control on sepiolite precipitation. High values of $a_{\text{SiO}_2}/a_{\text{Mg}^{2+}}$ may have been a major factor in sepiolite precipitation.

Different mixtures of dilute ground water and saline, alkaline lake water in pore fluids may largely account for the differences in clay mineralogy of cavity-filling clays. Sepiolite is the dominant clay mineral in lacustrine sediments of the Amboseli Basin, and the cavity-filling sepiolite may reflect a high proportion of lake water. The low-Al Ke/St may have formed from fluids with a higher proportion of ground water. Detrital clay was very likely a factor in forming the Al-Ke/St, for which $\delta^{18}\text{O}$ values suggest a saline environment.

Key Words—Kerolite, Meerschaum, Mixed-layered kerolite/stevensite, Oxygen isotope composition, Sepiolite, Stevensite.

INTRODUCTION

The white massive variety of sepiolite is commonly termed meerschaum (Etymol: German *Meerschaum* = “sea froth”). It is used for the manufacture of tobacco pipes. Meerschaum was extensively mined in the Amboseli Basin of northern Tanzania and southern Kenya in the 1950’s and 1960’s (Figure 1). The meerschaum occurs as veins and cavity fillings in highly deformed carbonate rocks and bedded sepiolite of the Sinya Beds, the oldest deposits of the basin. Geology of the Kenya part of the basin is described by Williams (1972), and the part in Tanzania is described by Sampson (1966). Sepiolite is reportedly the principal clay mineral in the

Amboseli Clay, a lacustrine deposit that unconformably overlies the Sinya Beds.

In 1975 Stoessell investigated the geochemistry and clay mineralogy of the Amboseli Basin, and he showed that water supplied to the Amboseli Basin from Mount Kilimanjaro, the principal recharge area, has a relatively high content of Mg^{2+} , and on evaporation it becomes supersaturated with respect to dolomite, sepiolite, and kerolite (Stoessell 1977, Stoessell and Hay 1978). Stoessell also reported the occurrence of kerolite in the Sinya Beds, which he inferred to be at least partly an alteration product of sepiolite. To explain the intense deformation and caliche-like features of carbonate rocks in the Sinya Beds of Kenya, Hay and Stoessell

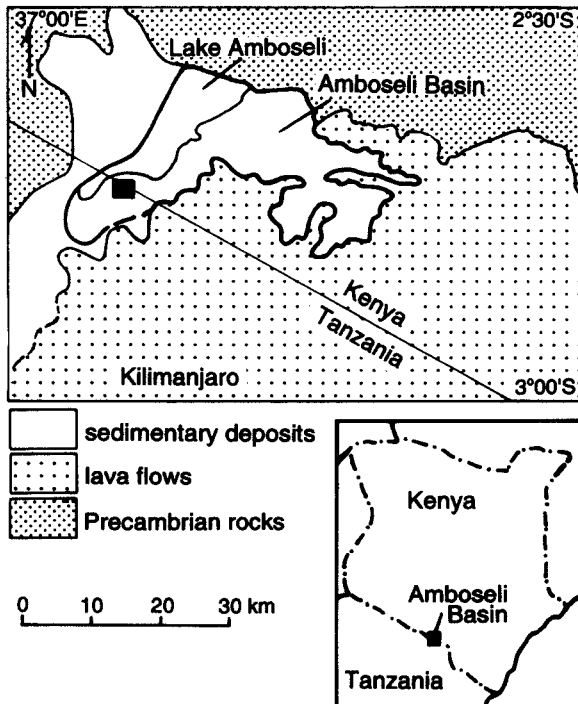


Figure 1. Regional geologic map showing the location of the Amboseli Basin and the study area (black rectangle). Map is slightly modified from Williams (1972) and Downie and Wilkinson (1964).

(1984) suggested that the carbonate rocks originated as diapiric caliche-breccia masses similar to those of the Amargosa Desert, Nevada and California (Hay *et al* 1986).

This report is based on a two-day trip by one of us (RLH) in 1983 to former meerschaum mines in Kenya and Tanzania for field study and sampling of the carbonate rocks and cavity-filling clays of the Sinya Beds. Samples were collected from the Sinya Beds in the major pits in Tanzania except for the southernmost, which was flooded (Figure 2). Sampling in Kenya was confined to the large southernmost pit, which was the main kerolite locality of Stoessell (1977). This pit lies near locality Q of Williams (1972) and will be termed Pit Q. Dr. Anna K. Behrensmeyer (Smithsonian Institution) provided samples from the northernmost pit in Kenya, which is near locality S and will be termed Pit S.

The principal goal of the present study is to describe the clay mineralogy and paragenesis of the cavity-filling clays of the Sinya Beds. Particular attention is given to the clays identified as kerolitic. Another goal is to provide new information about the nature and origin of carbonate rocks in the Sinya Beds, which contain a significant amount of authigenic Mg-rich clay minerals representing an early phase of Mg-clay mineral precipitation in the Amboseli Basin. Using chemical and ox-

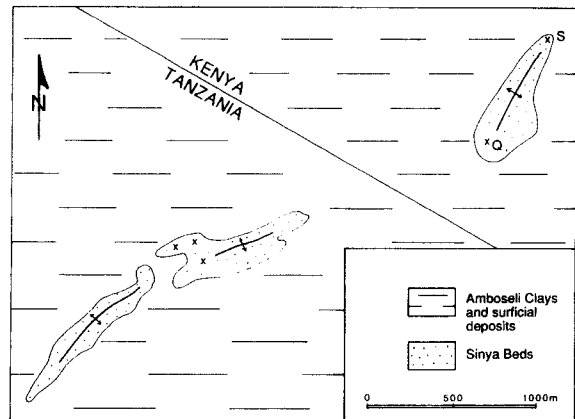


Figure 2. Geologic map showing domal exposures of the Sinya Beds in the Amboseli Basin. Principal sample localities in Tanzania are indicated by X; Pits Q and S in Kenya are indicated by Q and S.

xygen isotope data, this report attempts to establish what factor(s) controlled (1) the composition of Ke/St, and (2) the precipitation of sepiolite vs. Ke/St.

GEOLOGIC, HYDROLOGIC, AND CLIMATIC SETTING

The Amboseli Basin has an areal extent of about 400 km² and is bordered on the south and east by alkaline olivine basalt of the large volcano Kilimanjaro and on the north and west by low hills of Precambrian marble, granite gneiss, granite, and schist (Figure 1). The basin contains Lake Amboseli, a seasonally flooded plain, along its western edge and is underlain by lacustrine deposits over most of its extent. The basin sediments have been divided by Williams (1972) into three formations, which are from oldest to youngest the Sinya Beds, Amboseli Clays, and Ol Tukai Beds (Figure 3). All of these deposits were considered to be Pleistocene by Williams (1972). The Sinya Beds are chiefly chemical precipitates of solutes derived from weathering of Kilimanjaro, hence some of the deposits may be as old as 2.3 Ma, the oldest date obtained thus far on lavas of Kilimanjaro (Dawson 1992). Taking an age of 1.6 Ma for the base of the Pleistocene (Harland *et al* 1990), the lowermost part of the Sinya Beds may extend into the Pliocene.

The Sinya Beds are exposed in elongate domes, where they consist in Tanzania of as much as 7.3 m of carbonate rocks overlain by as much as 2.3 m of bedded sepiolitic mudstone (Sampson 1966.) In Kenya they consist of as much as 7 m of carbonate rocks overlain by as much as 2 m of sepiolitic claystone (Williams 1972). Both the carbonate rocks and bedded sepiolite are intensely deformed and locally brecciated. Drilling in Kenya shows that the Sinya Beds are at least 18 m thick (Williams 1972). The deformed carbonate rocks of Kenya are described as rubbly marl or clayey lime-

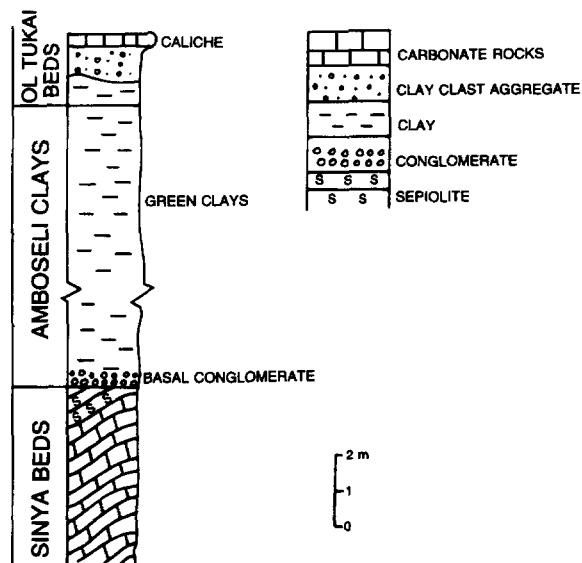


Figure 3. Schematic stratigraphic section of the Pleistocene sediments in the Amboseli Basin.

stone by Williams (1972); those of Tanzania are described by Sampson (1966) as dolomitic lacustrine limestone. Meerschaum and other clays fill cavities in the deformed carbonate rocks and sepiolite.

The Amboseli Clays unconformably overlie the Sinya Beds and underlie most of the basin at shallow depth. Drilling in Kenya indicates a thickness of at least 60 m under the dry lake bed of Lake Amboseli. The Amboseli Clays are lacustrine clays, the upper part of which contain gaylussite $[\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}]$, indicating a saline and highly alkaline ($\text{pH} = 9.5\text{--}10.0$) playa or lake. Later study of drill core from Kenya shows that illite and authigenic K-feldspar are also commonly present (Stoessell and Hay 1978).

The Ol Tukai Beds are a sequence of silts, clays, and other sediments with a maximum thickness of 25 m (Williams 1972). Most of the deposits are lacustrine, and the lower part of the lacustrine sequence contains sepiolite, analcime, a 10\AA clay mineral, and K-feldspar (Stoessell and Hay 1978).

Mt. Kilimanjaro is the major source of water to the Amboseli Basin. Melted snow and rain water flow northward into the basin as streams and ground water. The streams dry up in the foothills of Mt. Kilimanjaro, and ground water flows to the north and west towards Lake Amboseli. Ground water of Mt. Kilimanjaro and the Amboseli Basin ranges in solutes from 60–2060 parts per million (ppm). Analyzed samples range in pH from 6.5–8.8, in Mg^{2+} from 0.4–60.4 ppm, and in SiO_2 from 10.7–107 ppm (Stoessell and Hay 1978). The data show a general increase in $a_{\text{Mg}^{2+}}/a_{\text{H}^+}$ and a_{SiO_2} in water moving toward Lake Amboseli. About half of the analyzed ground waters are supersaturated with respect

to disordered dolomite, sepiolite, and disordered K-feldspar.

The present climate is hot and semiarid, with annual rainfall of 350–400 mm (Western and Van Praet 1973). The mean annual temperature (MAT) is about 25°C , as based on a lapse rate of $8^\circ\text{C}/\text{km}$ and the elevation of Amboseli 270 m below a locality with a MAT of 22.8°C at Olduvai Gorge, 120 km to the west (Hay 1976). The climate is now very likely as hot and dry as it has been over the past 2 Ma, as based on the oxygen and carbon isotope composition of pedogenic carbonates at Olduvai Gorge (Cerling and Hay 1986). The present climate is the result of an overall drift toward aridity from the late Pliocene, and at about 1.8 Ma the climate at Olduvai Gorge, and presumably at Amboseli, was moister, and the MAT approximately 7°C cooler than at present.

The isotopic composition of meteoric water has also changed over the past 2 m.y. at Olduvai Gorge and presumably Amboseli. In the early Pleistocene, ~ 1.6 Ma, meteoric water at Olduvai Gorge was as much as 5 to 10‰ (SMOW) lower in $\delta^{18}\text{O}$ than the present value of $\sim -1.0\text{‰}$ (Cerling and Hay 1986). Amboseli lies between Olduvai Gorge and the Indian Ocean, the principal source of meteoric water. Rainfall has a relatively high mean $\delta^{18}\text{O}$ value of -2.0‰ at Dar es Salaam, on the coast (Rozanski *et al* 1993). An average value of $\sim 0\text{‰}$ seems likely for Amboseli on the basis of its elevation 270 m below that of Olduvai Gorge.

METHODS

Staining with Alizarin Red (Friedman 1959) was used to distinguish limestone from dolomite in the field, and a saturated aqueous solution of methyl orange (Mifsud *et al* 1979) aided in the field distinction of sepiolite from Ke/St.

About 45 clay samples were analyzed by X-ray diffraction (XRD) with Cu , K_α radiation. Nearly all of the clays forming veins and filling cavities are relatively hard and do not disperse in water. In early phases of the work, analyses were made of random mounts and bulk smears, which gave poor reflections of the 00/ series. Later phases of the study used oriented mounts of the $<2\ \mu\text{m}$ fraction of samples micronized with a McCrone® mill. During this investigation and in concurrent studies of flint clays, we have found that grinding these types of clays in wet-grinding mills such as the McCrone® micronizer dramatically improves sample preparation and in the Amboseli samples increased the ethylene glycol solvation of Ke/St. Mounts were made by transferring wet clay films from Millipore filters to glass slides as described by Moore and Reynolds (1989). By this procedure, most of the hard wax-like clays yielded well-defined 001 peaks at $\sim 18\ \text{\AA}$ on glycolation. Even in these oriented mounts, the smaller peaks of the 00/ series are generally poorly defined, probably because of the non-platy shape and poor ori-

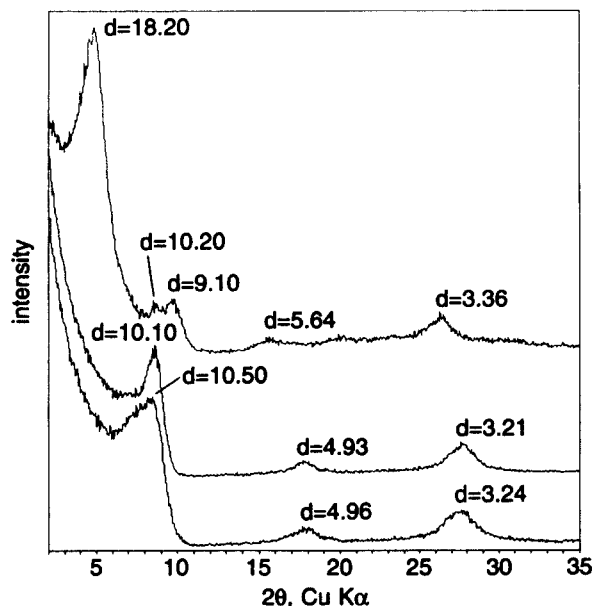


Figure 4. XRD patterns from oriented mounts of sample 13K, which is principally Ke/St with 30–35 percent kerolite layers. The lower trace is of an air-dried mount, the middle trace is a mount heated at 375°C for 1 hour, and the upper trace is of a mount glycolated for 1 week. The small peak at 10.2 Å is attributed to a small amount of kerolite-rich Ke/St.

entation of clay particles. Analyses were made of air-dry samples, after glycolation, and after heating at 375°C for one h. A few samples were heated at 550°C for one h. Several samples were glycolated for varying lengths of time up to two weeks in order to distinguish illite from kerolite, which expands slowly (Brindley *et al* 1977). Also analyzed was the acid-insoluble fraction of 10 samples of carbonate rock after dissolution in a 10% aqueous solution of acetic acid. Eleven samples were studied by scanning electron microscope (SEM), using a JEOL JSM-840E with the KEVEX system for qualitative chemical analysis. Clay samples were chemically analyzed using X-ray fluorescence (XRF) by X-Ray Assay Laboratories of Don Mills, Ontario.

NEWMOD® (Reynolds 1985) was used to model XRD traces of mixed-layered kerolite/stevensite (Ke/St) clays. Parameters used to model Ke/St were d 001 stevensite = 17.1 Å, d 001 kerolite = 9.35 Å, defect-free distance = 2, “high N” = 5–7, and “R” = 0–1. Both patterns displayed in Figure 5 used R = 0 and N = 7.

The oxygen-isotope composition of clay samples was determined at the University of Saskatchewan using the BrF₅ technique of Clayton and Mayeda (1963). Samples were heated overnight at 110°C before analysis. The stable isotope composition of carbonate minerals was determined by David E. Haymes at the University of Illinois, Champaign-Urbana. The CO₂ was obtained by reaction with 100% H₃PO₄ at 25°C. The

differing reaction rates of calcite and dolomite were used to obtain measurements for the calcite and dolomite in mixtures (Haymes 1988). All values are reported relative to SMOW for oxygen and PDB for carbon.

RESULTS AND DISCUSSION: CARBONATE ROCKS

Carbonate rocks exposed in Pits Q and S are dolomite, whereas both limestone and dolomite are present in the pits of Tanzania. The carbonate rocks vary greatly in degree of deformation. In Pit Q, bedding is generally unrecognizable, and dolomite forms sheared, folded, and fractured masses of varying size, many of which have reticulate surface cracks (e.g., Stoessell and Hay 1978, Figure 4). Deformation is less intense in the Tanzanian pits, where folded limestone and dolomite beds have dips of as much as 60°. The carbonate rocks are locally brecciated and in some other places are disrupted into rounded to irregular nodular masses with reticulate surface cracks. Rootmarkings are present in carbonate rocks of all the pits.

Calcite and dolomite are also present in cavities of the deformed carbonate rocks. In Tanzanian pits, they most commonly occur as horizontal layers filling the lower parts of cavities. In Kenya, dolomite is disseminated in some of the cavity-filling clays.

Dolomite and limestone are indistinguishable in the field except by staining. The distribution of limestone and dolomite in the Tanzanian pits is irregular and bears no obvious relation to bedding, suggesting a replacement origin. Limestones analyzed by XRD contain dolomite, generally in minor amounts. The dolomite of both Kenya and Tanzania is disordered, as based on attenuation of the (015) ordering reflection, and contains about 55% CaCO₃, as based on the (104) spacing (Goldsmith and Graf 1958).

The deformed carbonate rocks contain very little non-carbonate material except for sepiolite and Ke/St, which average 7 wt. percent of 4 samples from Tanzanian pits and 16 percent in 6 samples from Pits Q and S. Clay is generally fine grained and disseminated, but in Pit Q it also lines or fills root channels and fractures, and clay pellets, possibly transported by wind, are common in some of the dolomites. No fossils were noted in the field or in thin sections.

It seems likely that the carbonate sediment was deposited in saline, alkaline marshland and/or shallow water of a lake or ponds. Fossils such as ostracodes and molluscs are lacking, and rootmarkings show that vegetation was present, at least intermittently. The principal problem concerning the origin of the deformed carbonate rocks is in accounting for the lithologic difference between the hard, commonly nodular carbonate rocks of the domes and the soft carbonates and clays lateral to the domes where penetrated by drilling. The explanation suggested here is that car-

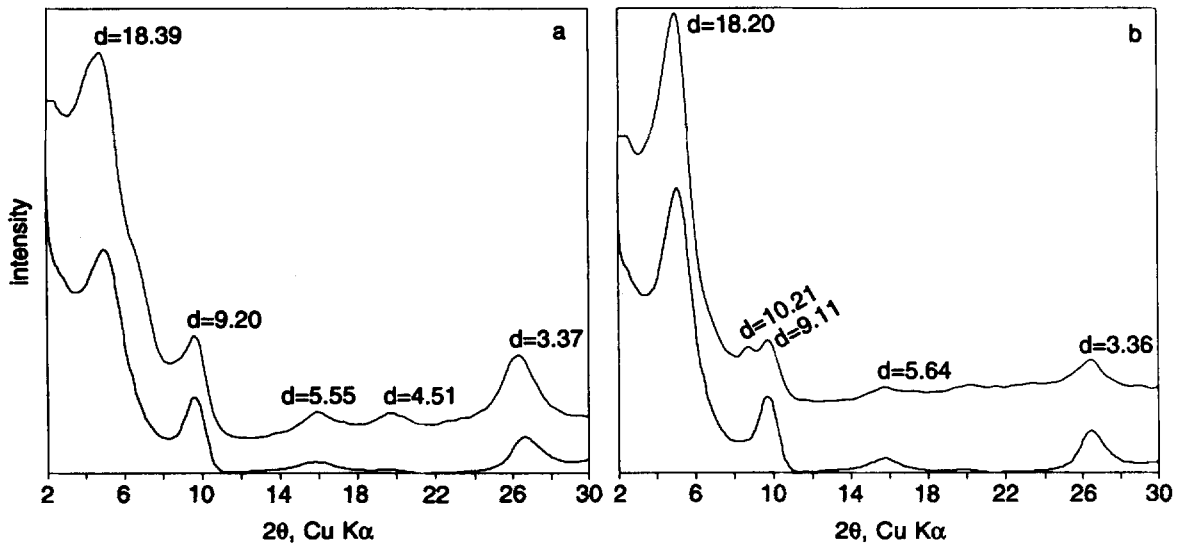


Figure 5. NEWMOD® modeling of XRD traces of Ke/St. a) Superposition of trace of 14L above NEWMOD® modeled trace for 51% stevensite and 49% kerolite. b) Superposition of trace of sample 13K above modeled trace for 70% stevensite and 30% kerolite.

bonates rocks of the domes were initially unconsolidated deposits that were hardened and extensively modified to form nodules and nodular masses by recrystallization in the vadose zone, analogous to the calcretization process in soils, during the early stages of deformation. As evidence of vadose recrystallization, nodules with reticulate surface cracks resemble those found in some caliche soils (e.g., Reeves 1976, Figure 3-14A; Hay and Wiggins 1980, Figure 7C). In Tanzania, relict bedding in nodular masses with reticulate cracks indicates that the nodular masses did not originate as diapiric caliche breccia masses as proposed by Hay and Stoessel (1984). This study sheds no light on the cause(s) of the domal uplift and intense deformation of the carbonate rocks and overlying bedded sepiolite.

Stable isotope data from bedded carbonate rocks of the Sinya Beds (Table 1) are compatible with a lacustrine origin and an early or middle Pleistocene age. The $\delta^{13}\text{C}$ values for calcite and dolomite of the Sinya Beds are +2.0 to +3.5‰ (PDB) and overlap with those from the lacustrine Amboseli Clay. These values of +2.0–3.5‰ are within the range of closed-basin lakes (Talbot and Kelts 1990) and outside the range for pedogenic carbonates of Olduvai Gorge over the past 2 Ma (Cerling and Hay 1986). Calcite and dolomite of deformed rocks in the Sinya Beds are ~6‰ lower in $\delta^{18}\text{O}$ than calcite and dolomite from drill core of the Amboseli Clay (Table 1). Calcite of the Sinya Beds has $\delta^{18}\text{O}$ values of 27.8–28.9‰, averaging 28.2‰ relative to SMOW. Dolomite ranges from 28.8–31.1‰, averaging 30.0‰. This large difference in $\delta^{18}\text{O}$ values between carbonate minerals of the Sinya Beds and Amboseli Clay is com-

patible with an early or middle Pleistocene age (1.6–0.7 Ma) for the Sinya Beds, when meteoric water had substantially lower $\delta^{18}\text{O}$ values than at present.

The $\delta^{18}\text{O}$ values of cavity-filling dolomite are +29.3–30.7‰, averaging 30.0‰. These values are about the same as those of dolomite from deformed rocks, suggesting formation from fluids of similar oxygen isotope composition. The one sample of cavity-filling calcite has a $\delta^{18}\text{O}$ value of +31.1‰, midway between values for calcite of deformed carbonate rocks and calcite of the Amboseli Clay. Its high $\delta^{13}\text{C}$ value of +6.6‰ is in the range of calcite formed in methanogenic saline and highly alkaline lakes such as that of Bed I, Olduvai Gorge (Cerling and Hay 1986).

Oxygen isotope data suggest that dolomite was formed from fluids more dilute than those in which limestones were precipitated. The disordered dolomite-water fractionation factor is ~3‰ greater than that for calcite-water at low temperatures (Fritz and Smith 1970), and assuming similar temperatures, the dolomite crystallized from fluids about 2‰ lower than associated calcite. By this line of reasoning, the cavity-filling dolomite crystallized from fluids about 4‰ lower than the cavity-filling calcite. Dolomite of the Sinya Beds may well have formed from ground water. This can account for both the $\delta^{18}\text{O}$ values and the irregular distribution of dolomite in the Tanzanian carbonate rocks. As supporting evidence, about half of the analyzed samples of present-day ground water are supersaturated with respect to disordered dolomite (Stoessel and Hay 1978).

For later comparison with oxygen isotope data for clays, $\delta^{18}\text{O}$ values for water in equilibrium with carbonate minerals at 20°C are given in Table 1. The

Table 1. Stable isotope composition of carbonate minerals in the Sinya Beds and Amboseli Clays¹.

	Sample	Loc.	Cal.	Dol.	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}_{\text{H}_2\text{O}}^2$
Sinya Beds (deformed)	13A	T	X		+27.8	+2.3	-1.7
	13A ₂	T	X		+27.8	+2.1	-1.7
	13M	T	X		+28.9	+2.5	-0.6
	13A ₂	T		X	+29.3	+3.0	-3.2
	13H	T		X	+28.8	+2.0	-3.7
	14B ₂	Q		X	+29.5	+2.3	-3.0
	14M	Q		X	+30.5	+3.5	-2.0
	AKB-5	S		X	+31.1	+2.9	-1.4
Sinya Beds (cavity fill)	AKB-6	S		X	+30.7	+2.1	-1.8
	13M ₁	T	X		+31.1	+6.6	+0.6
Sinya Beds (cavity fill)	13G	T		X	+29.9	+2.6	-2.6
	13I	T		X	+29.3	+1.9	-3.2
	13M ₂	T		X	+30.7	+5.6	-1.8
Amboseli Clays ³	4-64	LA		X	+36.5	+6.8	+4.0
	F17-19	LA	X		+34.2	+2.4	+5.9

¹ Abbreviations are Loc., locality; Cal., calcite; Dol., dolomite. Localities are T, Tanzania; Q, Pit Q in Kenya; S, Pit S in Kenya; LA, drill core from Lake Amboseli. $\delta^{18}\text{O}$ values are given in ‰ relative to SMOW for oxygen and PDB for carbon.

² $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values are calculated for 20°C.

³ Sample 4-64 consists of coarse (~1 mm) calcite crystals associated with gaylussite and is from a depth of 19.5 m in borehole M-4, about 460 m north-northeast of Pit S; sample F-17-19 is from a depth of 5.2 m in borehole F-17, about 4 km northeast of Pit S (Williams 1972).

calcite-water fractionation factor was obtained from $\Delta_{\text{calcite-water}} = 2.78 (10^6/T^2) - 2.89$ (O'Neill *et al* 1969).

CAVITY-FILLING CLAYS

Clay forms veins and fills cavities in both deformed carbonate rocks and bedded sepiolite. Veins range from less than a millimeter to about 5 cm in thickness. Cavity fillings are of highly varied shapes and sizes but are most commonly lenticular and generally range from about 1 cm to 30 cm in thickness. Veins and cavity fillings range from undeformed to sheared and brecciated, showing that they were deposited during and after the major deformation of the Sinya Beds. Except for samples from Pit S, nearly all of the clays forming veins and filling cavities are relatively hard and do not disperse in water without crushing. Sepiolite and mixed-layered kerolite/stevensite (Ke/St) are the principal minerals of the veins and cavity fillings. Illite is a minor constituent in a few samples. Regarding the use of Ke/St, we have chosen the convention of adding lower case letters to distinguish this phase from mixed-layered kaolinite/smectite (K/S).

Clay mineralogy

Sepiolite occurs in cavities chiefly as the meerschau variety. Friable green and gray sepiolitic clays of waxy luster that readily disperse in water were noted in a few cavities at one locality in Tanzania. XRD patterns are typical for sepiolite except for highly variable intensities of the (131) peak at 4.35 Å and the (331) peak at 3.20 Å. These spacings are absent in the XRD pattern from a random mount of sample 14E, which contains 30% sepiolite. The main peak of sepiolite, with an air-dry *d*-value of 12.3 Å, expands to

12.6–12.7 Å on glycolation, as do many sepiolites and palygorskites (Jones and Galan 1988). After heating at 375°C, the main peak of Amboseli sepiolite is reduced in intensity by 50 to 90 percent, and a shoulder is developed at ~10.5 Å, reflecting dehydration and structural collapse. The amount of sepiolite in mixtures was estimated from the intensity of the (110) peak at 12.6 Å after glycolation to displace the (001) peak of smectite to lower angles. The content of Al is low, generally ≤1% Al₂O₃ in chemically analyzed meerschau from Amboseli (Sampson 1966, Stoessel and Hay 1978). Of two meerschau samples analyzed by KEVEX, one contains no detectable Al and Fe, and the other contains small amounts. Sepiolite of meerschau occurs as fibers and fibrous mats as seen by SEM (Figure 6a).

The Ke/St clays are trioctahedral and have an (060) spacing of 1.521–1.524 Å. Two varieties of Ke/St are represented by different air-dry spacings. The more common variety has a spacing of 12.1–12.5 Å (generally ~12.5 Å), and the other has a spacing of 10.0–10.5 Å (Figure 4). Samples commonly exhibit both spacings, indicating mixture of the two types. For micronized samples, glycolation generally expanded the (001) peak of both varieties to 17.8–19.0 Å, but in a few samples glycolation raised the intensity of the low-angle background but did not yield a peak. In the low-Al Ke/St, the *d* spacing of the (001) peak was slightly increased by continued glycolation. Mixed-layering is indicated by non-integral spacings of the (00*l*) series and by low peak to saddle ratios in glycolated mounts.

The Ke/St giving an air-dry peak at ~10 Å deserves comment because other samples of this material were previously identified as kerolite (Stoessel and Hay 1978). In the early phases of the work, using random

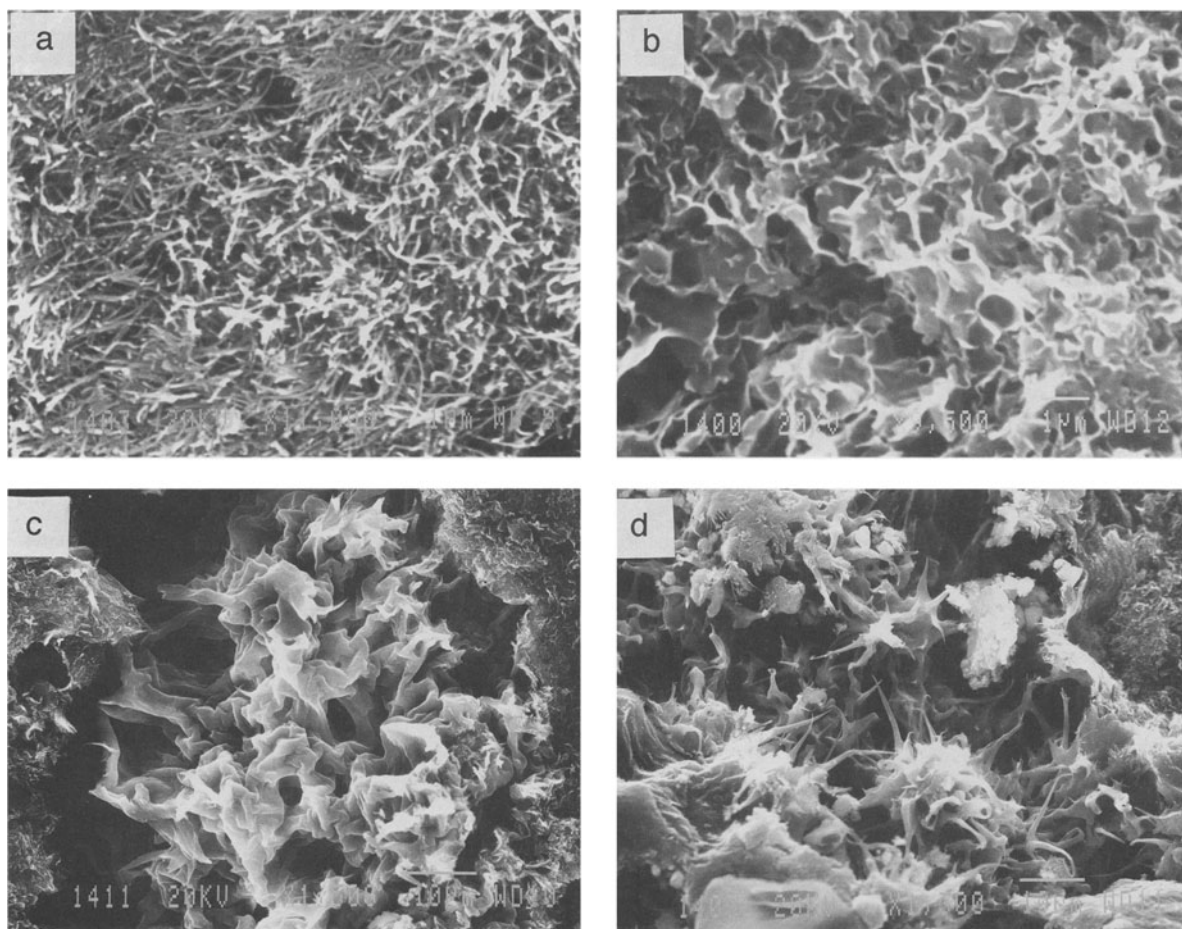


Figure 6. SEM photos of cavity-filling clays of the Sinya Beads. a), Fibrous sepiolite typical of the Amboseli meerschaum. Scale bar is 1 μm . b), Ke/St of relatively low specific gravity and earthy luster, which is a boxwork of wavy sheets. Scale bar is 1 μm . c), Pore-filling of Ke/St in Al-Ke/St (sample AKB-5). Fe was detected but Al was not in KEVEX analysis of pore filling. Scale bar is 10 μm . d), Ke/St and sepiolite lining pore in meerschaum. Tapered fibers attributed to sepiolite lie on wavy surface of Ke/St (lower left). Scale bar is 10 μm .

mounts and bulk smears, glycolation increased the low-angle intensity but only rarely resulted in a low-angle peak. A peak or shoulder at ~ 10 \AA remained after glycolation, and this combination of features gave the impression of kerolite with an undetermined amount of an expandable mineral. In later work, using oriented mounts of micronized samples, glycolation resulted in a well-developed 001 peak at ~ 18 \AA , and the peak at ~ 10 \AA was resolved into the 002 peak of smectite, at 9.1–9.5 \AA , and the 001 peak of kerolite-rich Ke/St, at 9.8–10.4 \AA .

The content of kerolite in the Ke/St is estimated at about 25 to 50 percent by applying to Ke/St the $\Delta 2\theta$ 002/003 method for estimating the percent of illite in illite/glycolated smectite (Moore and Reynolds 1989). The least kerolitic samples are from Pit S and the most kerolitic are from Pit Q. Kerolite contents of chemically analyzed samples determined by this method are AKB-6 = 25%, 13K = 30–35%, 14I = 40%, and 14L

= 45–50%. Results of this method suggest that the hard waxlike Ke/St clays classified as kerolite by Stoessel and Hay (1978) contain 30 to 50 percent interstratified kerolite. Within the hard waxlike claystones, the content of kerolite bears no obvious relation to development of an air-dry 001 peak at about 10 \AA .

XRD patterns of Ke/St were closely approximated by modeling using NEWMOD[®] (Reynolds 1985). These patterns could be modeled more easily using a talc 001 d spacing of 9.35 \AA than the 9.65 \AA spacing of kerolite. Figures 5a and 5b show the superposition of the XRD trace above the NEWMOD[®] model trace for samples 14L and 13K. In Figure 5a, the match is excellent except for the high-angle shoulder on the 18.39 \AA peak, which is due to sepiolite. The comparison of real data and NEWMOD[®] trace is excellent for 13K, excepting the peak at 10.21 \AA on the sample tracing, which is attributed to a minor amount of kerolite-rich Ke/St that is inadequately modeled by NEWMOD[®].

Table 2. XRF analyses of clays forming veins and filling cavities in the Sinya Beds.

	AKB-6	13K	14E	14I	14L
SiO ₂	53.9	53.6	49.5	55.0	53.6
TiO ₂	0.23	0.09	0.15	0.52	0.06
Al ₂ O ₃	3.42	0.92	1.58	0.19	0.44
Fe ₂ O ₃	2.09	0.52	1.03	0.07	0.24
MnO	0.04	<0.01	0.01	<0.01	<0.01
MgO	24.9	26.2	22.6	27.3	27.2
CaO	0.05	0.24	0.15	2.48	0.48
Na ₂ O	1.72	1.08	2.50	0.13	0.16
K ₂ O	1.70	1.01	1.08	0.17	0.32
P ₂ O ₅	0.03	0.11	0.03	0.02	0.02
L.O.I.	11.4	16.1	21.4	14.8	17.5
Total	99.5	99.9	100.0	100.8	100.0

AKB-6, Na-exchanged <2 μm fraction of soft green clay lens in dolomite of Pit S; ~85% Al-Ke/St, 10% illite, and ≤5% sepiolite.

13K, hard pale green waxy clay from cavity in carbonate rock of Tanzanian pit; Ke/St with minor kerolite-rich Ke/St.

14E, hard sub-waxy pale yellow clay from sheared clay lens 10–15 cm thick in dolomite of Pit Q; 70% Ke/St and 30% sepiolite.

14I, hard sub-waxy white clay of vein 1.5 cm thick in bedded sepiolite of Pit Q; Ke/St with minor sepiolite.

14L, hard white waxy clay from lens 30 cm thick in bedded sepiolite of Pit Q; Ke/St with minor sepiolite.

The content of kerolite as based on modeling agrees with that obtained by the Δ2θ 002/003 method.

Heating of Ke/St to 375°C causes either complete collapse of the 001 peak to 10 Å or incomplete collapse in which the intensity of the 12.5 Å 001 air-dry peak is reduced in size and a weak to moderate peak is developed at ~10 Å. Heating of the latter samples at 550°C for one hour collapsed the 001 peak to ~10 Å. Incomplete collapse at 375°C characterizes most of the Ke/St clays from Pit Q and some of the Ke/St in samples from Tanzania.

All of the samples have a high MgO content, and the amount of Al₂O₃ + Fe₂O₃ ranges from 0.3% for sample 14I to 5.5% for sample AKB-6 (Table 2). The structural formula for sample 14L is close to that of kerolite, and the other analyzed Ke/St-rich clays have Si:Mg ratios higher than kerolite (Table 3). Sample AKB-6, from Pit S, has substantial Al and Fe and will be designated Al-Ke/St. Calculated layer charges of the samples with high contents of Ke/St and Al-Ke/St range from ~0.10 to ~0.50 (Table 3). The relatively high content (0.52%) of TiO₂ in sample 14I warrants comment as Ti⁴⁺ (or TiO₂) is considered as relatively insoluble, yet the sampled deposit was chemically precipitated. It should be noted that the structural formulas only approximately indicate the composition of Ke/St, as all analyzed samples contain small to moderate amounts of other clay minerals.

Brucite-like interlayers are probably an additional component of much of the Ke/St. The structural formulae for samples 14I and 14L have insufficient Si to

Table 3. Unit formulae set to 22 charges for clays¹ of the Sinya Beds.

		AKB-6	13K	14E	14I	14L
Tetrahedral	Si	3.79	3.92	3.89	3.91	3.94
	Ti	0.01	0.01	0.01	0.03	0.00
	Al	0.20	0.07	0.10	0.02	0.04
	Σ	4.00	4.00	4.00	3.96	3.98
Octahedral	Al	0.08	0.01	0.05	0.00	0.00
	Fe ³⁺	0.11	0.03	0.06	0.00	0.01
	Mg	2.61	2.86	2.64	2.89	2.98
	Σ	2.80	2.90	2.75	2.89	2.99
Interlayer	Ca	0.01	0.02	0.02	0.19	0.04
	Na	0.23	0.15	0.39	0.02	0.02
	K	0.15	0.09	0.11	0.02	0.03
Charge	Tet	0.20	0.07	0.10	0.06	0.06
	Oct	0.21	0.19	0.39	0.22	0.01
	Σ	0.41	0.26	0.49	0.28	0.07
	Int	0.40	0.28	0.54	0.42	0.13

¹ Structural formulae are based on chemical analyses in Table 2.

give a tetrahedral charge of 4.00 per O₁₀(OH)₂, probably because some of the analyzed Mg occurs as brucite-like interlayers or pillars, which can account for the impeded collapse of these samples on heating. The inferred interlayer Mg may be present chiefly as Mg(OH)⁺ rather than as Mg(OH)₂ in view of the expansion of the (001) peak on glycolation (Brindley and Kao 1980).

A kerolitic component is a minor constituent of many samples of Ke/St. This identification is based on a small peak at ~10 Å in glycolated mounts that generally changes in size and position with increased glycolation time. Most commonly the peak increases in size and may shift to lower angles after continued glycolation, as in sample 13K, where it shifts from 10.1 to 10.2 Å. In two samples the peak decreased in size and shifted to 9.8 Å after increased glycolation. This 10 Å component is interpreted as kerolite-rich Ke/St, and the differing behaviors on glycolation may reflect differences in kerolite content and/or ordering of the Ke/St.

Illite is present in a few samples, as based on a 10.0 Å peak that does not change in size or position after continued glycolation. It is most common in Al-Ke/St-rich samples from Pit S, and the maximum amount is about 10% as determined from intensities of the (003) smectite peak and the (002) illite peak using calculated intensities for illite and Fe-saponite (Reynolds 1989, Table 12). The illite does not give an identifiable (060) *d* spacing, despite slow scans (0.05° 2θ/min.). We suggest that it is probably an authigenic illite with a high content of Fe and Mg, and the 060 peak falls within the Ke/St peak at 1.52–1.54 Å. Authigenic illites of this type are common in deposits of saline, highly alkaline lakes such as Searles Lake, California, where the illites commonly have 060 *d* spacings of 1.514–1.518 Å (Hay *et al* 1991).

As seen in SEM, waxy Ke/St has either a dense, fine-grained cornflake texture (e.g., Stoessell 1988, Figure 1) or is a dense meshwork of flattish fibers 0.05–0.10 μm wide, with cornflake sheets in pores. Al and Fe are below detection limits in KEVEX analysis of 14I, and Ca was confirmed as the dominant interlayer cation. Ke/St of relatively low specific gravity and earthy luster is a boxwork of wavy sheets (Figure 6b). Small amounts of Al, Fe, and Cl were detected in sample 14E. The Cl may represent NaCl, which would account for some of the Na in the chemical analysis. The Al-Ke/St has a cornflake morphology, with rumpled sheets in pores (Figure 6c). Substantial Al and Fe were detected throughout a sample examined by SEM. A euhedral quartz crystal 3 μm in length was noted in a cornflake-textured Ke/St sample from Pit Q.

Paragenesis and associations

The earliest clay minerals of the Sinya Beds are the sepiolite and Ke/St in the deformed carbonate rocks. Bedded clays overlying the carbonate rocks are reportedly sepiolite (Sampson 1966, Stoessell and Hay 1978), and the one sample analyzed in the present study is sepiolite with minor smectite or Ke/St. Deposited last were the clay veins and cavity fillings in the carbonate rocks and bedded sepiolite.

Veins and cavity fillings are composed of two or more clay minerals, and at least trace amounts of sepiolite are present in all samples analyzed by XRD. The type of clay mineral in veins and cavities differs to some extent in the various areas sampled. Sepiolite of the meerschaum variety is widespread but appears to be most abundant in the Tanzanian pits. Rare cavity fillings of soft green and gray sepiolite-rich clay were noted in one pit in Tanzania. These clays contain subordinate Ke/St, illite, and less commonly disordered K-feldspar of end-member composition. Meerschaum is interbedded with the soft sepiolitic clays of one cavity. These green and gray clays may well represent the Amboseli Clays, as they are similar in appearance and mineral composition, and K-feldspar has not been identified in any other samples from the Sinya Beds.

Hard, waxlike Ke/St is most common in Pit Q, where it occurs chiefly as lenses in bedded sepiolite. It occurs as layered fracture fillings as much as 45 cm thick, which are commonly deformed (Stoessell and Hay 1978, Figure 5) and locally brecciated. Where observed, the contact between bedded sepiolite and cavity-filling Ke/St is sharp, and no evidence was found for replacement of sepiolite by Ke/St. Al-Ke/St was found only in Pit S, where it is associated with illite. The amount of illite, even if Al-rich, is too small account for the Al in the analyzed sample.

The depositional sequence of clays filling cavities at all localities is from dominantly Ke/St to sepiolite (meerschaum), with or without minor Ke/St. This sequence was determined by stratigraphic and structural

relationships in the cavity-fillings. Clay fillings are commonly laminated and were filled from the base upward, hence the depositional sequence can be determined by stratigraphic position. Age relationships in deformed fillings are indicated by undeformed veins and lenses cutting deformed clays, and by clasts of early-formed clay in a matrix of less-deformed or undeformed clay. In both Pit Q and the Tanzanian pits, the earlier clays are waxlike Ke/St with minor sepiolite. Limited study suggests an increase of sepiolite in the Ke/St clays through time prior to the deposition of meerschaum. Clasts of meerschaum are in the basal conglomerate of the Amboseli Clays (Williams 1972), showing that at least some of the meerschaum was formed prior to the Amboseli Clays. Carbonates with disseminated clay form the lowermost and earliest deposits in some of the cavities in Tanzania, and dolomite is disseminated in some of the early-deposited clays in Pit Q.

SEM study shows that small amounts of Ke/St were deposited after sepiolite. Wavy sheets of Ke/St were found in pores of one meerschaum sample, showing that they followed sepiolite. Rounded fibers, presumably of sepiolite, line some other pores in the same sample, and in a very few pores sepiolite fibers appear to grow on wavy sheets of Ke/St (Figure 6d), suggesting the sequence was sepiolite \rightarrow Ke/St \rightarrow sepiolite.

Stable-isotope composition

Clays consisting largely of Ke/St range in $\delta^{18}\text{O}$ value from 22.5‰ to 25.6‰, whereas the two meerschaum samples have intermediate values of 23.5 and 24.7‰ (Table 4). Within the Ke/St clays, the $\delta^{18}\text{O}$ values vary inversely with the content of kerolite (Figure 7). Samples AKB-5 and AKB-6, with \sim 25 percent kerolite, have values of 25.2 and 25.6‰, and samples 14I and 14L, with 40–50 percent kerolite, have values of 22.5 and 22.7‰. Sample 13K, with 30–35 percent kerolite, has an intermediate $\delta^{18}\text{O}$ value of 24.0‰. In Pit Q, sepiolitic samples have higher $\delta^{18}\text{O}$ values than analyzed samples of Ke/St. In Pit Q, samples 14I and 14L of the early-deposited Ke/St clays have the lowest values, 22.5 and 22.7‰, and the sample of meerschaum (S102), the latest clay, has the highest value, of 24.7‰. Sample 14E, of intermediate age and Ke/St-sepiolite composition has a value of 23.7‰. The $\delta^{18}\text{O}$ value of 22.7‰ for bedded sepiolite falls near the low end of values for cavity-filling clay.

Clay mineral-water fractionation factors were obtained from structural formulas for chemically analyzed samples using bond-type calculations (Savin and Lee 1988) with the computer program of Dr. Eric Daniels (Chevron Research Corp.). Clay mineral composition was used to estimate the chemical composition and structural formula for samples not chemically analyzed. The calculated fractionation factors vary rather little because the framework of all clays consists largely

Table 4. Oxygen-isotope composition of clays of the Sinya Beds and calculated equilibrium values for H₂O at 20°C.

	Sample ¹	Loc. ²	Clay Mineral Comp. ³	$\delta^{18}\text{O}^4$	$\Delta_{\text{cm-H}_2\text{O}}^5$	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$
Bedded clay	14G	Q	95 Sp, 5 S	+22.7	22.9	-0.2
Cavity filling	13B*	T	90 Sp, 10 S	+23.5	23.0	+0.5
Cavity filling	13K	T	95 S, 5 K	+24.0	22.7	+1.3
Cavity filling	14E	Q	70 S, 30 Sp	+23.7	22.8	+0.9
Cavity filling	14I	Q	95 S, 5 Sp	+22.5	22.8	-0.3
Cavity filling	14L	Q	95 S, 5 Sp	+22.7	22.9	-0.2
Cavity filling	S102*	Q	Sp, trace S	+24.7	23.0	+1.7
Cavity filling	AKB-5	S	85 Sa, 5-10 Sp, 5-10 I	+25.6	22.7	+2.9
Cavity filling	AKB-6	S	85 Sa, 10 I, 5 Sp	+25.2	22.7	+2.5

¹ Samples marked with * are meerschaum, which are latest in the depositional sequence.

² Localities are Q, Pit Q; S, Pit S; and T, Tanzanian pits.

³ Abbreviations are S, dominantly stevensitic Ke/St; Sa, Al-Ke/St; K, kerolite-rich Ke/St; Sp, sepiolite; and I, illite. Estimated clay mineral composition is given in percent.

⁴ $\delta^{18}\text{O}$ values are given in per mil (‰) relative to SMOW.

⁵ Fractionation factors are based on bond-type calculations of Savin and Lee (1988) as explained in text.

of MgO and SiO₂. Using a temperature of 20°C, the $\delta^{18}\text{O}$ values of water in equilibrium with the clays range from -0.3 to +2.9‰, averaging 1.2‰. The cavity-filling calcite has a water value of +0.6‰ at 20°C, within the range of the clays, and the cavity-filling dolomite has an average water value of -3.5‰, much lower than all the clays (Table 1).

CLAY MINERAL GENESIS

The chemical environment of the bedded sepiolite in the Sinya Beds is not known, as neither fossils nor evidence of saline minerals has been recorded. The bedded sepiolite overlies chemically precipitated carbonate rocks, and the change from dominantly carbonate minerals to sepiolite may represent the evaporative sequence in a carbonate-rich highly alkaline

lake (Hardie and Eugster 1970). In support of this possibility, the calculated $\delta^{18}\text{O}$ water value of the analyzed sample of sepiolite is -0.2‰, compared to calculated water values of -0.6 to -3.7‰ for the underlying deformed limestones and dolomites (Table 1).

The correlation of $\delta^{18}\text{O}$ value with Ke/St composition in the cavity-filling clays (Figure 7) suggests that higher salinities favored higher stevensite contents. This supports the conclusion of Jones (1986) that kerolite/smectite interstratification is favored by increased salinity. A similar correlation between $\delta^{18}\text{O}$ value and stevensite content is found in Pliocene Mg-rich clay minerals of the Amargosa Desert, Nevada (Hay *et al* 1986). A sample of the Ke/St richest in kerolite, the kerolite of Eberl *et al* (1982), has a $\delta^{18}\text{O}$ value of 16.3‰, whereas eight Ke/St samples with much higher contents of stevensite have values of 17.0–22.0‰, averaging 19.1‰ (Hay *et al* 1986).

As $\delta^{18}\text{O}$ values for sepiolite fall near the middle of the range for Ke/St, salinity was probably not the main control in determining whether sepiolite or Ke/St was formed. Another possible factor is the presence or absence of a precursor clay. Sepiolite is readily precipitated from laboratory solutions (Wollast *et al* 1968), whereas a preexisting phyllosilicate substrate is commonly involved in precipitation of trioctahedral 2:1 phyllosilicates (Jones 1986). In Lake Abert, for example, stevensite and/or kerolite have formed as interlayers in detrital montmorillonite (Jones and Weir 1983). The presence of detrital clay may well have been a factor in the formation of the Al-Ke/St found in Pit S. Precursor clay cannot, however, be called upon to explain the low-Al Ke/St. Differences in $a_{\text{SiO}_2}/a_{\text{Mg}^{2+}}$ may account for the precipitation of cavity-filling sepiolite and low-Al Ke/St at different times. High $a_{\text{SiO}_2}/a_{\text{Mg}^{2+}}$ would favor sepiolite, and one mechanism for varying the $a_{\text{SiO}_2}/a_{\text{Mg}^{2+}}$ is by mixing ground water with lake water. Sepiolite is the dominant clay mineral formed in lacustrine deposits of the Amboseli Basin, at least

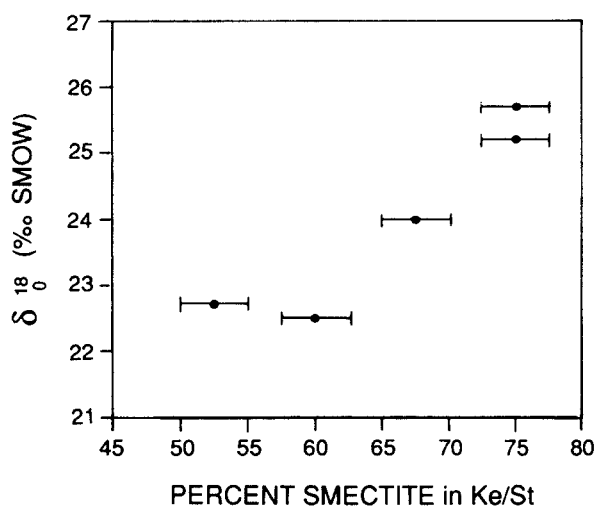


Figure 7. $\delta^{18}\text{O}$ values of Ke/St plotted against percent stevensite layers in Ke/St. Content of stevensite layers was determined by $\Delta\theta$ 002/003 as discussed in text, and bars represent error limits based on uncertainties in the 002 and 003 measurements.

some of which were deposited in saline and highly alkaline water. Saline, highly alkaline lake water commonly has 100–140 ppm SiO_2 , <2 ppm Mg^{2+} and a pH of 9.5–10.0 (Jones 1966). Ground water of the Amboseli Basin is dilute, slightly alkaline and generally has 10–20 ppm Mg^{2+} and 50–60 ppm SiO_2 (Stoessell and Hay 1978). Mixtures of these waters should decrease the $\text{SiO}_2/\text{Mg}^{2+}$ activity ratio over that in lake water, thus favoring Ke/St. The $\delta^{18}\text{O}$ values for clay minerals of Pit Q are in accord with this hypothesis, as the values for Ke/St are lower than those for sepiolitic clays. Mixing saline, highly alkaline lake water with ground water should raise the $a_{\text{Mg}^{2+}}/a_{\text{H}^+}$, which may have been a factor in forming brucite-like interlayers. Short-term fluctuations in water chemistry are indicated by the sequence of sepiolite \rightarrow Ke/St, and probably of sepiolite \rightarrow Ke/St \rightarrow sepiolite in meerschaum examined by SEM. These mineralogic fluctuations could reflect variations in lake level and/or ground water discharge.

The change from dominantly low-Al Ke/St clays to dominantly sepiolite in Pit Q and the Tanzanian pits may have been caused by an increase in the contribution of lake water over that of ground water to the pore fluid. This inference is based partly on the fact that sepiolite is the dominant Mg-rich clay mineral in lacustrine deposits of the Amboseli Basin. The presence of detrital clay may have been an important factor in forming the Al-Ke/St in Pit S, as high $\delta^{18}\text{O}$ values of the clay suggest relatively undiluted saline lake water.

CONCLUSIONS

1. Limestones, dolomites, and bedded sepiolite of the Sinya Beds were probably deposited in marshland and/or shallow lakes or ponds. The carbonate rocks contain significant amounts of disseminated sepiolite and Ke/St, and the change from dominantly carbonate sedimentation to deposition of the bedded sepiolite may represent the evaporative sequence in a carbonate-rich highly alkaline lake. The stable isotope composition of carbonate rocks suggests that they were deposited in the middle or early Pleistocene, when meteoric waters had $\delta^{18}\text{O}$ values on the order of 5 to 10‰ lower than at present.

2. The dominant clay minerals in veins and filling cavities in the Sinya Beds are sepiolite (meerschaum) and Ke/St. Most of the Ke/St has 25 to 50 percent stevensite layers, and some samples contain minor amounts of kerolite-rich Ke/St. The waxlike clays identified as kerolite by Stoessell and Hay (1978) are most likely Ke/St with 30–50 percent kerolite layers. At one locality the Ke/St contains significant amounts of Al and Fe (Al-Ke/St). Brucite-like interlayers are probably present in the Ke/St with 40–50% kerolite layers. No 7 Å phyllosilicate was identified.

3. Cavity-filling clays were chemically precipitated,

and the sequence of cavity-filling clays was from dominantly Ke/St to dominantly sepiolite (meerschaum), although minor Ke/St followed sepiolite in at least some of the meerschaum.

4. The oxygen isotope composition of cavity-filling clays suggests that salinity controlled the contents of stevensite and kerolite in the Ke/St, with high salinities favoring a high content of stevensite. The $a_{\text{SiO}_2}/a_{\text{Mg}^{2+}}$ of pore fluid may have been the main control on precipitation of sepiolite and low-Al Ke/St.

5. SiO_2 and Mg^{2+} for Mg-rich clays were supplied by lake- and ground water. Different mixtures of dilute, relatively Mg-rich ground water with saline, alkaline lake water may account for precipitation of sepiolite and low-Al Ke/St at different times, with high proportions of lake water favoring sepiolite. Detrital clay was very likely a factor in forming the Al-Ke/St.

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