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SILICATE REACTIONS IN THREE LITHOFACIES OF A SEMI-ARID BASIN, OLDUVAI GORGE, TANZANIA

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Abstract

Authigenic minerals containing Al or Si are abundant in Pleistocene sediments of three environments in the Olduvai region: a saline, alkaline lake; intermittently flooded, lake-margin terrain; and an alluvial plain and fan. Minerals in all three sedimentary facies were formed by reactions involving sodium-carbonate solutions, and each sedimentary facies contains a different assemblage of authigenic minerals, reflecting differences in salinity, available detritus, and hydrologic environment.

Lake deposits of Beds I and II are about 80 percent claystone, and the remainder is chiefly tuff. Tuffs are altered to K-feldspar and phillipsite; nontuffaceous claystones contain 15 to 20 percent analcime and K-feldspar. Clinoptilolite and erionite are present in a few claystones and searlesite and jarosite occur rarely in tuff. Chert nodules are widespread. Zeolites were formed by reaction of class and detrital clay with lake water at shallow burial depths; K-feldspar was formed later from zeolites. Chert nodules formed from a sodium-silicate mineral precipitated on the lake floor.

Lake-margin deposits of Bed II in the Side Gorge are about 50 percent zeolitic limestone, 40 percent zeolitite, and 10 percent claystone. Massive, impure zeolitites are 25–40 percent phillipsite, clinoptilolite, and erionite; rare laminated zeolitites may be nearly pure clinoptilolite. Claystones average about 13 percent clinoptilolite. Chert nodules are widespread in the Side Gorge, and opal nodules and kenyaite occur in lake-margin deposits of Bed II in the Main Gorge. Clinoptilolite of the laminated zeolitite probably formed, together with chert, from a bedded sodium-silicate precursor. The massive zeolitites may have formed either from an authigenic aluminosilicate gel or from detrital amorphous clay. Biogenic opal supplied SiO_2 for kenyaite, opal nodules, and some of the clinoptilolite.

Alluvial deposits of Beds III, IVa, and the upper part of Bed II are 73 percent claystone, the remainder including tuffs and mudflow deposits. Tuffs are zeolitized, and claystones average about 10 percent zeolites, reaching a maximum of 40 percent. Claystones richest in zeolites characteristically contain volcanic detritus and form hard, reddish-brown beds that contain authigenic illitic clay. Analcime is the principal zeolite; chabazite and phillipsite are common, and natrolite and dawsonite are relatively rare. Where altered, the mudflow deposits resemble mineralogically the hard, reddish-brown claystones except for the common occurrence of dawsonite. Zeolites, dawsonite, and illite were formed in the alluvial deposits by reaction of detrital clay with sodium carbonate solutions concentrated at the land surface by evapotranspiration. During zeolitic alteration silica and alumina were redistributed within the alluvial deposits.

Introduction

Scope and method. To a spectacular degree, the Pleistocene deposits of Olduvai Gorge, Tanzania, illustrate reactions of aluminosilicate materials with sodium-carbonate solutions at surface conditions. Varied materials were altered, and many different minerals were formed. This paper documents the nature and distribution of authigenic minerals in sediments of three environments: a saline, alkaline lake; lake-margin terrain; and an alluvial plain and fan. An attempt is made, with varying degrees of success, to establish the nature of the reactions yielding K-feldspar, zeolites, quartz, dawsonite ($NaAl(OH)_2CO_3$), and kenyaite ($NaSi_{11}O_{20.5}(OH_4\ 3H_2O)$). The overall pattern of silicate authigenesis in Olduvai Gorge is given elsewhere (Hay, 1966, p. 39–44), and studies have been published on "zeolitic weathering" of tuffs (Hay, 1963a), paleogeography of the Olduvai deposits (Hay, 1967a), revised stratigraphy (Hay, 1967b), and the nature and origin of chert (Hay, 1968).

Olduvai Gorge was studied and sampled over five field seasons during the period 1962–1969. Laboratory study at the University of California at Berkeley included microscopic examination, X-ray diffraction, and chemical analysis. Amounts of authigenic silicate minerals in claystones were estimated by comparing diffractometer patterns of bulk samples with those of prepared mixtures. The phillipsite, chabazite, clinoptilolite, and K-feldspar used in the mixtures were obtained from samples collected in Olduvai Gorge. Estimates of analcime and K-feldspar were based on the height of two or more diffractometer peaks; a single peak was used for estimating clinoptilolite (8.9 Å), chabazite (9.3 Å), erionite (11.4 Å), and phillipsite (7.08 Å). As little as 2 to 3 percent analcime or erionite can be detected by X-ray methods; 5 percent is usually necessary to identify phillipsite, chabazite, clinoptilolite and K-feldspar.

Climatic and geologic setting. Olduvai Gorge is cut 45 to 90 m into Pleistocene deposits of a small basin to the west of the major faults and volcanoes of the Eastern Rift Valley in Tanzania (Fig. 1). The climate is hot and dry, and the annual rainfall averages 40 to 50 cm per year, as gauged from 1962 to 1969. The climate was probably not greatly different during most of the Pleistocene (Hay, 1963b).

The Rift Valley adjacent to Olduvai Gorge is rich in sodium carbonate-bicarbonate, as reflected in the composition of lakes, spring water, and saline, alkaline soils. Sodium carbonate has been supplied both by weathering of sodic volcanic rocks and by "carbonatite" volcanism. Oldoinyo Lengai, a nephelinite volcano 90 km northeast of the gorge, has repeatedly erupted alkali-carbonate ash over the past 60 years (Dawson, 1962) and the extinct nephelinite volcano, Kerimasi, probably supplied nephelinite and carbonate ash to Bed IVb (Dawson, 1964). The

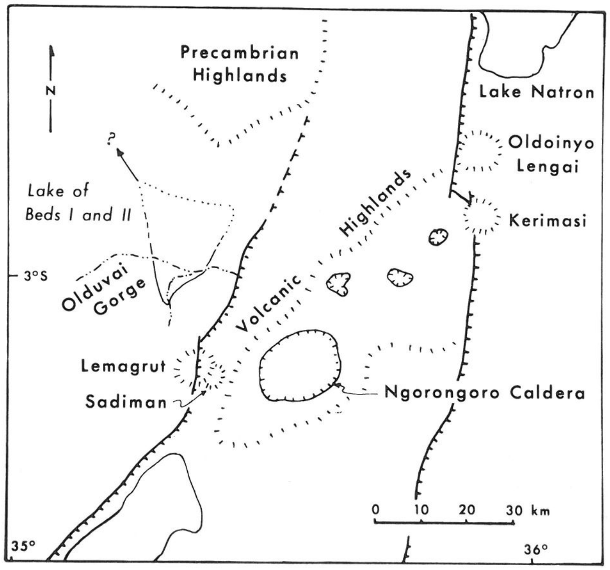

FIG. 1. Map showing major geologic features in the vicinity of Olduvai Gorge. Lake in the Olduvai region is generalized for Beds I and II. If the lake overflowed its Olduvai basin at times of flooding, it probably drained northwest, toward Lake Victoria.

nephelinite volcano, Sadiman, was probably active during the time of Beds I and II.

From the standpoint of paleogeography and volcanism, the Olduvai deposits can be subdivided into three parts. The lower part, comprising Bed I and the lower part of Bed II, contains deposits of a perennial saline, alkaline lake and of marginal terrain and alluvial fans rising southeastward to the volcanic highlands. Claystone is the principal lacustrine sediment, and reworked trachyte tuffs predominate in the alluvial-fan deposits. The distribution of lake- and lake-margin sediments indicates that the northwest-southeast diameter of the lake generally fluctuated between 8.5 and 12.5 km (Fig. 2). Lacustrine sediments are about 30 m thick in the axis of the basin. Tuffs within Bed I give seemingly reliable K-Ar dates of 1.65 to 2.0 m.y., and sedimentation rates based on these dates suggest that the lake was formed about 2.5 m.y. ago and lasted approximately 1.2 m.y. (Hay, 1968).

The middle part of the sequence, deposited after faulting commenced in the Olduvai Basin, comprises the upper part of Bed II, Bed III, and Bed IVa, which have an aggregate thickness of 20 to 40 m (Hay, 1967b). These sediments are largely claystone and were deposited mostly by streams.

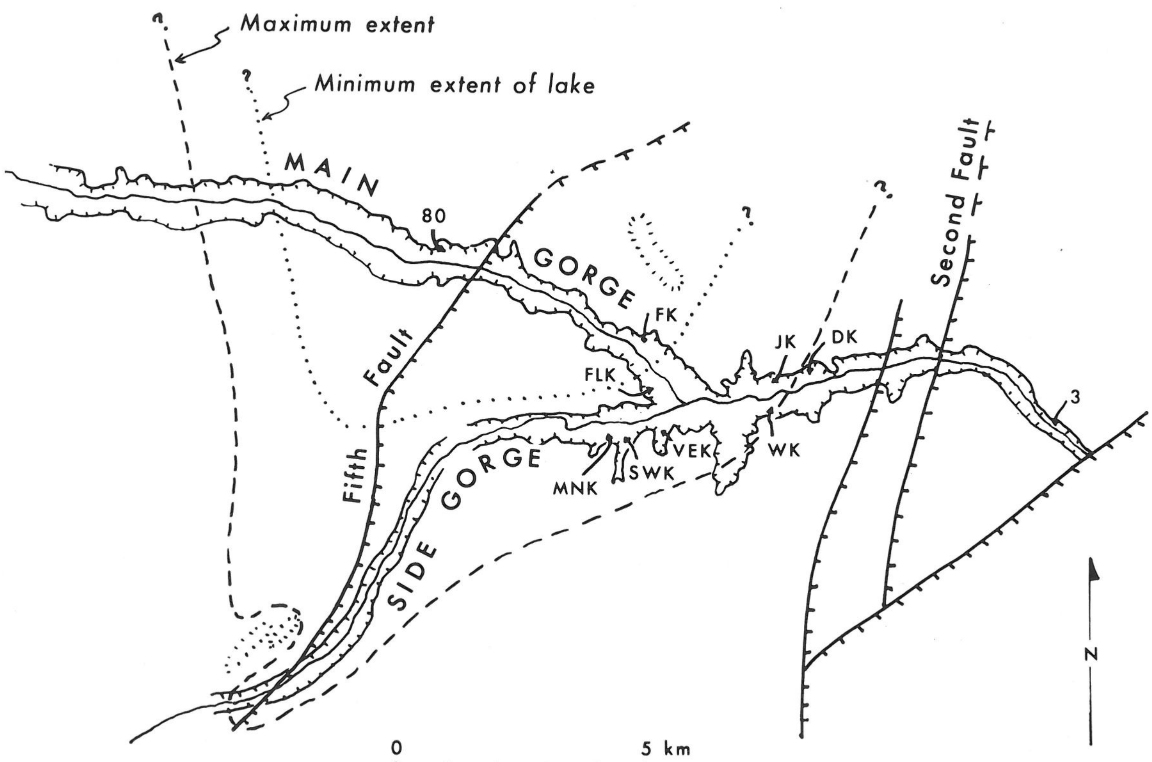

FIG. 2. Map showing Olduvai Gorge and the shorelines along the southern half of the lake during the deposition of Bed 1. Maximum shoreline marks the limit of the lake at the end of deposition of Bed I, about 1.5 m.y. ago; minimum shoreline outlines the lake about 1.6 m.y. ago. The lake fluctuated between approximately the same limits during deposition of the lower part of Bed II. Capital letters (*e.g.*, FLK) mark archeological sites of Leakey (1965) where stratigraphic sections were measured; numbers mark other stratigraphic sections.

This part of the Olduvai sequence spans the period from about 1.3 m.y. to possibly 0.25 m.y. ago, as estimated from fossils and the Acheulian archeologic assemblage of Bed IVa.

The upper part of the sequence was deposited during a period of intermittent faulting, nephelinite volcanism, and erosion of the gorge. It comprises Beds IVb and deposits previously referred to Bed V (Hay, 1963a) but now subdivided into two new formations—the Ndutu and Naisiusiu Beds. Bed IVb is generally conformable on Bed IVa and is unconformably overlain by the Ndutu Beds. All of these formations contain a large proportion of eolian (wind-worked) nephelinite tuffs that were zeolitized by reaction with sodium-carbonate solutions concentrated at the land surface by evapotranspiration (Hay, 1963a). Downstream from the Second Fault, Bed IVb contains a middle unit generally 5–10 m thick that consists largely of claystones resembling those of Bed IVa in lithology and origin. Data from the claystones of Bed IVb are included in this paper; zeolitized nephelinite tuffs are not considered further.

Lake Deposits

Stratigraphy and lithology. Lacustrine deposits form a well-defined lithologic facies 30 m thick within Beds I and II in the central part of the Olduvai Basin (Hay, 1968, Fig. 5). Near the inferred axis of the former lake basin, lacustrine sediments of Bed I total 25 m and those of Bed II about 5–6 m. Lake beds extend about 5 km to the west, where they intergrade with lake-margin sandstones and tuffs. The sequence is downfaulted to the east of the Fifth Fault, which bisects the basin (Fig. 2), and the eastern half of the lacustrine facies of Bed I does not crop out. Lake deposits of Bed II, about 5 m thick, are, however, exposed 3 km southeast of the Fifth Fault, at Site FK (Fig. 2).

The lake beds are about 80 percent claystone, 15 percent tuff, and 5 percent dolomite, limestone, and sandstone. Tuffs are interbedded through the entire sequence but are most abundant in the upper 5 m of Bed I. A single, widespread horizon of chert nodules lies near the middle of the lacustrine sequence of Bed I, and nodules lie at three horizons within the lower 5 m of Bed II in the axial part of the Basin.

1. Claystones. Claystones are generally wax-like, massive, and pale olive to greenish gray. Most of them contain illite and montmorillonite in various proportions, but purely montmorillonitic claystones are common, particularly near the base. A few claystones in the upper part of the facies are almost entirely illitic. Mixed-layer illite-montmorillonite is commonly present but is nowhere the dominant species of clay mineral. Authigenic minerals form substantial proportions of nearly all claystones (Table 1). The most common of these are calcite, dolomite, K-feldspar, zeolites, and altered pyrite. Fluorite is in three samples from Bed II, and gaylussite (?) replaced by calcite

Table 1. Authigenic Minerals in Claystones and Trachytic Tuff of Olduvai Gorge[a]

		Calcite	Dolomite	Pyrite	Jarosite	Fluorite	Quartz	Opal	Kenyaite	Dawsonite	Natrolite	Analcime	Chabazite	Phillipsite	Erionite	Clinoptilolite	Montmorillonite	Illite	K-feldspar
Lake Deposits (Beds I and II)	Claystone	××	××	××	–	×	××	–	–	–	–	××	–	–	×	×	–	–	××
	Trachytic Tuff	××	×	×	×	–	×	–	–	–	–	–	–	××	–	–	–	–	××
Lake-Margin Deposits (Bed II)	Claystone	××	×	–	–	–	×	×	×	–	–	–	×	×	–	××	–	–	–
	Trachytic Tuff	×	–	–	–	–	–	×	–	–	–	–	×	××	–	–	×	–	–
Alluvial Deposits (Beds II, III and IVa)	Claystone	××	×	–	–	–	–	–	–	×	×	××	××	××	–	–	–	××	–
	Trachytic Tuff	×	×	–	–	–	–	–	–	×	×	××	××	××	–	–	–	–	–

[a] × refers to relatively rare minerals, ×× to common minerals, and – to absent minerals.

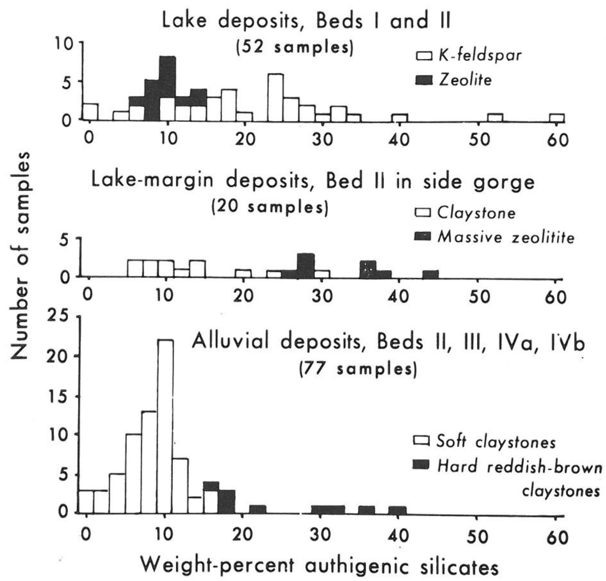

FIG. 3. Histograms showing amounts of authigenic tectosilicate minerals in 141 samples of claystone and 8 of massive zeolitite. Data from four samples of clayey mudflow deposit are included with data for alluvial claystones. K-feldspar and zeolites are shown separately for lacustrine clays; other deposits contain only zeolites.

was noted at a single horizon in Bed I. Most claystones contain a few percent of euhedral calcite that is 0.1 to 2.0 mm long and a few percent or less of altered pyrite. Calcite crystals are reworked and concentrated to form clayey limestones at a few horizons in the upper part of Bed I. Fine-grained dolomite is disseminated through many beds, particularly those lacking calcite crystals, and all gradations exist between claystone and nearly pure dolomite.

A zeolite or K-feldspar was identified in diffractograms of 44 out of 46 claystone samples, collected from the exposed western half of the facies and in all 13 samples collected from Bed II to the east. Amounts of zeolite and K-feldspar for 52 samples are shown in Figure 3; the other seven samples were analyzed before procedures were standardized. An unidentified silicate (?) mineral is in one of the two samples lacking K-feldspar or zeolite. K-feldspar occurs in 37 of the 46 samples from the western half of the facies and two of the 13 samples from the area to the east. The amount of K-feldspar ranges from about 5 to 60 percent, averaging 21 percent (Fig. 3). The three samples with 40 percent or more of K-feldspar are tuffaceous; nearly all the others appear to be lacking tuffaceous matter. The amount of K-feldspar varies erratically in samples collected at 1- to 1.3-m intervals, supplemented by spot samples through the thickness of the facies in Section 80, in the former axial part of the basin (Fig. 4). Analcime is in three samples and clinoptilolite and erionite each in one from the same section. Analcime is in all ten samples collected from Bed II to the east, at FK; and analcime and K-feldspar occur together in two other samples from the eastern part of the facies. A curious feature is the occurrence of either a zeolite or K-feldspar, but not both, in claystones from the central and western parts of the facies. Fluorite was found only in a few samples from Bed II in in the western half of the facies.

2. Tuffs. Tuffs form laterally extensive beds 1–45 cm thick that are white, pale orange, or yellow. They range from fine-grained to lapilli tuff, and most are crystal-vitric or vitric tuffs of original trachyte composition. The remainder are either mafic or a mixture of trachytic and mafic materials. All of the glass in these tuffs is altered. Zeolites and K-feldspar are the principal authigenic silicate minerals; searlesite, montmorillonite, and quartz were noted in some samples. K-feldspar, with or without phillipsite, is the authigenic silicate mineral in most or all of the tuffs less than 2.5 cm thick; phillipsite is the dominant authigenic silicate mineral in most of the thicker, coarser tuffs, some of which contain K-feldspar. Analcime, phillipsite, and chabazite are generally in tuffs that originally contained mafic glass. Some mafic tuffs contain K-feldspar and montmorillonite in addition to zeolites.

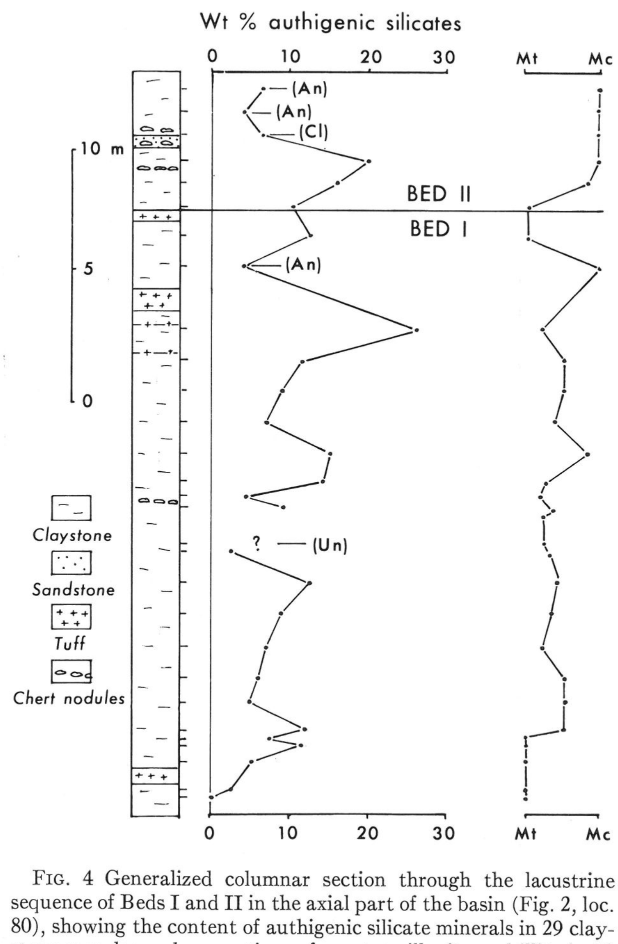

FIG. 4 Generalized columnar section through the lacustrine sequence of Beds I and II in the axial part of the basin (Fig. 2, loc. 80), showing the content of authigenic silicate minerals in 29 claystone samples and proportions of montmorillonite and illite in 30 samples. K-feldspar is the authigenic mineral unless otherwise indicated by (An)—analcime, (Cl)—clinoptilolite, and (Un)—unidentified mineral. Proportions of montmorillonite (Mt) and illite (Mc) are based on relative areas under the (001) peak in diffractograms of unoriented bulk samples.

Nature and occurrence of authigenic minerals

1. K-feldspar. Authigenic K-feldspar is very fine-grained, and in claystones it is in the fraction finer than 2 microns. Its mean refractive index is 1.520, suggesting a pure K-feldspar, and its X-ray pattern is characteristic of the K-feldspar of saline, alkaline lake deposits (Hay and Moiola, 1963; Sheppard and Gude, 1969). It forms overgrowths as much as 5 microns thick on plagioclase in a single sample from Bed I. This is the youngest occurrence of K-feldspar overgrowths of which I am aware.

2. Phillipsite. Phillipsite forms a cement and replaces glass in trachyte tuffs. It generally forms aggregates of anhedral crystals 10 to 50 microns in diameter. Its birefringence is low, and refractive indices generally lie between 1.476 and 1.480. An analyzed sample from a tuff of Bed I is rich in alkalis and has a $Si:Al+Fe^{3+}$ ratio of 2.55 (Hay, 1964, p. 1375).

3. Analcime. Analcime occurs in claystones as fine disseminated crystals not recognizable microscopically. The Si:Al ratio is 2.0 in the analcime of one sample, using the ($\bar{6}39$) *d* and the determinative curve of Sheppard and Gude (1969).

4. Other zeolites. Chabazite, clinoptilolite, and erionite were identified in X-ray patterns and are visible microscopically as fine specks having a low refractive index. No other data were obtained.

5. Montmorillonite. Authigenic montmorillonite is apparently restricted to tuffs containing mafic pyroclastic materials, where it occurs through the matrix and as pseudomorphs after shards. Montmorillonite of the claystones is probably detrital inasmuch as the montmorillonite-rich claystones lack vitroclastic texture and are most common in the lower part of the section, which has the smallest proportion of tuffs.

6. Quartz. Authigenic quartz occurs chiefly as nodules but also as fine disseminated crystals in a sample of claystone forming the matrix for chert nodules. Together with K-feldspar, fine-grained quartz forms a soft, chalklike bleb 1 cm thick within a harder phillipsitic tuff in the upper part of Bed I. Chert nodules are irregular, lobate, or spinose, and they have reticulate surface patterns. Most weigh 20 to 250 g and are 5 to 15 cm long (Hay, 1968).

7. Other minerals. Calcite, dolomite, and pyrite altered to iron oxide are common authigenic minerals. Relatively rare are fluorite, searlesite, jarosite, calcite pseudomorphs after gaylussite (?), molds of bladed trona (?), and an unidentified mineral, probably an aluminosilicate. The unidentified mineral was found in a single claystone sample, where it occurs as moderately birefringent fine-grained aggregates having wavy extinction and N_2 less than 1.500. Its principal spacings are 4.65 Å (1=4), 3.08 Å (1=5), and 2.78 Å (1=10).

Depositional and diagenetic environments. This facies accumulated in a lake, as indicated by (1), a low content of silt and sand, either as beds or within the claystones; (2), even bedding and uniform thickness of tuff beds; (3), even beds of fine-grained dolomite; (4), rarity or absence of desiccation cracks, cross bedding, channeling and rootmarking; (5), absence of fossils other than rare bones of small fish at very few horizons; and (6) lateral gradation or intertonguing to the west, south, and southeast with lake-margin deposits.

This lake was saline, alkaline, and rich in dissolved sodium-bicarbonate. The assemblage of authigenic minerals —particularly K-feldspar, phillipsite, analcime, searlesite, fluorite, and dolomite—strongly suggests a saline, alkaline lake (Hay, 1966), and the chert is of a type known to form only in deposits of sodium-carbonate lakes (Eugster, 1967, 1969; Hay, 1968). Molds of trona (?) and calcite pseudomorphs after gaylussite (?), if correctly identified, prove that there were at least temporarily high concentrations of sodium carbonate. Saline water rich in dissolved sodium carbonate presently seeps from the lake beds into the sides of the gorge, and at least a part of the sodium carbonate was probably trapped in the sediments when they were deposited. Finally, remains of flamingoes have been found at two horizons in lake-margin deposits of Bed I (L. S. B. Leakey, pers. commun., 1967). Flamingoes in East Africa presently live mainly in or near saline, alkaline lakes.

Nature of reactions.

1. Zeolites and montmorillonite in tuffs. Trachytic glass reacted to form phillipsite in saline, alkaline water, probably at burial depths of a few meters or less (Hay, 1964). Although glass is totally dissolved in altering to phillipsite, hydration is the principal chemical change (Hay, 1963a):

(a) $$\text{trachyte glass} + H_2O \rightarrow \text{phillipsite}$$

Montmorillonite in the mafic tuffs probably reflects the high content of Mg and Fe in mafic glass; chabazite and analcime in addition to phillipsite probably reflect Si:Al and K:Na ratios lower than those of trachyte glass. The reaction can be written:

(b) $$\text{mafic glass} + H_2O + Na^+ + K^+(+H^+) \rightarrow \text{alkali zeolites} + \text{montmorillonite} + Ca^{2+}$$

where H^+ is derived from hydrolysis of aqueous CO_2 (Jones, 1966), and Ca^{2+} is precipitated from alkaline waters as carbonate.

2. Zeolites in claystones. By analogy with modern sodium-carbonate lakes such as Natron in Tanzania (Hay, 1966), zeolites of the claystones formed rapidly in the surface layers of mud. It is difficult to prove whether the analcime was precipitated directly from lake water or formed by reaction of detrital clay. However, analcime in nonlacustrine claystones of Olduvai Gorge almost certainly formed from detrital clay, and thus chemical precipitation is not required to account for zeolites of the lacustrine claystones. Another problem now arises, for the amount of zeolite (and K-feldspar) varies independently of the clay-mineral composition (Fig. 4) suggesting that neither illite nor montmorillonite was altered selectively. Either the finer-grained particles of detrital clay reacted to form zeolites, regardless of their mineralogy, or an amor-

phous fraction of the detrital muds was the reactant. In the present state of uncertainty, the reactions that yielded zeolites in the nontuffaceous claystones are generalized as follows:

(c) clay (amorphous?) + Na^+ (+SiO_2?) → analcime + H^+

(d) clay (amorphous?) + Na^+ + K^+ + SiO_2 → clinoptilolite or erionite + H^+

3. K-feldspar. K-feldspar of the lake beds most likely formed by reaction of early-formed zeolites. The K-feldspar of tuffs probably formed by reaction of phillipsite with interstitial fluids, for although replacement textures were not observed in Olduvai tuffs, K-feldspar visibly replaces the coarser zeolites including phillipsite in other lake deposits (Iijima and Hay, 1968; Sheppard and Gude, 1968, 1969). The stratigraphic succession of phillipsite and K-feldspar in altered rhyolite tuffs of Pleistocene age in Searles Lake, California, is circumstantial evidence strongly suggesting that phillipsite was the initial reaction product of alkali-rich glass, and was gradually altered to K-feldspar (Hay, 1966, p. 95). The uppermost tuffs in drill cores from Searles Lake are phillipsite, the lowermost K-feldspar, and a tuff recently obtained from an intermediate level, near the top of the Mixed Layer, is a mixture of K-feldspar and phillipsite. It should be emphasized that nowhere in saline-lake deposits has authigenic K-feldspar been observed in contact with unaltered glass. Zeolites nucleate and grow much more rapidly than alkali feldspars at low temperatures, thus explaining why trachytic glass, rapidly dissolving in a highly alkaline solution, yielded phillipsite rather than K-feldspar, the more stable phase. The distribution of K-feldspar and phillipsite in tuffs of Searles Lake suggests that 250,000 years or more may be required to convert the phillipsite of a tuff to K-feldspar. The phillipsite-K-feldspar reaction can be written as follows, using analyzed phillipsite from Bed I (Hay, 1964) and neglecting small amounts of Fe, Ca and Mg.

(e) $\underset{\text{phillipsite}}{Na_{0.55}K_{.45}AlSi_{2.7}O_{7.4}\cdot 2.3H_2O} + 0.3SiO_2 + 0.55K \rightarrow KAlSi_3O_8 + 0.55Na^+ + 2.3H_2O$

K-feldspar may have formed selectively in the thinner, finer-grained tuffs either because of their finer grain size and greater effective surface area exposed to reaction, or because there was not sufficient SiO_2 or K^+ available in the interstitial water adjacent to the thicker tuffs in order to convert completely their phillipsite to K-feldspar.

K-feldspar in the nontuffaceous claystones very likely formed principally from analcime. It is difficult otherwise to account for the mutually exclusive occurrence of zeolites (principally analcime) and K-feldspar in nearly all claystones. Moreover, K-feldspar can be observed to replace analcime in the Green River Formation (Iijima and Hay, 1968), and replacement can be inferred in the drill cores of Searles Lake, where the content of analcime decreases irregularly and that of K-feldspar increases downward (Hay and Moiola, 1963; Hay, 1966, Fig. 2). Using the Si:Al ratio of 2.0 indicated by the ($\bar{6}39$) *d* spacing of analcime, this reaction is

(f) $NaAlSi_2O_6\cdot H_2O + SiO_2 + K^+ \rightarrow KAlSi_3O_8 + Na^+ + H_2O$

As the reaction is partly one of dehydration, it is favored by high salinity as well as by a high $K^+:Na^+$ ratio, thus accounting for the dominance of K-feldspar in the axial part of the basin and of analcime in sediments deposited nearer the southeast margin, where the lake was diluted by fresh-water streams. In view of the large amount of K-feldspar, averaging about 20 percent, much SiO_2 and K^+ must have been available. In order to form 20 percent authigenic K-feldspar from analcime, for example, 4.3 percent additional SiO_2 and 1.7 percent K_2O are required. Reactions of clay minerals may have supplied the SiO_2 and K^+, but the lake beds provide no evidence of such a reaction in the form of a correlation between clay-mineral composition and amount of K-feldspar. It should be emphasized that the source of SiO_2 and K^+ required to balance zeolite-feldspar reactions in other saline-lake deposits is similarly enigmatic (Hay, 1966, p. 100; Sheppard and Gude, 1969, p. 32). The problem concerning claystones is reduced but not eliminated by postulating that K-feldspar formed by reaction of clay minerals rather than analcime.

4. Quartz. Chert nodules and quartz disseminated in claystones formed from one or more sodium-silicate minerals, as discussed later in this paper. The single occurrence of quartz associated with K-feldspar in a phillipsitic tuff may also involve a sodium-silicate precursor, although evidence is lacking.

Lake-Margin Deposits

Stratigraphy and lithology. Lake-margin deposits constitute a highly variable assemblage of sediments that lie between the lake beds and stratigraphically equivalent alluvial deposits of Beds I and II. Marginal deposits are exposed to the south, southeast, and west of the lacustrine facies, but only those of the southeast will be described here. Lake-margin deposits of Bed I have a thickness of 9 to 15 m and a lateral extent of 2.6 to 5 km, as measured along the Main Gorge. Lake-margin deposits of Bed II, stratigraphically equivalent to the lake beds described above are 6 to 12 m thick and have a width of 2.6 km.

1. Bed I. Lake-margin deposits of Bed I to the southeast of equivalent lake beds are about 50 percent tuff and 50 percent claystone. Claystones are montmorillonitic and commonly have a few percent of sand-size volcanic detritus and scattered pumice fragments. Pumice is locally zeolitic but elsewhere is fresh; authigenic silicate minerals were not detected in diffractograms of nontuffaceous samples.

Tuffs are trachytic and generally 10 cm to 2 m thick. Some are laminated, evenly bedded, and were deposited in quiet water; others are massive, undulating, rootmarked, and were deposited on land. The marker tuff at the top of Bed I commonly comprises a lower, laminated part 50 to 100 cm thick and an upper massive, rootmarked part 25 to 50 cm thick. The marker tuff is zeolitic throughout its western exposures and is generally fresh within the lake-margin facies farther east. In the transitional zone, the lower, laminated part is characteristically zeolitic whereas the upper, massive and rootmarked part is commonly unaltered. The pattern of alteration is roughly the same but is much less consistent in the other tuffs. Phillipsite is generally the only zeolite in altered tuffs, which commonly contain subordinate amounts of authigenic montmorillonite. Chabazite is also in a few tuffs.

2. Bed II in the Main Gorge. Lake-margin deposits of Bed II in the Main Gorge are about 80 percent claystone, 10 percent sandstone and conglomerate, and 10 percent tuff. A few beds of clayey "diatomite" are present at Site VEK (Fig. 2). Claystones are yellow or gray, commonly wax-like, and generally contain a few percent volcanic sand, principally anorthoclase. Paleosols are common within the claystones in the eastern part of the facies but are rare toward the west. Montmorillonite either predominates over illite or is the only clay mineral present. Some of the claystones in the eastern part of the facies contain a few percent of pumice fragments. About half of the claystones examined microscopically contain small amounts of biogenic opal (diatoms; tests of silicoflagellates (?); and phytoliths, or plant opal, mostly from grasses). Silicified plant debris and rootcasts are in some of the claystones with diatoms and opal phytoliths. About one-third of the claystones contain 5 to 10 percent fine disseminated clinoptilolite, chabazite, or phillipsite. Only very rarely do both biogenic opal and zeolites occur in the same beds.

A few conspicuous beds, 30 to 150 cm thick, of cream-colored, porous tuffaceous claystone contain substantial amounts of biogenic opal. These are massive, rootmarked deposits consisting of 10 to 20 percent tuffaceous material, 5 to 25 percent biogenic opal, and 60 to 80 percent montmorillonite. Trachytic glass is rare, but mafic glass, fresh or altered to montmorillonite, forms as much as 10 percent of a sample. Diatoms and phytoliths are commonly corroded, and there may be a few percent or less of a zeolite, principally erionite.

The clayey "diatomities" are soft, porous, cream-colored beds consisting of biogenic opal (principally diatoms and phytoliths) and montmorillonite in various proportions. The "diatomites" are massive, rootmarked, and were evidently exposed above the level of the lake. Opal of the "diatomites" gives a broad hump centering at 4.0 Å, indicating that the silica is amorphous. A chemically analyzed "diatomite" (Table 2, no. 14) has 74.0 percent silica.

Tuffs contain minerals, glass, and rock fragments from

TABLE 2. CHEMICAL ANALYSES OF SAMPLES FROM OLDUVAI GORGE[a]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	40.42	43.14	33.07	30.86	52.58	48.49	46.4	43.2	40.4	49.4	49.5	64.9	56.1	74.0	51.9
Al_2O_3	19.53	17.76	19.78	15.45	8.51	13.38	13.7	18.7	16.6	14.2	12.6	11.6	10.5	4.6	8.0
TiO_2	3.07	2.45	2.87	4.02	2.36	1.86	6.4	6.2	7.5	2.4	2.2	0.4	1.7	0.8	0.7
Fe_2O_3	15.03	12.42	15.71	24.04	8.64	9.84	10.2	10.1	12.3	12.5	12.5	1.7	6.4	3.2	6.0
FeO	0.53	0.29	2.98	tr.	0.67	0.30	—	—	—	—	—	—	—	—	—
MnO	0.23	0.29	0.36	0.49	0.06	0.07	0.3	0.2	0.2	0.2	0.2	0.03	0.08	0.04	0.1
MgO	0.93	1.16	1.26	2.35	8.11	3.84	3.2	1.5	2.5	2.5	3.0	1.2	3.5	2.2	12.5
CaO	1.49	1.63	0.80	1.99	0.22	1.74	0.7	1.9	2.3	1.4	0.7	0.4	1.9	0.6	0.7
Na_2O	4.26	5.56	2.62	1.24	2.28	1.47	2.8	6.7	2.9	1.8	2.4	3.6	4.7	2.0	3.1
K_2O	2.37	4.31	1.97	3.92	2.38	3.73	4.1	3.1	5.4	3.5	3.4	4.6	3.0	0.9	2.6
P_2O_5	0.29	0.25	0.66	0.79	0.05	0.24									
CO_2	0.58	0.71	0.60	0.90	0.03	0.82									
H_2O^+	6.31	5.29	8.97	7.42	5.55	5.36									
H_2O^-	4.65	4.26	5.59	4.94	7.65	7.87									
loss on ignition			17.33	14.55	14.37	15.61	12.1	8.4	9.8	12.3	13.7	11.6	11.5	11.7	14.4
Total	99.69	99.52	99.41	99.70	100.23	100.57	99.9	100.0	99.9	100.2	100.2	100.0	100.2	100.0	100.0

[a] Analyses 1–6 are by J. Muysson using wet-chemical methods; analyses 7–14 are by R. N. Jack, using X-ray fluoresence, and all iron is calculated as Fe_2O_3.
[b] Loss on ignition was used in totals for analyses 3–6, instead of reported CO_2, H_2O^+ and H_2O^- contents.

EXPLANATION FOR TABLE 2

1. Bulk sample of mudflow deposit in Bed II, from lower part of alteration profile (Fig. 10). Sample is yellowish brown and contains 9% phillipsite, 4% analcime, and a trace of dawsonite as estimated from diffractograms.
2. Bulk sample of mudflow deposit from upper part of alteration profile (Fig. 10). Sample is reddish-brown and contains 19% phillipsite and 9% analcime.
3. Clay fraction finer than 2 microns from mudflow sample (1). Clay minerals are montmorillonite with interlayered illite (dominant) and halloysite(?) (minor).
4. Clay fraction finer than 2 microns from mudflow sample (2). Clay minerals are illite with interlayered montmorillonite (dominant) and halloysite(?) (trace).
5. Clay fraction finer than 2 microns of montmorillonite from clinoptilolite-bearing claystone of Bed II in the Main Gorge. The structural formula is $K_{0.44}Na_{0.65}Ca_{0.03}Mg_?(Al_{1.18}Ti_{0.26}Fe^{3+}_{0.95}Fe^{2+}_{0.08}Mg_{1.77})(Al_{0.29}Si_{7.71})O_{20}(OH)_4$.
6. Clay fraction finer than 2 microns of illite with interlayered montmorillonite from claystone of Bed IVa to the west of the Fifth Fault.
7. Average of 3 analyses of gray, zeolite-bearing claystones from Beds II and IVa. Claystones contain 2–3% analcime or chabazite. Sand fractions include detritus from both volcanic and basement rocks.
8. Bulk sample of hard, reddish-brown claystone of Bed III containing 22% analcime and 8% phillipsite. Sand fraction is volcanic detritus.
9. Bulk sample of soft, reddish-brown claystone of Bed IVb containing 9% analcime. Sand fraction is volcanic detritus.
10. Clay fraction finer than 2 microns from reddish-brown, zeolitic claystone of Bed III containing volcanic detritus. Clay mineral is poorly crystalline illite with little interlayered montmorillonite.
11. Clay fraction finer than 2 microns from reddish-brown zeolitic claystone of Bed IVa that contains detritus of basement origin. Clay mineral is poorly crystalline illite with interlayered montmorillonite.
12. Clinoptilolite of thin layer associated with chert nodules in Bed II at SWK (Fig. 5). Its structural formula is $(Na_{3.1}K_{2.6}Mg_{0.78}Ca_{0.02})(Fe^{3+}_{0.57}Al_{6.1}Si_{29.1})O_{72}\cdot 17H_2O$
13. Massive impure zeolitite from bed beneath the main chert horizon at site FC, which lies in the Side Gorge north of MNK. Zeolitite contains 33% clinoptilolite, 10% erionite, and several percent volcanic sand, principally anorthoclase; most of the remainder is clay.
14. "Diatomite" from Bed II at site VEK (Fig. 6). Analyzed "diatomite" contains biogenic opal, montmorillonite, and a minor amount of volcanic sand.
15. Average of two analyses of montmorillonite finer than 2 microns from Bed I near Site FLK.

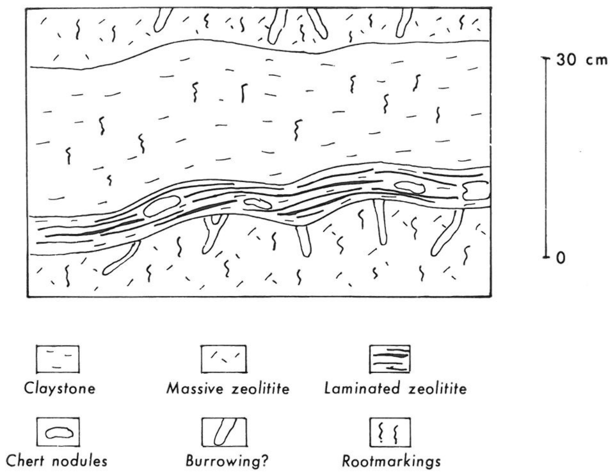

FIG. 5. Zeolitites, claystone and chert nodules at SWK, 4 m above the base of Bed II. Massive claystone above laminated zeolitite contains veins, rootcasts, and very small disseminated crystals of clinoptilolite.

trachytic, nephelinitic, and trachyandesitic (?) erruptions. A few are laminated and probably lacustrine; most are massive, rootmarked, and were deposited on land. Laminated tuffs are zeolitized, and massive tuffs may either be fresh or partly zeolitized. Phillipsite is the dominant zeolite, and authigenic montmorillonite is a major constituent of tuffs with mafic glass.

3. Bed II in the Side Gorge. The lower 4.5 to 5.5 m of Bed II in the Side Gorge is a zeolite-rich assemblage of sediments unlike any other in Olduvai Gorge. This sequence, exposed at SWK and MNK (Fig. 2), is about 50 percent zeolitic limestone, 40 percent zeolitite, 10 percent claystone, and less than 1 percent sandstone. The term *zeolitite* is used for beds other than altered tuffs in which zeolites are the principal single component. Bed II contains both massive and laminated zeolitites. By far the most abundant are massive, rootmarked, cream-colored, and forms beds 25 to 150 cm thick. These massive zeolitites are variable mixtures of zeolites (25 to 50 percent), volcanic detritus (10 to 20 percent) of sand size, and sand-sized clay pellets (20 to 30 percent). Calcite or dolomite may be present, and all gradations exist between zeolitites and zeolitic limestone or dolomite. Altered glass shards form 2 to 10 percent of most zeolitites. Zeolite rootcasts are abundant in most beds, and burrowings (?) 1 to 2 cm in diameter are common in a few (Fig. 5). Wood fragments and ostracod tests are replaced by zeolites in many of the samples examined microscopically. Clinoptilolite or phillipsite may be the only zeolite in a bed, but two or more zeolites may occur together. The most common assemblages are clinoptilolite-erionite, clinoptilolite-erionite-phillipsite, and phillipsite-erionite. The zeolite mineralogy of limestones is about the same as in the massive zeolitites. A chemically analyzed zeolitite (Table 2, no. 13) has a high content of alkalis and a Si:Al ratio of 4.5.

Thin zeolitite layers were found at two horizons at SWK. Four meters above the base of Bed II are white zeolitite layers as much as 5 mm thick interlayered with zeolitic claystone through a thickness of 5 to 8 cm over an exposed lateral distance of 15 m. Clinoptilolite and less commonly erionite are the zeolites of this laminated sequence, which also contains chert nodules 2 to 8 cm long (Fig. 5). Some of the zeolitite laminae are nearly pure clinoptilolite, one sample of which (Table 2, no. 12) yielded only 0.03 weight percent detrital mineral grains using heavy liquids. Approximately 1 m higher is a 2-cm bed of clinoptilolite-bearing clayey zeolitite with abundant chert nodules.

Claystones are greenish-gray to light olive gray; they have little sand and may either be wax-like or have an earthly lustre. Rootmarkings are uncommon, and paleosols are absent. All twelve samples contain zeolites, principally clinoptilolite, which ranges from about 6 to 30 percent and averages 13 percent (Fig. 3). The zeolites are generally fine-grained and disseminated but may also form veinlets or rootcasts. Illite is the principal clay mineral, but montmorillonite is commonly present and predominates in a few samples.

Chert nodules are widespread in the Side Gorge 4 m above the base of Bed II where they lie in a matrix of zeolitite, zeolite-rich claystone, or zeolitic limestone. At Site SWK, nodules also occur about 1 m and 5 m above the base of Bed II. Those of the lower horizon are dispersed through a 30-cm thickness of claystone; those of the upper horizon are embedded in a 2-cm zeolitite. Clinoptilolite is generally the only zeolite in beds containing chert nodules.

Nature and occurrence of authigenic minerals

1. Zeolites. Zeolites are abundant in the altered tuffs of Beds I and II and are in many of the nontuffaceous claystones of Bed II. They are the principal minerals through about 40 percent of the lower 4.5 to 5.5 m of Bed II in the Side Gorge. Phillipsite is the principal zeolite in most lake-margin tuffs. Clinoptilolite is most abundant in claystones of the Side Gorge, and clinoptilolite, phillipsite, and chabazite may be about equally common in claystones of Bed II in the Main Gorge. Either phillipsite or clinoptilolite can be the only zeolite in massive zeolitites of the Side Gorge, but clinoptilolite and erionite commonly occur together, with or without phillipsite. Clinoptilolite forms nearly pure layers 1 to 5 mm thick at one locality. A sample of relatively pure clinoptilolite, chemically analyzed by X-ray fluorescence, is similar except for a slightly higher content of iron, to clinoptilolites formed from rhyolitic glass in saline-lake deposits (Sheppard and Gude, 1969). Physical properties were not measured on zeolites of the lake-margin deposits.

2. Montmorillonite. Authigenic montmorillonite commonly replaces mafic shards and pumice in the tuffs and claystones of Bed II. Mafic glass is locally altered to orange or reddish-brown palagonite, which probably contains montmorillonite. Montmorillonite occurs with ze-

olites in trachytic tuffs, and itcan be the dominant alteration product of finely tubular, highly porous trachytic pumice.

3. Opal. Opaline silica commonly replaces plant debris and roots in claystones of Bed II. The opalized materials are soft, white, and give a low diffractometer hump centering at about 4.0 Å. Nodules and discontinuous layers of hard clayey opal lie within soft montmorillonitic claystones interbedded with clayey diatomites about 2 m above the base of Bed II at VEK (Fig. 6). The hard opal gives a strong, well-defined diffractometer peak at 4.09 Å, the principal peak of alpha cristobalite. Hard opal and opal-rich claystone are cut by veins of kenyaite, with or without chalcedony.

4. Kenyaite. Kenyaite has been found at a single locality within Bed II (Fig. 6), where it forms veinlets and sponge-like intersecting concentrations of veinlets in clayey opal and opal-cemented claystone. Veinlets are generally 1–3 mm thick, 1–2 cm long, have walls of spherulitic kenyaite, and are open in the center. Spherulites are 0.1 to 0.2 mm in diameter and consist of acicular crystals arranged radially. Chalcedony partly replaces kenyaite in some of the spherulites, and the fibrous structure of the chalcedony parallels the radial structure of kenyaite.

5. Quartz. Authigenic quartz is present as chert nodules, within the soft rinds of nodules, and as a chalcedonic replacement of kenyaite. Three-quarters or more of the nodules have reticulate surface textures, and some of them have soft white rinds 1–3 mm thick. Dense chert of the nodule interiors is finely crystalline quartz; the soft rinds are a mixture of cryptocrystalline quartz and clinoptilolite.

6. Unidentified silica (?) phase. An unidentified silica (or silicate) phase with 15 to 30 percent of intergrown clinoptilolite forms soft white rinds around the chert nodules of the uppermost horizon at SWK. The material forms fine-grained aggregates having the textures of fine-grained chert and chalcedony. Its birefringence is slightly less than that of quartz, and the minimum and maximum refractive indices are approximately 1.522 and 1.528, respectively. Its spacings are 4.40 Å (I=25), 3.34 Å (I=100), 3.11 Å (I=20), and 2.64 Å (I=10). The 3.34 Å peak is broader than that of quartz, and the 4.26 Å peak of quartz is lacking.

7. Other minerals. Authigenic calcite is ubiquitous. It forms beds and occurs as concretions, veins, euhedral crystals, oolites, pore-filling cement, and replacements. Dolomite is present in many samples from the Side Gorge, and a few beds are chiefly dolomite. Gypsum rosettes ("desert roses") replaced by calcite have been found at two localities within Bed I.

Depositional and diagenetic environments. The lake-margin facies of Bed I contains abundant evidence that the terrain was alternately flooded by the lake and exposed to the air. Pelecypods and fresh-water gastropods have been found in a few places, and remains of crocodiles and fish are widespread. There are remains of shore birds other than

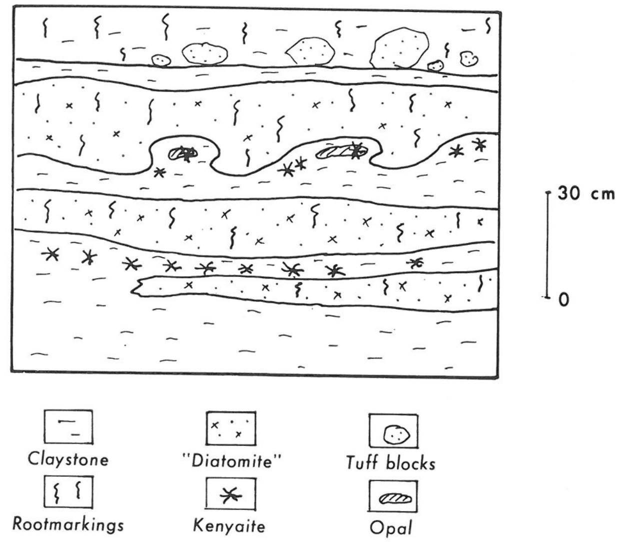

FIG. 6. Kenyaite and opal in claystone interbedded with clayey "diatomite" at site VEK, 2 m above the base of Bed II. The claystone with tuff blocks is tuffaceous and rich in biogenic opal.

flamingoes, and the semiaquatic mammals include reedbuck, waterbuck, hippopotamus, etc. (Leakey, 1965). There is equally convincing evidence for dry land at other horizons: paleosols, hominid occupation sites, and remains of horses, gazelles and rodents.

Lake-margin deposits of Bed II in the Main Gorge accumulated in an environment much like that of Bed I in the same area. Fossilized remains of aquatic or paludal types include gastropods, ostracods, fish, diatoms, crocodiles, and *Deinotherium*. Oolitic sandstones with concentrations of heavy minerals indicate wave agitation in shallow lake water. Evidence for dry land includes paleosols; finely textured rootmarkings, probably of grass; hominid occupation sites; and stream channels as much as 4.5 m deep, now filled by conglomerates.

The lake-margin deposits of Bed II in the Side Gorge contain a higher proportion of lacustrine sediments than do equivalent beds of the Main Gorge. The principal fossils are ostracods, fish bones, rootcasts of reeds(?), and plant debris. The claystones contain little sand, and paleosols are lacking. There is, however, good archeological evidence that the principal chert horizon was exposed widely above lake level, possibly for an appreciable period of time. Stone tools made of chert are scattered through the principal chert-bearing stratum, and a "workshop site" developed on the stratum was recently excavated, yielding many thousands of chert artifacts. Only at SWK does this horizon lack evidence of exposure at the surface.

Lake water flooding the marginal terrain probably ranged from fresh to saline, with highest salinities toward the west, nearer the central part of the lake. This is documented by the distribution of fossils at one horizon in Bed I, where flamingo remains are present in the westernmost exposures, and varied mammal fossils and *Papyrus*(?) rhizomes have been found at DK, to the east. The eastward decrease in zeolitic alteration of tuffs in Bed I very likely reflects the same pattern of salinity and pH. By analogy with present-day desert lakes, the mud flats exposed by a drop in lake level very likely contained saline pore fluid and were locally coated with efflorescent sodium carbonate. The gypsum rosettes replaced by calcite are evidence that Ca^{2+} and SO_4^{2-} were among the ions concentrated within the surface layers of mud.

The lower 4.5 to 5.5 m of Bed II in the Side Gorge may have been deposited in rather highly saline, alkaline lake water and on saline mudflats. Remains of mammals and vertebrates, common in equivalent deposits of the Main Gorge, are absent or rare here, and zeolites and chert are unusually abundant.

Nature of reactions

1. Zeolites and montmorillonite in tuffs. Trachytic glass reacted with alkaline solutions to form zeolites, principally phillipsite, and montmorillonite. Lacustrine tuffs were probably altered by lake water, and landlaid tuffs may have been zeolitized either by lake water saturating the tuffs during a period of flooding or by reaction with sodium-carbonate solutions concentrated at the land surface by evapotranspiration during exposure to air (Hay, 1963a). Montmorillonite may reflect a lower pH and salinity, and possibly a higher Mg^{2+} activity, than in the central part of the basin, where phillipsite alone is the characteristic reaction product.

2. Zeolites in claystones. Zeolites in nontuffaceous claystones of the lake-margin facies may have formed by the reaction of amorphous(?) detrital clay with an alkaline sodium-carbonate solution (reactions c and d).

Diatoms also seem a probable reactant on the basis that most claystones contain either a zeolite or fine-grained biogenic opal, but not both. The solution of diatoms and opal phytoliths could account for the common occurrence of the siliceous zeolite clinoptilolite in claystones of the lake-margin facies. A sodium-silicate mineral or aluminosilicate gel may have been an additional reactant in some of the claystones richest in clinoptilolite. This possibility is discussed more fully below.

3. Massive zeolitites. Either an authigenic aluminosilicate gel or detrital amorphous clay seems the most likely precursor for massive zeolitites of the Side Gorge. The amount of volcanic glass originally present was far too small to account for the zeolites, and reaction of clay minerals in place seems unlikely, as detrital clay pellets embedded in a zeolite matrix show no petrographic evidence of solution or alteration, and only rarely of replacement by calcite. Little Magadi, Kenya, provides a modern example of aluminosilicate gels that could readily yield zeolites in an alkaline environment (Eugster and Jones, 1968). The gels, which have Si:Al ratios of 1.6 to 3.8. are deposited by alkaline hot springs near the lake margin and are periodically washed into the lake. A zeolite could be formed by crystallization of a gel:

$$\text{(g)} \qquad \text{Al}=\text{Si gel} \rightarrow \text{alkali zeolite} + H_2O$$

Detrital amorphous clay, *e.g.*, allophane, is a possible alternative reactant, although additional silica would be required to raise the Si:Al ratio sufficiently high to form clinoptilolite (reaction d). A basic difficulty here is that the amorphous clay fraction would have to be separated, physically or chemically, from the clay minerals of a detrital mud and concentrated into beds. I do not know of any mudflat mechanism that could effect such a separation.

4. Laminated zeolites. Either of two origins seems possible for the laminated, nearly pure zeolitites at SWK: (a) crystallization of aluminosilicate gel (reaction g), or (b) reaction of a sodium-silicate mineral such as magadiite. Chert nodules in the laminated sequence seem to favor reaction of a sodium-silicate mineral, as they indicate that a sodium-silicate mineral was originally present in the laminated sequence. In the field, the laminated zeolitite-claystone sequence with chert nodules strikingly resembles laminated magadiite with chert at Lake Magadi (Eugster, 1967, 1969). To convert magadiite to clinoptilolite requires the addition of Al and an alkali ion, as idealized below using Na^+:

$$\text{(h)} \quad \underset{\text{magadiite}}{NaSi_7O_{13}(OH)_3 \cdot 3H_2O} + H^+ + 0.4Na^+ + 1.4Al(OH)_4 \rightarrow \underset{\text{clinoptilolite}}{1.4NaAlSi_5O_{12} \cdot 4H_2O} + 2.2H_2O$$

A source of Al is not evident, although dawsonite ($NaAl(OH)_2CO_3$) spherulites and veinlets in non-lacustrine deposits of Olduvai Gorge prove that Al can be highly mobile in alkaline environments. The clinoptilolite commonly intergrown with cryptocrystalline quartz rinds of chert nodules I interpret as forming by addition of Al to a sodium-silicate mineral (reaction h). In conclusion, these facts do not eliminate the possibility that the laminated clinoptilolite and associated chert formed from laminated gels containing masses of magadiite.

5. Opal. Fine particles of biogenic opal were dissolved to supply the silica of authigenic opal. As evidence, most of the diatoms in lake-margin deposits are corroded, and layers and nodules of opal occur only in claystones interbedded with "diatomites" (Fig. 6). Opal in the "diatomites" is amorphous, whereas that of nodules gives a diffractometer pattern of alpha cristobalite, indicating:

$$\text{(i)} \qquad SiO_2 \text{ (amorphous)} \rightarrow SiO_2 \text{ (cristobalite)} + H_2O$$

6. Kenyaite. The kenyaite was precipitated in fractures, suggesting:

$$\text{(j)} \quad Na^+ + OH^- + 11SiO_2 + 4.5H_2O \rightarrow \underset{\text{kenyaite}}{NaSi_{11}O_{20.5}(OH)_4 \cdot 3H_2O}$$

Soluble silica was readily available in the nearby porous "diatomites" (Table 2, no. 14), and Na^+ and OH^- were probably provided by the lake water.

7. Quartz. The chert nodules have all the characteristics of chert formed from a sodium-silicate precursor (Hay,

1968), and chalcedony has clearly formed from kenyaite at VEK (Fig. 6). The chemical basis for converting sodium-silicate minerals to quartz is unclear, and alternatives are discussed below. Eugster (1969) stresses the importance of $Na^+:H^+$ ratio and has suggested leaching of sodium by dilute waters (rainfall, etc.) as the conversion mechanism:

(k) $$\underset{\text{magadiite}}{NaSi_7O_{13}(OH)_3 \cdot 3H_2O} + H^+ \rightarrow 7SiO_2 + Na^+ + 4H_2O$$

Percolating waters or intermittent wetting and drying have clearly favored the conversion of magadiite in the High Magadi Beds, for layers of chert above the present lake grade abruptly into magadiite beds at lake level. However, for most of the year the fluid in the surface layers of rock and soil is probably highly saline and alkaline, as indicated by efflorescent sodium carbonate (*e.g.*, Eugster, 1969, Fig. 1). Leaching by dilute solutions cannot apply to the formation of quartz in the Evaporite Series[1] where penetrated by Drill Core B (see Hay, 1968). Here magadiite, kenyaite, or makatite ($NaSi_2O_3(OH)_3$ H_2O) is present through most of the drill core between depths of 14 and 29 m (Sheppard and others, in press). Authigenic quartz first appears at a depth of 32.6 m as veinlets of small crystals in clayey trona, and chert is interbedded with trona at depths of 41–47.4 m. The quartz associated with trona has formed from a precursor in continuous contact with a brine. No samples were obtained between 29 and 32.6 m, so the nature of the transition zone is unknown.

A decrease in the activity of silica should cause sodium-silicate minerals to alter to quartz, and this mechanism may have been important in forming the cherts of Lake Magadi and Olduvai Gorge. This can be understood from the magadiite-silica equilibrium diagram (Fig. 7), based on the solubility of magadiite in distilled water (Bricker, 1969), Figure 7, taken from Eugster (1969, Fig. 19), shows the boundaries for magadiite-amorphous silica (lower line) and magadiite-quartz (upper line). Results for kenyaite are similar although the kenyaite-quartz boundary lies above that for magadiite-quartz in Figure 7. It should be noted that these equilibrium boundaries are given as straight lines whereas they are probably curved at a pH above 9, where silica exists in solution as several species. However, using the lines as plotted, the brines of Lake Magadi are undersaturated with respect to amorphous silica but supersaturated with respect to quartz. With regard to the kenyaite-quartz equilibrium they are even more supersaturated with respect to quartz.

Evidence that kenyaite and magadiite have altered directly to quartz without an intermediate stage of amorphous silica includes: (1) thin sections from both surface samples and drill core show quartz in direct contact with sodium silicate; (2) in the drill core, quartz increases and sodium silicates decrease in amount with depth, while no amorphous silica was found in insoluble residues from any

[1] The base of the Evaporite Series is taken at 47.4 m on the basis of a lithologic break rather than at a depth of 37.4 m on the basis of presumed correlation with surface exposures (Eugster, 1969).

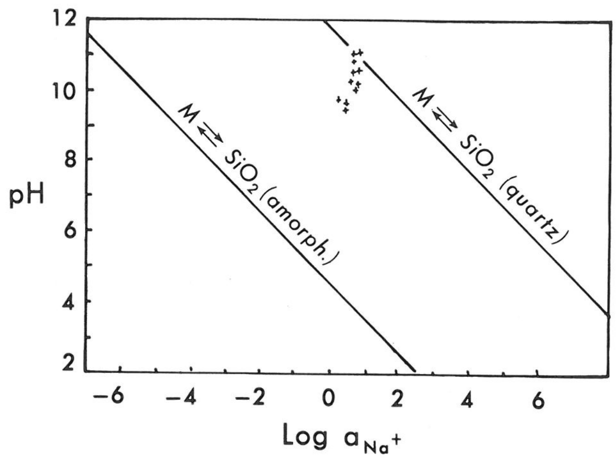

FIG. 7. Conversion boundaries for magadiite (M), SiO_2 (amorphous), and SiO_2 (quartz) in terms of pH and a_{Na^+}, taken from Eugster (1969). Boundaries are drawn for $a_{H_2O}=1$. Crosses represent Magadi brines. Magadiite is stable on the right-hand side of both boundary lines.

level. This indicates that the magadiite-quartz and kenyaite-quartz are the relevant boundary lines, and leaching is not necessary to form quartz. In fact, leaching by dilute solutions should produce amorphous silica rather than quartz. All that is required in order to form quartz is to lower and maintain the activity of silica in solution at the low level of equilibrium with quartz. Sorption or reaction of silica with clay minerals might be involved in lowering the activity of silica (Jones et al., 1969). Judging from the pH effect on hydrothermal crystallization of quartz from amorphous silica (Campbell and Fyfe, 1960), the high pH of a sodium-carbonate brine may well shorten the time necessary to reach equilibrium with quartz, which is the stable phase of silica at surface conditions. Judging from the transition of sodium-silicate minerals to quartz at a depth of about 30 m in Drill Core B, 5,000 to 10,000 years were required to convert sodium-silicate minerals to quartz in the Evaporite Series (Hay, 1968). Breakdown of sodium-silicate minerals in response to a low silica activity can be represented by:

(l) $$\underset{\text{magadiite}}{NaSi_7O_{13}(OH)_3 \cdot 3H_2O} \rightarrow 7SiO_2 + Na^+ + OH^-$$

Other factors are involved in the formation of quartz above the water table or lake level. High surface temperatures and dehydration may be responsible for converting soft magadiite rinds on chert nodules of the High Natron Beds to hard quartzose porcelanite after exposure at the surface (Hay, 1968, p. 271). A lowering of the $Na^+:H^+$ ratio should accelerate the conversion. In view of the uncertain role of leaching by dilute solutions, oxygen isotopes of chert should be determined as a possible means of estimating the salinity of fluids in which the chert was formed.

Alluvial Deposits

Stratigraphy and lithology. This part of the paper focusses on a 20- to 40-m thickness comprising the upper part of Bed II, Bed III and Bed IVa. All but the lowermost

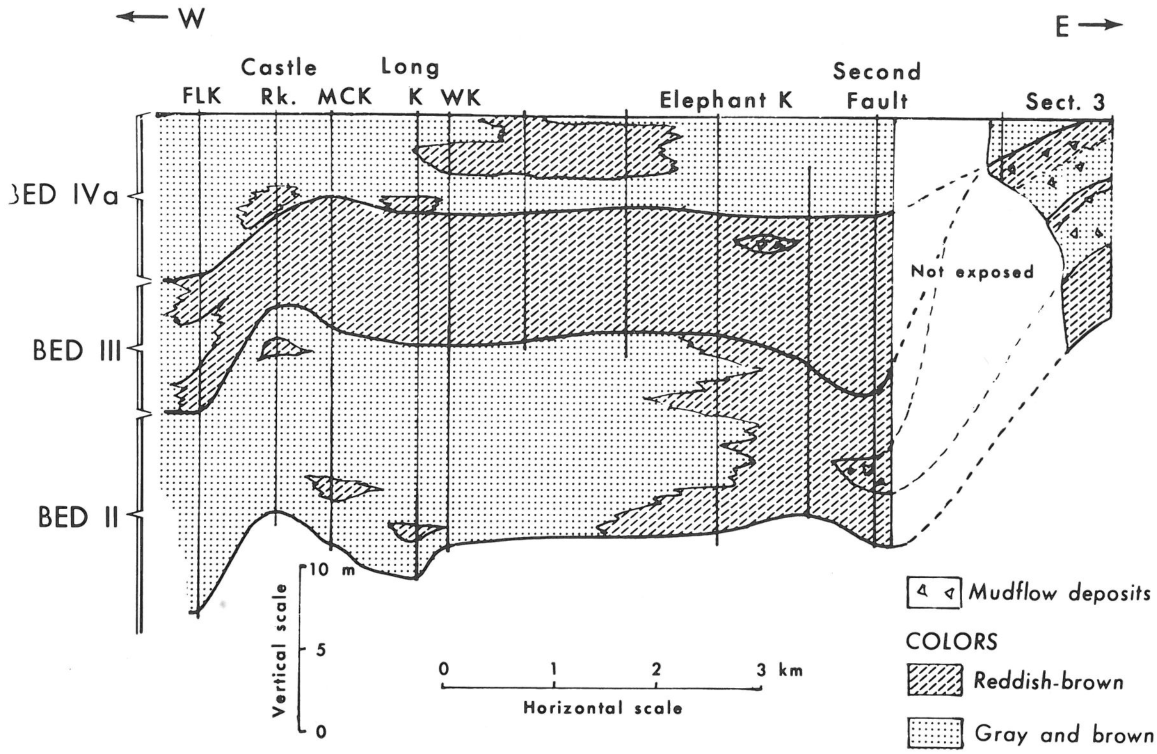

FIG. 8. Diagrammatic east-west section of Beds III, IVa, and the upper part of Bed II in the Main Gorge between FLK and Section 3, near the mouth of the Gorge. The top of Bed IVa is arbitrarily taken as a horizontal datum. Vertical lines indicate measured sections on which diagram is based, all but one of which are on the south side of the Gorge. Leakey (1965) gives locations of MCK, Long K, Elephant K and Castle Rock; Fig. 2 shows Section 3, the Second Fault, WK, and FLK. Within Bed IVa, volcanic detritus predominates to the east of WK and in the two reddish-brown areas shown to the west; within Bed III, volcanic detritus predominates to the east of FLK and basement detritus to the west.

part of this sequence is younger than the lake and lake-margin deposits described above. Most of the following lithologic and mineralogic data are based on samples collected in the southeastern 9 km of the gorge (Fig. 8). Here the sequence is about 25 m thick and is approximately 73 percent claystone, the remainder consisting of sandstone (14%), tuff (6%), conglomerate (4%), mudflow deposits (2%), and limestone (1%). Tuffs and mudflow deposits are most common in Bed II.

The upper part of Bed II contains chiefly volcanic debris eroded from the volcanic highlands to the southeast; quartzose metamorphic detritus from the basement complex is intermixed with volcanic detritus toward the west. Bed III consists largely of volcanic sediments, which interfinger to the northwest with quartzose sediments (Fig. 8). Bed IVa consists of quartzose sediments interfingering to the southeast with volcanic deposits resembling those of Bed III. Bed III and upper Bed II are dominantly reddish-brown claystone toward the southeast and gray or brown claystone to the northwest. Within Bed III the volcanic sediments are characteristically reddish-brown and most of the metamorphic sediments gray or brown; within Bed II, the transition from reddish-brown to gray is within purely volcanic sediments. Within Bed IVa, volcanic sediments are chiefly gray or brown.

1. Claystone and sandstone. Claystones are characteristically silty or sandy, massive, and rootmarked. Many layers, particularly in Beds II and IVa, have closely spaced vertical prismatic fractures of the type common in paleosols. The amount of detrital sand and silt generally is 5 to 40 percent, averaging about 15 percent. Anorthoclase, rock fragments, and less commonly plagioclase and pyroxene constitute most of the volcanic sand and silt; quartz, plagioclase and microcline form the bulk of sand and silt eroded from the basement rocks. Soluble salts are ubiquitous and average 4.3 percent of nine samples leached with distilled water. Sodium carbonate-bicarbonate is the principal salt. Conglomerates and sandstones generally form lenticular beds, many of which fill stream channels. Most sandstones contain the same detrital minerals as the associated claystones. Bed II contains a few sheetlike bodies of calcareous oolitic sandstone in the area west of DK.

Clay minerals of Bed II include montmorillonite, illite, and mixed-layer illite-montmorillonite. Illite generally predominates to the west and montmorillonite to the east of DK, a pattern corresponding generally to the presence or absence of metamorphic detritus in the sand fraction. Significant exceptions to this distribution pattern are the hard, reddish-brown, zeolite-rich claystones of the eastern area, which contain a poorly crystalline illite, with or without expandable interlayers. Illite and mixed-layer clay minerals are the only clay minerals found in Beds III and IVa. The illite of claystones with metamorphic detritus generally gives a rather well-defined diffractometer pattern in which the (001) peak at 10 Å is asymmetric to larger spacings and shows further broadening with glycolation. Illite of red claystones with volcanic detritus gives a weaker pattern with low, broad peaks suggesting a poorly crystalline illite, probably with some interlayered montmorillonite. Chemically, the clay fractions of gray and red claystones are about the same (Fig. 9; Table 2, nos. 6, 10 and 11). All of them have Si:Al ratios of about 3.0 and relatively high contents of MgO and Na_2O, suggesting that the illites contain interlayered montmorillonite. By contrast, bulk samples of red claystone have Si:Al ratios of 2.1–2.2 whereas gray claystones have Si:Al ratios of 2.7–2.9 (Fig. 9; Table 2, nos. 7, 8 and 9). This difference partly but not entirely reflects the greater content of zeolite in the reddish-brown claystones. Montmorillonite of Beds I and II deserves comment because of its unusually high Si:Al ratio of about 5:1 (Table 2, nos. 5 and 15; Fig. 9). This reflects low Al, High Fe^{3+}, and a very high Mg content of the octahedral layer. Its unusual composition is probably a result of the mafic composition of the source rocks that were weathered.

Nearly all of the claystones have been modified by chemical processes. Most conspicuous of the changes is the reddish-brown color of many claystones, particularly of those with volcanic detritus. More than nine-tenths of the claystones contain analcime or, less commonly, chabazite or phillipsite. Natrolite and dawsonite were noted in a few reddish-brown claystones of Bed II from the marginal parts of the basin and are locally common in claystone interlaminated with tuff at one horizon in Bed IVa. Pyroxene and plagioclase are etched in many samples and quartz is etched in a few, particularly from Bed IVb.

Illite and mixed-layer clay minerals have formed, and montmorillonite altered in at least some and perhaps most of the zeolite-rich, reddish-brown claystones containing volcanic detritus. These changes are indicated in Bed II by hard, reddish-brown, illitic claystones in an area where the softer, less-altered claystones contain chiefly montmorillonite.

Zeolites form, on the average, about 10 percent of all claystones, reaching a maximum of 40 percent (Fig. 3). They average about 12 percent in beds formed of volcanic detritus and 8 percent in beds formed of basement detritus. Volcanic detritus characterizes all of the claystones with more than 16 percent zeolites. Similarly, zeolites are more common in volcanic sandstones than in quartzose sandstones, and they are also more common in clayey sandstones than in well-sorted sandstones. Both the amount and species of zeolite vary gradually within claystone sequences, and the content of zeolite may remain about the same through thicknesses of several meters. As an example,

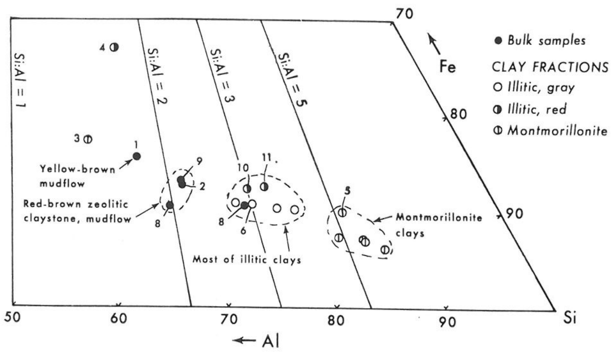

FIG. 9. Chemical analyses of samples from Olduvai Gorge plotted in the silica-rich part of a ternary diagram having Si, Al and Fe as end members. Atomic Si:Al ratios of 1, 2, 3 and 5 are also shown. Numbers refer to analyses of Table 2. Other analyses are unpublished. Small amounts of halloysite(?) are present in addition to montmorillonite in No. 3 and to illite in No. 4, both from a mudflow deposit of Bed II.

the amount of analcime ranges from 8 to 13 percent and averages 11 percent in eleven samples collected at 1-m intervals from one stratigraphic section.

Zeolites in claystones occur most commonly as veinlets; they also cement sandstones. Porous, sandy claystones may have zeolites as veinlets, disseminated crystals, and cement. Veinlets range from paper-thin and a few millimeters long to 2–4 mm thick and 1 m long. The larger veinlets are sandy, subvertical and fill fractures formerly open at the land surface. Intersecting veinlets may form zeolite boxworks, which constitute as much as 20 percent of a bed. Sandy claystones with more than 15 percent zeolites are characteristically hard, bright reddish-brown, and have a bricklike appearance.

Zeolites were probably formed and claystones reddened at or near the surface. Clasts of zeolitic claystone in one channel-filling conglomerate of Bed III show that the claystone was altered at depths a few meters or less. The clasts have an atypical color and unusually dense concentration of analcime veinlets and were almost certainly derived from a distinctive bed of similar claystone exposed in the wall of the channel. Although red zeolitic claystone clasts are present in some zeolitic, reddened conglomerates, there is no proof that the clasts were reddened and cemented by zeolites before they were deposited in the conglomerate.

2. Mudflow Deposits. A massive volcanic mudflow deposit 2.5 to 3.6 m thick forms the uppermost bed of Bed II near the mouth of the gorge. It consists of large and small blocks of basalt and trachytic lava and welded tuff in a detrital matrix of clay, rock fragments, and crystals of feldspar, pyroxene, and altered olivine. Where overlain by Bed IVb, the bed exhibits an alteration profile (Fig. 10) that was studied in detail to determine the mineralogical and chemical changes in altering a soft clay-rich volcanic sediment to a hard, reddish-brown rock with abundant zeolites.

The upper zone, 1 to 2 m thick, is friable to hard and light brown

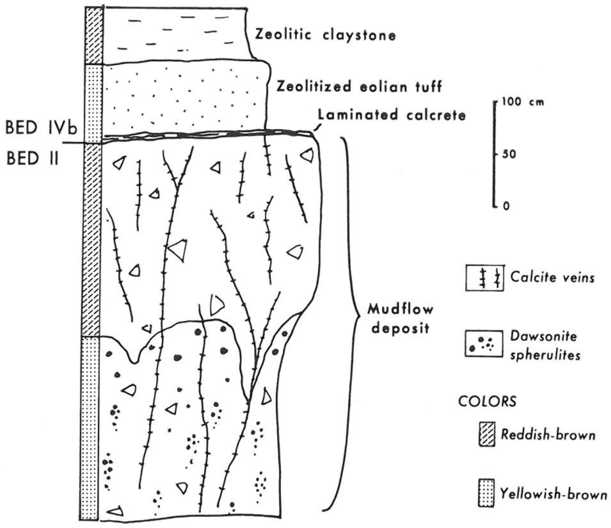

FIG. 10. Alteration profile developed on a clayey volcanic mudflow deposit of Bed II (Fig. 8, Section 3). The upper, reddish-brown part of the profile is rich in zeolites; the lower part is relatively poor in zeolites. The mudflow deposit is overlain disconformably by 1–2 cm of calcrete ("steppe limestone") and 50–100 cm of eolian nephelinite tuff of Bed IVb. Calcrete and zeolites of Bed IVb were formed in surface alteration ("zeolitic weathering") of nephelinite tuff prior to burial.

(5YR 5/6) to moderate reddish-brown (10R 4/6) in the rock color chart of the Geological Society of America. The base of the zone is uneven and extends downward along fractures and calcite veins. The composition of samples examined microscopically is estimated as 30–40 percent mineral grains and fragments of volcanic rocks, mostly of sand size; 25–30 percent ferruginous clay; and 20–30 percent zeolites, both disseminated and as veins. Anorthoclase, the principal detrital mineral, forms about 10 percent, and etched pyroxene forms 0.7 percent of one disaggregated sample. On the basis of diffractometer patterns, three samples average 27 percent analcime, chabazite and phillipsite. Calcite veins are common, and a few of the larger veins extend to the base of the deposit. The fraction finer than 2 microns gives a very low 7.0 to 7.6 Å peak (of halloysite?) and a weak pattern of illite in which the (002)-(003) d spacing of 5.04 Å in a glycolated sample suggests 45 percent of expandable layers (Burst, 1969, p. 77). A bulk sample analyzed chemically (Table 2, no. 2) has a notably high content of alkalis ($K_2O=4.31\%$, $Na_2O=5.56\%$). The fraction finer than 2 microns has a composition appropriate for illite with interlayered montmorillonite (Si:Al=1.7; $K_2O=3.92$, $Na_2O=1.24\%$, $MgO=2.35\%$). The analyzed sample has a bulk density of 2.06 g/cc and a porosity of 26.5 percent.

The lower zone, 2 to 2.5 m thick, is friable and moderate yellowish-brown (10YR 10/4). Samples are estimated to be 35–50% mineral grains and rock fragments, 35–50% ferruginous clay, 5–10% zeolites, and 1–2% dawsonite. Along vertical fractures the deposit may be reddened and rich in zeolites. Dawsonite is present chiefly as spherulites, but it also occurs in narrow veins lined by analcime and chabazite. Natrolite is present in the center of some veins, and it may alternate with dawsonite along the length of a vein. Dawsonite spherulites are widely scattered and relatively large (5–10 mm across) near the top of the zone; lower in the zone most are 2–4 mm across and concentrated in nests that may average 20% dawsonite. The largest concentrations are subvertical, and are as much as 50 cm×20 cm ×12 cm. The fraction finer than 2 microns gives a weak 7.0–7.6 Å peak (of halloysite?) and a weak to moderately strong pattern of montmorillonite with 30–35% illite layers. A bulk sample analyzed chemically (Table 2, no. 1) has 2.37% K_2O and 4.26% Na_2O. The fraction finer than 2 microns is chemically compatible with a mixture of halloysite and montmorillonite with interlayered illite (Si:Al=1.4, $K_2O=1.97\%$, $Na_2O=2.62\%$, and $MgO=1.26\%$). However, the low Si:Al ratio suggests either that halloysite is more abundant than the diffractometer pattern suggests, or else an amorphous aluminosilicate (allophane?) is present. The analyzed sample has a bulk density of 1.61 g/cc and a porosity of 41.5 percent.

The reactions involved in the zeolitic alteration are discussed in a later section. Table 3 is a chemical balance sheet based on analyses of bulk samples.

Unlike most of the zeolitic alteration of alluvial deposits in Olduvai Gorge, the alteration profile (Fig. 10) probably post-dated the mudflow deposit by a rather long time. The profile is overlain by zeolitic eolian tuff and laminated calcrete of Bed IVb, and a profile is lacking where the mudflow deposits are overlain by claystones of Beds II or IVa. Thus the profile was very likely developed either shortly before or at the same time that the overlying tuffs were deposited and altered to zeolites.

Another dawsonite-bearing clayey mudflow deposit, 0.8 to 1.2 m thick, is interbedded with analcimic claystones of Bed III a short distance southwest of the Second Fault. Like the deposit of Bed II, it varies from yellowish-brown and poor in zeolites to zeolitic and reddish brown. There is, however, no profile of alteration but rather an irregular distribution of reddish-brown and yellowish-brown areas. Dawsonite is largely confined to the reddish-brown, zeolitic parts of the deposit.

These descriptions of mudflow deposits have emphasized the occurrence of dawsonite. Although it is more common

TABLE 3. CHEMICAL BALANCE SHEET FOR ZEOLITIC ALTERATION OF MUDFLOW DEPOSIT

	1	2		3
		(a)	(b)	
SiO_2	40.42	54.06	+ 33.8%	+36.8%
Al_2O_3	19.53	22.26	+ 14.0	+16.4
TiO_2	3.07	3.07	—	+ 2.2
Fe_2O_3[a]	15.61	15.96	+ 2.2	+ 4.2
MnO	.23	.36	+ 57	+62
MgO	.93	1.45	+ 56	+60
CaO	1.49	2.04	+ 37	+40
Na_2O	4.26	6.95	+ 63	+67
K_2O	2.37	5.39	+127	+132
P_2O_5	.29	.31	+ 7	+11
H_2O	10.96	11.95	+ 8.9	+11.3

[a] All Fe is calculated as Fe_2O_3.

1. Composition of least-altered sample (Table 2, no. 1).

2(a). Composition of most-altered sample (Table 2, no. 2) recalculated assuming the amount of TiO_2 in (1).

2(b). Gains (+) and losses (−) in zeolitic alteration, assuming constant TiO_2, which are percentage differences in components between (1) and (2a).

3. Percentage difference between equal volumes of the most-altered and least-altered samples, as calculated using bulk densities measured on the analyzed samples.

in mudflow deposits than in claystones of Beds II and III, it is present in less than half the exposures I examined. High contents of zeolites are present in nearly all the exposures, either as local concentrations or throughout the deposit.

3. Tuffs. Vitric tuffs of Beds III, IVa, and the upper part of Bed II are reworked and generally form massive, lenticular beds 25 to 120 cm thick. Most are trachytic, and all are zeolitic with the exception of a tuff in Bed II at a single locality. Phillipsite is the dominant zeolite but is commonly accompanied by chabazite or analcime. Analcime is the dominant zeolite in a widespread, dominantly trachytic tuff as much as 2 m thick which lies near the middle of Bed IVa. At Sites JK and WK, it is laminated reddish brown and contains thin interbeds of claystone. The tuff and claystone are highly veined by analcime and minor chabazite. Veins at a few horizons are 2 to 4 mm thick and form a polygonal pattern resembling that of mud cracks. Natrolite and dawsonite are present in the center of many veins and the depositional sequence established in thin section is (1) chabazite, (2) analcime, and (3) natrolite or dawsonite.

Nature and occurrence of authigenic minerals

1. Zeolites. Analcime occurs as veins and cement, and as a massive replacement in tuffs. Single crystals are generally globular to euhedral and between 5 and 100 microns in diameter. Their refractive index ranges from 1.485 to 1.489 ± 0.002. The $(\bar{6}39)$ d gives a Si:Al ratio of 2.1–2.2 in two tuffs, and 1.7 to 2.1, averaging 1.9, in nine claystones. Associated with analcime are phillipsite, chabazite, natrolite and dawsonite. Chabazite and analcime are commonly associated within clusters, suggesting that they grew together; natrolite and dawsonite invariably post-date analcime and chabazite.

Chabazite occurs in veins, as a cement, and as a replacement of glass. Crystals are rhombic and 0.01–0.10 mm long; birefringence is low, and the mean refractive index is 1.465–1.468. Sodium is the dominant cation, and the Si:Al+Fe ratio is 2.5 in one analyzed sample from Bed II (Hay, 1964).

Phillipsite may coat or fill cavities and replace trachytic glass. Its crystals are euhedral to anhedral and 0.01 to 0.10 mm long. Their physical properties are similar to those of lacustrine phillipsite, described above. Analcime and chabazite are common associates.

Natrolite generally occurs in veins, where it is commonly associated with analcime and dawsonite. Crystals are euhedral and 0.01 to 0.10 mm long. N_1 is 1.480–1.485 and N_2 is about 1.492 in the few samples studied.

2. Dawsonite. Dawsonite ($NaAl(OH)_2CO_3$) occurs as aggregates of white fibrous crystals which form thin veins and colloform spherulites as much as 10 mm in diameter. It was identified on the basis of d and optical properties. Natrolite and analcime are the most common associates.

3. Illite and mixed-layer clay. Red illitic clay is an alteration product of montmorillonite in zeolitic mudflows and zeolite-rich claystones with volcanic detritus. The authigenic illite is poorly crystalline and contains interlayered montmorillonite. The clay fraction in one claystone has a Si:Al ratio of 3.0 (Table 2, no. 10); that from a mudflow deposit has a Si:Al ratio of 1.7 (Table 2, no. 4). Both have comparable amounts of MgO, Na_2O, and K_2O.

4. Other minerals. Authigenic calcite is widespread and abundant in the non-lacustrine beds. It occurs chiefly as nodules in claystones and as a cement in sandstones. Dolomite was identified in few veins of calcite, and zeolite was recognized in sandy claystone and as a cement in a few sandstones. The reddish-brown ferric oxide coloring the claystones, etc., is authigenic, and although it is probably anhydrous Fe_2O_3, appropriate d are absent.

Depositional and Diagenetic Environments. More than nine-tentns of the sequence was deposited by streams: sandstones and conglomerates fill channels, and the fractured, rootmarked claystones accumulated on floodplains. Volcanic sediments, including mudflows, were deposited on alluvial fans from the volcanic highlands. Sediments derived from the basement complex were deposited on a broad alluvial plain. The zones of interfingering metamorphic and volcanic detritus within Beds III and IVa represent the depositional axis of the basin, which shifted in response to faulting.

Interlaminated tuff and claystone near the middle of Bed IVa appear to be playa-lake deposits. Thin, even laminations suggest sedimentation in quiet water, and the red color and horizons of desiccation cracks indicate intermittent exposure to the air. Similar deposits are at JK and WK, .8 km apart, and the playa was probably at least this long.

Oolitic sandstones in the western exposures of Bed II were deposited in shallow water along the eastern margin of the perennial lake that disappeared in response to faulting during the deposition of Bed II.

Remains of horses, gazelles, pigs and rhinos in Beds II and IVa (Leakey, 1965) suggest an open, grassy plain. Hippo, crocodile, and catfish remains are common in Bed IVa and indicate that perennial fresh-water streams flowed across the alluvial plain. Fossils are relatively rare in Bed III and suggest a deficiency of vegetation, fresh water, or both on the alluvial fan from the volcanic highlands.

The surface layers of alluvium probably were alkaline and contained sodium carbonate concentrated by evapotranspiration. Sodium carbonate is presently concentrated in the surface layers of soil and rock in the Olduvai region (Hay, 1963a), and similar concentrations of salt during the Pleistocene seem likely on the basis of past and present dry climates (Hay, 1963b). Moreover, claystones of Beds II, III and IVa contain remarkably high concentrations of sodium carbonate, much of which may have been trapped at the time of burial. Nephelinite-carbonatite volcanism almost certainly supplied alkali carbonate ash to the Olduvai region during the deposition of Bed IVb (Dawson, 1964), and carbonate ash may have accompanied the nephelinite tuffs of Bed II. The alkali carbonate ash of Bed IVb may indeed be responsible for the profile of alteration developed on a mudflow deposit of Bed II (Fig. 9). In view

TABLE 4. CHEMICAL REACTIONS IN PLEISTOCENE DEPOSITS OF OLDUVAI GORGE[a]

	Glass	
(a)	trachytic glass$+H_2O \rightarrow$phillipsite	[1, 3]
(b)	mafic glass$+Na^+ + K^+ + H_2O + H^+ \rightarrow$alkali zeolites $+$montmorillonite$+Ca^{2+}$	[1, 2]
	Clay	
(c)	clay (amorphous?)$+Na^+(+SiO_2?) \rightarrow$analcime$+H^+$	[1,/3]
(d)	clay (amorphous?)$+Na^+ + K^+ + SiO_2 \rightarrow$clinoptilolite or erionite$+H^+$	[1,/2?]
(m)	montmorillonite$+$amorphous clay$+$halloysite$+Na^+$ $+K^+ \rightarrow$illite$+$analcime$+H^+(+H_2O?)$	[3]
(n)	$Al_2Si_2O_5(OH)_4$(halloysite)$+2Na^+ + CO_3^{-2}$ $\rightarrow NaAlSi_2O_6 \cdot H_2O$(analcime) $+NaAl(OH)_2CO_3$(dawsonite)	[3]
(o)	montmorillonite$+Na^+ + K^+ \rightarrow$illite$+$analcime $+H^+ + SiO_2$	[3]
(p)	illite$+Na^+ \rightarrow$analcime$+K^{++}H^+(+SiO_2?)$	[1?, 3]
	Zeolites to form K-feldspar	
(e)	$Na_{0.55}K_{0.45}AlSi_{2.7}O_{7.4} \cdot 2.3H_2O$(phillipsite)$+0.3SiO_2$ $+0.55K^+ \rightarrow KA1Si_3O_8 + 0.55Na^+ + 2.3H_2O$	[2]
(f)	$NaAlSi_2O_6 \cdot H_2O$(analcime)$+SiO_2 + K^+$ $\rightarrow KA1Si_3O_8 + Na^+ + H_2O$	[1]
	Opal	
(i)	SiO_2(amorphous)$\rightarrow SiO_2$(cristobalite)$+H_2O$	[2]
(j)	$Na^+ + 11SiO_2$(diatoms)$+5.5H_2O \rightarrow NaSi_{11}O_{20.5}(OH)_4$ $\cdot 3H_2O$(kenyaite)$+H^+$	[2]
	Aluminosilicate gel	
(g)	Al-Si gel$+Na^+ + K^+ \rightarrow$alkali zeolites$+H_2O$	[2?]
	Magadiite	
(h)	$NaSi_7O_{13}(OH)_3 \cdot 3H_2O + H^+ + .4Na^+ + 1.4Al(OH)_4^-$ $\rightarrow 1.4NaAlSi^5O_{12} \cdot 4H_2O$(clinoptilolite)$+2.2H_2O$	[2?]
(k)	$NaSi_7O_{13}(OH)_3 \cdot 3H_2O + H^+ \rightarrow 7SiO_2 + Na^+ + 5H_2O$	[1, 2]
or		
(l)	$NaSi_7O_{13}(OH)_3 \cdot 3H_2O \rightarrow 7SiO_2 + Na^+ + OH^- + 4H_2O$	

[a] [1] refers to reactions in lake beds, [2] to those in lake-margin deposits, and [3] to those in alluvial deposits. The more questionable reactions are indicated by [?].

of the evidence for sodium carbonate at the land surface, the playa lake of Bed IVa was probably highly alkaline and rich in sodium carbonate.

Modern examples show that surface concentrations of sodium carbonate can produce zeolites and cause reddening in non-tuffaceous sediments. The Luboi Plain, at the north end of Lake Hannington, Kenya (McCall, 1967), is an area where brown claystones are presently being transformed to zeolitic redbeds resembling those of Olduvai Gorge. The Luboi Plain is a gently sloping alluvial fan about 0.5 km wide and 1.5 km long, measured perpendicular to the shoreline. The plain supports a scanty growth of grass, brush and trees, and thin efflorescences were widespread over the surface when I visited it in July, 1967. The sediments are chiefly rootmarked sandy claystones, the surface 15–100 cm of which is extensively reddened and both veined and cemented by analcime. The analcimic red claystones grade downward into soft brown claystones containing little or no zeolite. Zeolitic redbeds occur well above lake level, and no likely Holocene rise in lake level would have flooded the plain. Thus the zeolites and reddening are attributable to alkaline solutions concentrated at the surface rather than by intermittent flooding with alkaline lake water as on the Peninj delta of Lake Natron (Hay, 1966, p. 38).

Analcime in saline, alkaline soils of the semi-arid San Joaquin Valley of central California (Baldar, 1968) provides another analogy with zeolitic alluvial sediments of Olduvai Gorge. The soils are developed on non-tuffaceous alluvium and have a pH of 8.5 to 10.2. Very fine-grained analcime has formed in the A and B horizons, 50–75 cm thick, and is absent in the underlying alluvium. Both the soils and alluvium are gray or brown.

Nature of reactions

1. Zeolites and dawsonite in tuffs. Phillipsite and chabazite formed directly from glass, (reaction a, Table 4), judging from remnants of glass associated with phillipsite and chabazite in a tuff of Bed II. Analcimic tuffs lack unaltered glass and contain no textural evidence as to whether the analcime is a reaction product of glass or of an alkali-rich zeolite such as phillipsite, which is the usual precursor of analcime in vitric tuffs (Hay, 1966; Sheppard and Gude, 1969). It is not clear what reactions yielded natrolite and dawsonite in the analcime-rich interlaminated tuffs and claystones of Bed IVa. The natrolite and dawsonite postdate chabazite and analcime and may have formed by reaction of either clay or early-formed zeolites. If the dawsonite and natrolite formed from the chabazite and analcime, then SiO_2 must have been leached. B. F. Jones (1969, pers. commun.) has suggested leaching by capillary-evaporated sodium-carbonate waters as a mechanism for removing silica.

2. Zeolites and dawsonite in mudflow deposits. Clearly the clay fraction reacted to form zeolites, illite with interlayered montmorillonite, and dawsonite in the alteration profile developed on a mudflow deposit of Bed II (Fig. 10). Although etched pyroxene is present, the degree of etching (5–10%) and small amount of the mineral (0.7%) shows that it could not have been a significant source of silica. Montmorillonite and an amorphous component rich in Al were probably the principal reactants. Although montmorillonite is the principal clay mineral indicated by diffractograms of the least-altered samples, the Si:Al ratio of 1.4 in the clay fraction is much too low for Oldvai montmorillonites. Although halloysite is present, the small size of its (001) peak relative to that of montmorillonite suggests that halloysite alone does not account for the low Si:Al ratio. Halloysite may nevertheless have been an additional reactant as its (001) peak height decreases in the highly zeolitic samples. Thus, on the basis of mineralogical changes, the zeolitic alteration can be written:

(m) montmorillonite + amorphous clay + halloysite

$$+ Na^+ + K^+ \rightarrow \text{illite} + \text{analcime} + H^+ + H_2O$$

If the illite formed from montmorillonite and did not react further, this generalized equation may be written in two steps:

$$(m_1)\quad \text{montmorillonite} + K^+ \rightarrow \text{illite} + Na^+ + H_2O + SiO_2$$

$$(m_2)\quad \text{amorphous clay} + \text{halloysite} + SiO_2 + Na^+ \rightarrow \text{analcime} + H^+ + H_2O$$

Yellowish-brown ferric oxide dehydrated to yield red anhydrous(?) ferric oxide, and altering montmorillonite probably contributed additional Fe_2O_3.

The chemical budget based on two chemical analyses (Table 3, Fig. 10) indicates that the zeolitic rock gained relatively large amounts of several components, including Si and Al. Assuming Ti constant, the zeolitic rock gained 34 percent SiO_2 and 14 percent Al_2O_3, amounts sufficient to form 19 percent analcime, or about three-quarters of the zeolite present in this sample. Essentially similar results are obtained using bulk densities and comparing the amounts of different components in equal volumes of the analyzed samples. TiO_2 and Fe_2O_3 were immobile, within the limits of accuracy of the bulk-density determinations. The large amounts of Si and Al gained by the upper part of the mudflow deposits probably originated in the lower part, and the relative difference in amounts gained suggest that Si was the more mobile of the two.

Dawsonite is confined to the lower, montmorillonitic part of the mudflow deposit and could have formed by reaction of sodium carbonate with either amorphous clay or halloysite:

$$(n)\quad \underset{\text{halloysite}}{Al_2Si_2O_5(OH)_4} + 2Na^+ + CO_3{}^{2-} \rightarrow \underset{\text{analcime}}{NaAlSi_2O_6 \cdot H_2O} + \underset{\text{dawsonite}}{NaAl(OH)_2CO_3}$$

Reaction of clay to form dawsonite and a zeolite is more convincingly documented by the mudflow deposit of Bed III, in which abundant analcime and dawsonite were formed within the same small volumes of rock. Analcime invariably predates dawsonite in the mudflow deposits, and if reaction (n) is applicable, analcime must have precipitated nearer the site of reaction than the dawsonite. Natrolite was also deposited later than analcime in a given sample, and it may have been precipitated at intermediate distances, reflecting an intermediate activity or mobility of silica. The large spherulites of dawsonite are another line of evidence that Al was extensively transported colloidally or in solution within the mudflow deposits.

Alternative reactions for dawsonite in the mudflow deposits can probably be dismissed. No spacings of gibbsite were identified in the least-altered samples, and although dawsonite and natrolite formed from nepheline in Bed IVb, the mudflow deposits contain only basaltic and trachytic materials, only a little of which is vitrophyric.

3. Zeolites in claystones. The clay fraction must have supplied the major part of the Si and Al in zeolites of the nontuffaceous claystones. Montmorillonite of Beds I and II has an unusually high Si:Al ratio of about 5:1, and the Si:Al ratios of about 3.0 in authigenic clay and 2.0–2.6 in zeolites indicate either that a component more aluminous than montmorillonite was originally present (Fig. 9; reaction m), or else SiO_2 was lost:

$$(o)\quad \text{montmorillonite} + Na^+ + K^+ \rightarrow \text{illite} + \text{analcime} + H^+ + SiO_2$$

Some evidence suggests that both possibilities occurred. An aluminous noncrystalline component is apparently still present in the least-altered part of a mudflow deposit, and as the mudflow and the detrital clays were derived from the same sources, they may originally have had the same type of clay. Silica has been redistributed within the alluvial sequence, judging principally from the mudflow deposits, which gained SiO_2 in zeolitic alteration and only locally contain dawsonite.

Within claystones of metamorphic origin, zeolites were probably formed by reaction of illitic clay:

$$(p)\quad \text{illite} + Na^+ \rightarrow \text{analcime} + K^+ + Na^+ (+SiO_2?)$$

The illite has interlayered montmorillonite and an Si:Al ratio of 3.0–3.4, indicating either a more aluminous component was also a reactant or SiO_2 was lost, in forming analcime.

Reactions (o) and (p) may seem contradictory inasmuch as illite is a reactant in one case and a reaction product in the other. Two possibilities are evident: (1), only the degraded, weathered illite reacted to form analcime; or (2), illite in reaction (o) is an intermediate reaction product in the alteration of montmorillonite and would disappear if the reaction ran to completion. Clearly much more work is necessary on the detailed nature of the clays and their reactions.

Comparison With Other Examples

Lake deposits. Lacustrine sediments of Beds I and II resemble deposits of other saline, alkaline lakes in their content of authigenic silicate minerals. K-feldspar and analcime, for example, are common in lacustrine tuffs and claystones of Searles Lake, Pleistocene Lake Tecopa, and the Barstow Formation of California (Hay and Moiola, 1963; Sheppard and Gude, 1968, 1969), the Green River Formation of Wyoming and the Peninj Group of Tanzania (Hay, 1966). Likewise, the chert of Beds I and II Olduvai Gorge is a type characteristic of sodium-carbonate lakes (Eugster, 1967, 1969; Hay, 1968).

Lake-margin deposits. Lake-margin deposits of Beds I and II in the Main Gorge can be compared in silicate diagenesis with Pleistocene sediments of the Waucoba Lake Beds of California (Hay, 1964), where fresh and zeolitized tuffs alternate in a vertical section, reflecting variation in salinity and pH in a desert lake that did not have a permanent outlet. Claystones of Bed II, like those in a drill core from Owens Lake, California (Hay, 1966, p. 34), vary widely in their content of zeolites, reflecting lower salinities. K-feldspar is lacking in these sediments, probably because salinities were lower than in those lake beds where K-feldspar is formed. Zeolitites of lake-margin deposits of Bed II in the Side Gorge seem to be unique among examples in the literature and the zeolitites and nontuffaceous claystones rich in clinoptilolite appear to be exceptional.

Alluvial deposits. The alluvial sequence does not appear to have any close parallel in the literature, but it has some similarity with analcimic redbeds of Mesozoic age (see Hay, 1966, p. 31). Analcime is a common constituent in reddish-brown claystones, and it may be the principal mineral in some beds ("analcimolites"). Sediments of these Mesozoic examples were deposited largely on floodplains and in saline playa lakes. These Mesozoic claystones differ from the reddish-brown zeolitic claystones of Olduvai Gorge in the coarse, disseminated nature of the analcime and in a lack of phillipsite and chabazite. These differences may be partly a function of age, and the Olduvai redbeds, if not eroded, would have come to resemble more closely the Mesozoic redbeds. Given sufficient time, the phillipsite and chabazite would likely have disappeared, and the analcime would have become coarser and possibly more uniformly distributed (Hay, 1966, p. 72–76). No potential analcimolites are present in Olduvai Gorge, however.

The occurrence of dawsonite in Olduvai Gorge compares to some extent with that in the saline (nahcolite) facies of the Green River Formation of Colorado (Smith and Milton, 1966). In the Piceance Basin of Colorado it is disseminated in fine-grained lacustrine deposits and is a major constituent of many tuffs. Unlike most or all of that in Olduvai Gorge, however, dawsonite probably formed by reaction of analcime or another zeolite under high P_{CO_2} determined by equilibrium with nahcolite:

$$\underset{\text{analcime}}{NaAlSi_2O_6 \cdot H_2O} + CO_2 \rightarrow 2SiO_2 + \underset{\text{dawsonite}}{NaAl(OH)_2CO_3}$$

Evidence for this is in the distribution pattern of analcime, dawsonite and quartz in 34 tuff samples from depths of 196 to 700 m in Drill Core 14-1 by the Wolf Ridge Minerals Corp. (N$\frac{1}{2}$ Sec. 14, T. 1 S., R. 98 W.). These samples were examined by A. Iijima and myself. Tuffs highest in the section, above the saline facies, commonly contain analcime, with or without authigenic feldspars and quartz. Lower in the section, from the Mahogany Marker Tuff downward, tuffs commonly contain either analcime or dawsonite, but only rarely both, in addition to feldspars. The complementary distribution of analcime and dawsonite is to be expected if the dawsonite formed from analcime. Samples with 15–50 percent dawsonite usually contain 20–40 percent quartz, which is also to be expected from decomposing analcime.

In nontuffaceous samples of a different drill core (Hite and Dyni, 1967), the amount of quartz is proportional to dawsonite, which would be expected if both were formed from the same precursor. However, the ratio of quartz to dawsonite is about 2.5, which is too high to explain simply by decomposition of analcime. Probably other aluminosilicate reactions are also involved.

This explanation of the dawsonite in the Green River Formation relies heavily on studies of modern saline, alkaline lakes, in which analcime forms in muds on the lake bottom, and in which volcanic glass alters to zeolites at depths of a few meters or less over a few thousand years.

Summary and Conclusions

1. Authigenic silicate minerals form a substantial proportion of lake-margin, and alluvial sediments of Pleistocene age in the Olduvai region. Lacustrine claystones average 15 to 20 percent authigenic silicate minerals, principally K-feldspar and analcime, and claystones of alluvial origin average about 10 percent zeolite, principally analcime. Lake-margin deposits lack authigenic silicates in some places and contain high concentrations of zeolites in others. Maximum concentrations of zeolites are about the same in claystones of all three lithologic facies (Fig. 3).

2. Different assemblages of authigenic minerals characterize the different lithologic facies (Table 4). K-feldspar is the most abundant mineral in lacustrine claystones, clinoptilolite predominates in lake-margin claystones of Bed II, and analcime is most abundant in alluvial deposits. Minerals restricted to a single lithologic facies include K-feldspar, searlesite, and fluorite in the lake deposits, kenyaite and opal in lake-margin deposits, and dawsonite and natrolite in alluvial deposits.

3. Authigenic minerals of the different facies differ in their crystal size and mode of occurrence. Zeolites and K-feldspar are fine-grained and disseminated in lacustrine claystones, whereas in alluvial deposits the zeolites are coarser and commonly form veinlets. Zeolites occur both as veinlets and disseminated crystals in claystones of the lake-margin facies of Bed II. Zeolite veinlets and rootcasts and dawsonite spherulites are among the evidence that Si and Al were highly mobile in lake-margin and alluvial deposits.

4. Many different reactions involving sodium-carbonate solutions can either be demonstrated or inferred for the Pleistocene deposits of Olduvai Gorge (Table 4):

a. Trachytic glass altered to alkali-rich zeolites, a reaction widely documented elsewhere.

b. The clay fraction reacted extensively in deposits of all environments, but much remains to be determined about the nature of the reactions. Montmorillonite was extensively altered in the alluvial deposits, but there is no evidence that either montmorillonite or illite reacted selectively in the lake- and lake-margin deposits. Halloysite(?) altered in the mudflow deposits, and it may have been a reactant in many claystones derived by erosion of volcanic rocks. Amorphous clay may have been a major reactant in all three sedimentary facies, but this cannot be proved.

c. K-feldspar formed from a zeolite precursor, based principally on evidence from other deposits.

d. Diatoms and other biogenic opal contributed to the formation of kenyaite, opal nodules, and siliceous zeolites in the lake-margin deposits.

e. Zeolitites in lake-margin of Bed II in the Side Gorge apparently formed in unusual ways. Thin layers of clinoptilolite very likely formed by addition of Al and K to a sodium-silicate mineral, and the massive, impure zeolitites more likely formed either from an authigenic aluminosilicate gel or from high concentrations of detrital amorphous clay.

f. Chert and chalcedony formed from sodium-silicate minerals, as documented elsewhere in East Africa.

g. Most or all of the dawsonite of Beds II, III and IVa formed by reaction of clay.

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REFERENCES

BALDAR, N. A. (1968) *Occurrence and Origin of Soil Zeolites.*, Univ. Calif., Davis Ph.D. Diss.

BRICKER, O. P. (1969) Stability constants and free energies of formation of magadiite and kenyaite. *Amer. Mineral.* **54,** 1026–1033.

BURST, J. F. (1969) Diagenesis of Gulf Coast clay sediments and its possible relation to petroleum migration. *Amer. Ass. Petrol. Geol. Bull.,* **53,** 73–93.

CAMPBELL, A. S., AND W. S. FYFE, (1960) Hydroxyl ion catalysis of the hydrothermal crystallization of amorphous silica; a possible high temperature pH indicator. *Amer. Mineral.,* **45,** 464–468.

DAWSON, J. B. (1962) The geology of Oldoinyo Lengai. *Bull. Volcanol.* **24,** 349–387.

——— (1964) Carbonatitic volcanic ashes in northern Tanganyika. *Bull. Volcanol.,* **27,** 1–11.

EUGSTER, H. P. (1967) Hydrous sodium silicates from Lake Magadi, Kenya: Precursors of bedded chert. *Science* **157,** 1177–1180.

——— (1969) Inorganic bedded cherts from the Magadi area, Kenya. *Contr. Mineral. Petrology.,* **22,** 1–31.

———, AND B. F. JONES (1968) Gels composed of sodium-aluminum silicate, Lake Magadi, Kenya. *Science,* **161,** 160–163.

HAY, R. L. (1963a) Zeolitic weathering in Olduvai Gorge, Tanganyika. *Geol. Soc. Amer. Bull.,* **74,** 1281–1286.

——— (1963b) Stratigraphy of Beds I through IV, Olduvai Gorge, Tanganyika. *Science.,* **139,** 829–833.

——— (1964) Phillipsite of saline lakes and soils. *Amer. Mineral.,* **49,** 1366–1387.

——— (1966) Zeolites and zeolitic reactions in sedimentary rocks. *Geol. Soc. Amer. Spec. Pap.* **85,** 130 pp.

——— (1967a) Hominid-bearing deposits of Olduvai Gorge. *In* Time and Stratigraphy in the Evolution of Man, *Nat. Acad. Sci. Nat. Res. Counc.* [U. S.] *Publ.* **1469,** 30–42.

——— (1967b) Revised stratigraphy of Olduvai Gorge. *In* Bishop W. W. and J. D. Clark, eds., *Background to Evolution in Africa.* Univ. Chicago Press, 221–228.

HAY, R. L. (1968) Chert and its sodium-silicate precursors in sodium-carbonate lakes of East Africa. *Contr. Mineral. Petrology.,* **17,** 255–274.

———, AND R. J. MOIOLA (1963) Authigenic silicate minerals in Searles Lake, California. *Sedimentology,* **2,** 312–332.

HITE, R. J., AND J. R. DYNI (1967) Potential resources of dawsonite and nahcolite in the Piceance Creek Basin, northwest Colorado, *Col. Sch. Mines* Quart. **62,** 25–38.

IIJIMA, A., AND R. L. HAY (1968) Analcime composition in tuffs of the Green River Formation of Wyoming. *Amer. Mineral.,* **53,** 184–200.

JONES, B. F. (1966) Geochemical evolution of closed basin waters in the western Great Basin. *In* J. L. Rau (ed.) **2***nd Symp. Salt. Ohio Geol. Soc, Cleveland,* **1,** 181–200.

———, VANDENBURGH, A. S., TRUESDELL, A. H. AND RETTIG, S. L. (1969) Interstitial brines in playa sediments. *Chem. Geol.* **4,** 253–262.

LEAKEY, L. S. B. (1965) *Olduvai George 1951-1961. Vol.* **1,** *A preliminary report on the Geology and Fauna.* Cambridge Univ. Press, 118 pp.

MCCALL, G. J. H. (1967) Geology of the Nakuru-Thomson's Falls-Lake Hannington area. *Kenya Geol. Surv. Rep.* **78,** 122 pp.

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

———, AND ——— (1969) Diagenesis of tuffs in the Barstow Formation, Mud Hills, San Bernardino County, California. *U. S. Geol. Surv. Prof. Pap.* **634,** 35 pp.

———, ———, AND R. L. HAY (1970) Makatite, a new hydrous sodium silicate mineral from Lake Magadi, Keyna. *Amer. Mineral.* **55,** 358–366.

SMITH, J. W., AND C. MILTON (1966) Dawsonite in the Green River Formation of Colorado. *Econ. Geol.* **61,** 1029–1042.