

## THE NATURE OF ZEOLITE OCCURRENCES IN DEPOSITS OF THE OLDUVAI BASIN, NORTHERN TANZANIA

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**Abstract**—The Plio-Pleistocene deposits of the Olduvai Basin in northern Tanzania consist of a sequence of lacustrine and fluvial sediments. They contain various amounts of zeolite minerals, the formation of which is related to an interaction of volcanic material or detrital clays with saline alkaline lake water and groundwater. Petrographic characteristics of zeolite occurrences provide information about their conditions of formation. They were studied for all four main stratigraphical units that are recognized at Olduvai (Beds I to IV), sampled in the southeastern part of the basin. In the lake-margin deposits of Bed I and the lower part of Bed II, chabazite is the dominant zeolite mineral accompanied by phillipsite and minor amounts of erionite and clinoptilolite. Chabazite commonly occurs as part of altered volcanic rock fragments, characterized by partial or complete dissolution of volcanic glass and the formation of chabazite inside vesicles, following the development of thin smectite coatings. It also formed within the sediment matrix, requiring extended periods of impregnation of the deposits by saline alkaline solutions. Chabazite also occurs extensively as coatings and infillings of pores, developed during periods of subaerial exposure which were characterized by high groundwater levels. Phillipsite formed at a later stage, from more evolved solutions, with higher K/Na ratios than during chabazite formation. The fluvial deposits of Bed IV, Bed III and the upper part of Bed II have a high analcime content. They also contain various amounts of chabazite, phillipsite and natrolite. All zeolite minerals mainly occur in pores. The predominance of analcime indicates a higher salinity and alkalinity than during the preceding period with sedimentation and diagenesis in a lake margin environment. Early development of zeolite occurrences, shortly after the deposits became exposed during breaks in sedimentation, is recorded for some intervals, where zeolites are covered by illuvial clay coatings or by sparitic carbonate cement. In most intervals, however, zeolites mainly formed at a later stage.

**Key Words**—Analcime, Chabazite, Diagenesis, Olduvai, Phillipsite, Tanzania, Zeolites.

### INTRODUCTION

The Quaternary deposits of the Olduvai region in northern Tanzania represent a 2 my record of continental sedimentation in lake and alluvial plain environments. They are exposed along the sides of a branching gorge, where several important hominid sites have been excavated since 1913 (*e.g.* Leakey *et al.*, 1964). The deposits have a high zeolite content, which has been the subject of several publications, documenting basin-wide variations (*e.g.* Hay, 1970) or concentrating on specific stratigraphical intervals or environments (*e.g.* Hay and Kyser, 2001). Detailed studies of vertical variations covering all main stratigraphical units at one location are not available. Petrographic features of these zeolites have been reported in the literature but they are not extensively documented, except for one paleosol interval (Ashley and Driese, 2000).

This paper presents the results of a petrographic study of all main stratigraphical units (Beds I to IV; Reck, 1951) sampled in the southeastern part of the basin. In

this area, early Pleistocene lake-margin deposits of great significance for paleoanthropological research are exposed. The main objective of this study is an improved understanding of the mechanisms and timing of zeolite diagenesis at Olduvai, based on the nature of zeolite occurrences and their relationship with other (non-zeolitic) diagenetic features.

### GEOLOGICAL SETTING

Olduvai Basin is a rift-platform basin along the western flank of the Eastern Rift Valley (Ashley & Hay, 2002). To the east and south, it is bordered by the Ngorongoro Volcanic Highlands, composed of trachytic and basaltic rocks in the area supplying most sediments to the basin (Hay, 1976). To the west and north, the bedrock consists of Precambrian metamorphic rocks (gneiss, quartzite).

The centre of the Olduvai Basin was occupied by a perennial saline alkaline lake during the early part of its recorded history (2.0–1.7 my; Hay, 1976). During the next stage (1.7–1.2 my), the lake progressively shrank and the area of alluvial terrains increased, followed by a period during which sedimentation mainly took place in an alluvial plain environment (1.2–0.6 my; Beds III and IV). The deposits include a number of mostly trachytic

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tuff layers, containing variable amounts of non-volcanic material.

Lake water and groundwater have been characterized by high alkalinity at all times, up to the present. This high alkalinity is mainly due to weathering of sodic volcanic rocks within the catchment (Hay, 1963, 1970). Semi-arid climatic conditions, which persisted throughout the Quaternary in this region (Hay, 1976, 1990), resulted in the development of saline alkaline lake and soil water.

#### PREVIOUS STUDIES OF ZEOLITE OCCURRENCES IN THE OLDUVAI BASIN

In the saline alkaline lake deposits of Beds I and II, K-feldspar is the dominant authigenic silicate mineral (Hay, 1970). Claystone intervals also contain analcime and less commonly clinoptilolite or erionite (Table 1). Phillipsite is the dominant zeolite mineral in tuff layers. All zeolites formed by an interaction of volcanic glass or detrital clays with saline alkaline lake water, although the possibility of zeolite formation from lake water is not excluded (Hay, 1970).

In the lake-margin deposits of Beds I and II, clinoptilolite is the dominant zeolite mineral (Hay, 1970). Clinoptilolite, chabazite and phillipsite are present in claystone intervals, phillipsite is the dominant zeolite mineral in tuff layers, and erionite occurs in tuffaceous claystone. Paleosol intervals in the upper part of Bed I and the lower part of Bed II in the southeastern part of the basin contain analcime in pores, occurring as authigenic coatings and illuvial silts; these zeolites can cover Fe oxides or clay coatings, and they are locally intergrown with sparitic calcite (Ashley and Driese, 2000). Zeolite minerals in the lake-margin deposits formed by an interaction of saline alkaline lake or soil water with volcanic glass, detrital clays or authigenic silicates (X-ray amorphous compounds, sodium silicates) (Hay, 1970). Zeolites are generally scarce or absent in lake-margin deposits at the greatest distance

from the centre of the basin, where pore waters were less saline (Hay, 1966).

In the fluvial deposits of Beds II to IV, analcime is the dominant zeolite mineral in claystone and sandstone, occurring as veins, cements and isolated crystals (Hay, 1970). Chabazite and phillipsite are less common and natrolite is rare. Analcime and chabazite commonly occur together, suggesting that they formed at the same time, whereas natrolite always formed at a later stage. In tuff layers, phillipsite is the dominant zeolite mineral. All zeolites formed at or near an exposed paleosurface, whereby detrital clays acted as the main source of Al and Si (Hay, 1970).

Part of the zeolites in deposits of the Olduvai Basin formed after incision of the gorge. These zeolite occurrences, dominated by phillipsite, are recognized for deposits that post-date gorge incision (Hay, 1963, 1964, 1966, 1980), as well as for exposed older deposits (Hay, 1963, 1964).

#### MATERIALS AND METHODS

Samples of all main stratigraphical units that have been defined for the Olduvai Basin (Reck, 1951; Hay, 1976) were available for this study. These samples were initially collected as part of a study of paleosol occurrences by Peter Kafumu and Roland Paepe (Kafumu, 2000). A total of 132 samples was available, for four exposures in the southeastern part of the basin (Figure 1). X-ray diffraction (XRD) analyses of bulk samples were performed for all sampled intervals, using a Phillips X'pert System (CuK $\alpha$  radiation, scan time 1 s per 0.02°2 $\theta$ , range 3–60°2 $\theta$ ). Thin-sections were prepared for 68 samples, after impregnation of air-dried undisturbed fragments with a cold-setting polyester resin. The composition of all zeolite minerals was checked by energy-dispersive analysis, using undisturbed fragments of selected samples (Noran Vantage microanalysis system, Jeol JSM-6400 scanning electron microscope).

Table 1. Zeolite minerals occurring in deposits of the Olduvai Basin.

Name	Composition*	DEC**
Analcime	Na <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·1.6H <sub>2</sub> O	Na
Chabazite	(Ca <sub>0.5</sub> ,K,Na)AlSi <sub>2</sub> O <sub>6</sub> ·3H <sub>2</sub> O	Na,Ca,K
Clinoptilolite	(Na,K,Ca <sub>0.5</sub> ) <sub>7</sub> Al <sub>7</sub> Si <sub>29</sub> O <sub>72</sub> ·22H <sub>2</sub> O	Na,Ca,K
Erionite	K <sub>2</sub> (Ca <sub>0.5</sub> ,Na) <sub>7</sub> Al <sub>9</sub> Si <sub>27</sub> O <sub>72</sub> ·28H <sub>2</sub> O	Na,K,Ca
Natrolite	Na <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> ·2H <sub>2</sub> O	Na
Phillipsite	K <sub>2</sub> (Na,Ca <sub>0.5</sub> ) <sub>3</sub> Al <sub>5</sub> Si <sub>11</sub> O <sub>32</sub> ·12H <sub>2</sub> O	Na,K,Ca

\*Composition: Passaglia and Sheppard (2001)

\*\*DEC: dominant extra-framework cations, in order of abundance, for zeolites formed in saline alkaline environments, based on published data (Hay, 1964, 1966, 1980; Gude and Sheppard, 1978, 1988; Sheppard and Gude, 1968, 1969, 1973; Surdam and Eugster, 1976; Ratterman and Surdam, 1981).

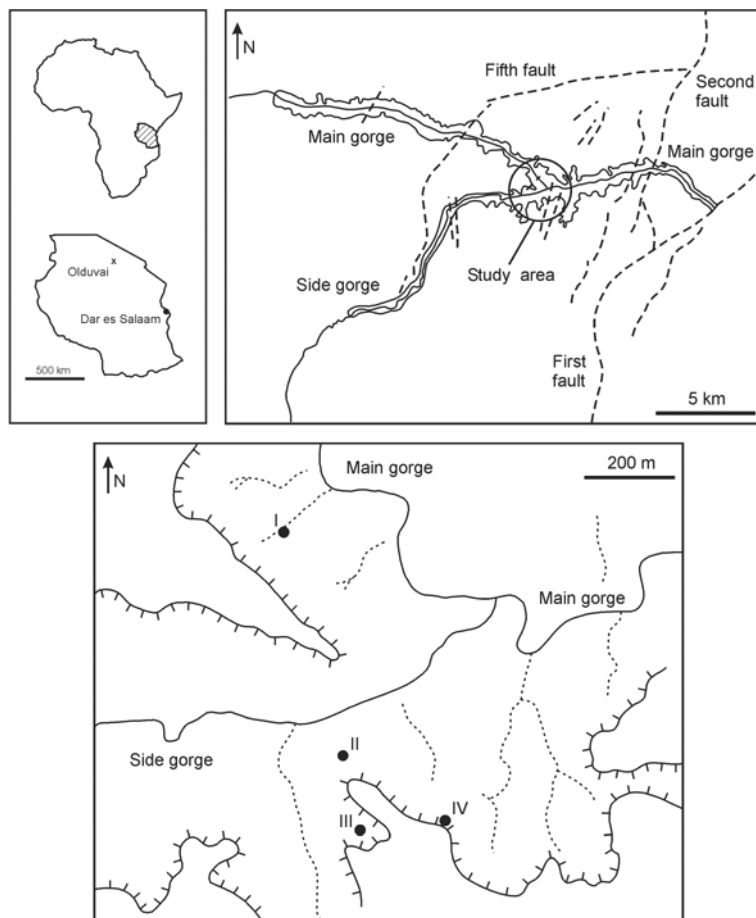


Figure 1. Location of the study area and the sampling sites. I–IV: Bed I to IV sites (I near site 45 of Hay, 1976; II to IV near site 85).

#### STRATIGRAPHY AND DEPOSITIONAL ENVIRONMENTS OF THE STUDIED DEPOSITS

The deposits of Bed I largely consist of claystone and sandy claystone (Figure 2), representing lake-margin deposits of a saline alkaline lake basin. They also include several tuff layers, containing mostly vitric volcanic material. In the lower part of Bed II, the deposits are mainly sand-free claystones, with several diatomaceous intervals (RS8, RS10, RS11). These Bed II sediments are lake-margin deposits, formed near the transition to an environment with continuous lacustrine sedimentation. The diatomaceous sediments are interpreted as spring-related perennial wetland deposits (Deocampo and Ashley, 1999; Ashley and Hay, 2002).

The clayey and diatomaceous lake-margin deposits of Bed II are covered by an eolian tuff (Tuff IIA) which corresponds to a stratigraphical unit the upper boundary of which represents a major unconformity (Hay, 1976). It is covered by sandstone with a high augite content (lower augitic sandstone; Hay, 1976), followed by a brownish clayey sandstone (Tuff IIB; Hay, 1976). The boundary between these sandstone intervals marks a change from lacustrine to fluvial sedimentation in this part of the basin (Hay, 1976). The deposits at the base of

the Bed III exposure are fluvial sediments that formed after further contraction of the lake and the development of a drainage way that extended from the east.

The Bed III deposits are typically reddish brown (sandy) claystones. These are fluvial sediments which formed after a major change in drainage patterns due to tectonic movements. The detrital fraction is dominated by volcanic detritus from southern and eastern source areas. The deposits of Bed IV largely consist of greyish brown claystones, representing fluvial deposits that were derived from metamorphic basement rocks in the north and northwest. They formed after a northward displacement of the drainage way that marks the boundary between zones with different sediment source areas.

Throughout Beds I to IV, many intervals show indications of subaerial exposure or pedogenesis, including the occurrence of root traces and soil structure development (Hay, 1976; Kafumu, 2000) (Figure 2).

#### RESULTS

##### *General features*

Features related to subaerial exposure or soil formation are recognized in thin-sections for many intervals.

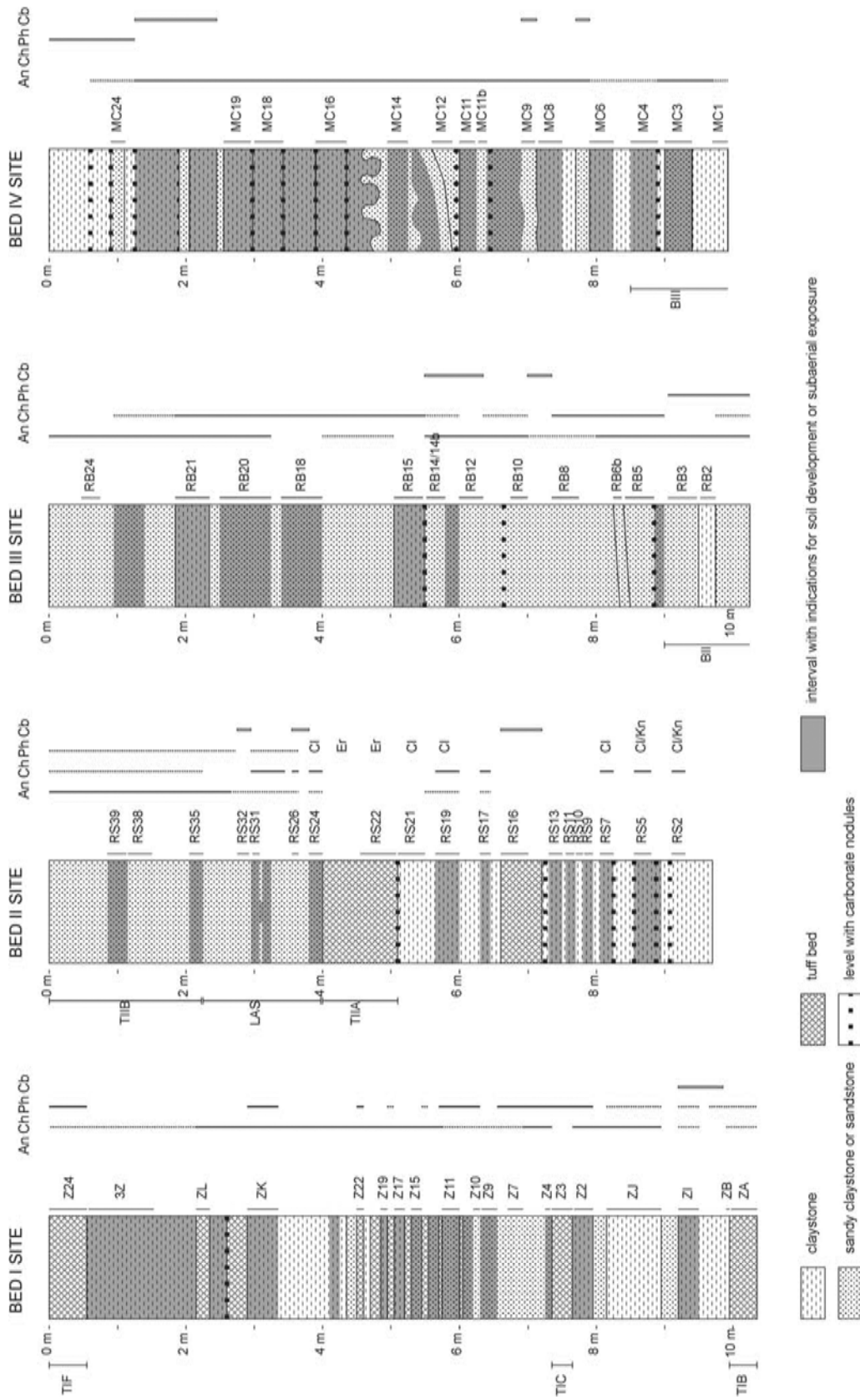


Figure 2. Stratigraphy, lithology and mineralogy of the studied exposures, and the positions of intervals for which thin-sections were prepared (stratigraphy and lithology modified from logs with initial stratigraphical interpretations and paleosol identifications by R. Paape and P. Kafumu, unpublished data). Stratigraphy: TIB, TIC, TIF, TIIA, TIIIB – Tuffs IB, IC, IF, IIA and IIB (Hay, 1976); LAS – lower augitic sandstone (Hay, 1976); BII – Bed II interval in the exposure at the studied Bed III site; BIII – Bed III interval in the exposure at the studied Bed IV site. Mineralogy: An – analcime, Ch – chabazite, Ph – phillipsite (major occurrences indicated by full lines, minor occurrences by dotted lines), Cl – clinoptilolite, Er – erionite, Kn – kenyaite, Cb – intervals with high carbonate content. Sampling levels: lines and sample codes indicate the intervals for which thin-sections were prepared.

They include features that can be considered to have developed during breaks in sedimentation, without being confined to the upper part of soil profiles, such as channels (small tubular pores related to faunal activity or root development), illuvial clay coatings (coatings consisting of translocated clay), sparitic calcite occurrences, Fe/Mn oxide nodules and Fe/Mn oxide impregnations along pores (see Tables 2 and 3). Other features are not necessarily associated with paleosurface levels because they might also have formed after incision of the gorge, *e.g.* some carbonate occurrences (*e.g.* micritic carbonate impregnation along pores) and certain types of

soil structure development. None of the mentioned features is unique to intervals identified as paleosol levels by Kafumu (2000).

Illuvial clay coatings, secondary carbonates and Fe/Mn oxides occur together in pores in some intervals. The most common sequences are clay coatings covered by sparitic calcite (RS5, RB2, RB5, RB12, MC11b), coarse clay coatings covered by fine clay (RS38, RB5, RB24) (see Figure 6d), and clay coatings with Fe/Mn oxide impregnation (RB2, RB6b, RB12, RB14, MC3, MC12). The reverse sequence is only observed for the last of these examples (Z11, RB21).

Table 2. Main features of zeolite occurrences in thin-sections, for the lake margin deposits of Beds I and II.

Unit	Sample	— Authigenic silicates —				— Other diagenetic features —				Mode	Associations
		An	Ch	Ph	Oth	fm	ch	cc	sc		
Bed II	RS32	-	-	-	-	-	-	-	xx		
	RS31	-	-	++	-	-	-	-	-	Ph-p/(r)	
	RS26	-	-	-	-	-	-	x	xx		
	RS24	-	++	-	Cl	-	xx	-	x	Ch-p	Ch → Cl
	RS22	-	-	-	Er	x	x	xx	-		
	RS21	-	-	-	-	-	-	-	xx		
	RS19	-	++	-	-	-	-	-	-	Ch-p-ic	
	RS17	-	++	-	Er	x	(x)	-	x	Ch-p	Ch → Er
	RS16	-	-	-	-	-	x	-	xx		
	RS13	-	-	-	-	-	-	-	-		
	RS13c	-	-	-	-	-	-	-	xx		
	RS11	-	-	-	-	-	-	-	-		
	RS11c	-	-	-	-	x	-	-	xx		
	RS10	-	-	-	-	-	-	-	x		
	RS9	-	-	-	-	-	-	-	-		
	RS7	-	++	-	-	-	x	-	-	Ch-p/(g)-i	
	RS5	-	++	-	Kn	-	x	-	-	Ch-p-i	Ch → Kn
	RS2c	-	-	-	-	-	-	-	xx		
Bed I	Z24	-	++	++	-	xx	-	-	-	Ch-g/(r), Ph-p/r	Ch → Ph
	3Z	-	++	-	-	-	-	-	-	Ch-p-ic	
	ZL	-	++	+	-	xx	-	(x)	-	Ch-g/r, Ph-p/r	Ch → Ph
	ZK	-	++	+	-	x	xx	x	-	Ch-g/r/p-i, Ph-p	Ch → Ph, Ch → afc → Ch
	Z22	-	++	+	-	xx	x	x	xx	Ch-g/(r), Ph-p/r	Ch → Ph
	Z19	-	++	-	-	x	-	-	-	Ch-g	
	Z17	-	++	-	-	x	-	-	-	Ch-p/(r)-i	
	Z15	-	++	+	-	xx	xx	-	-	Ch-g/(r), Ph-p/r	Ch → Ph
	Z11	-	++	+	-	xx	xx	xx	-	Ch-g/p/r, Ph-p/r	Ch → Ph
	Z10	-	++	+	-	xx	xx	xx	x	Ch-g/r, Ph-p/r	Ch → Ph
	Z9	-	++	-	-	(x)	xx	-	-	Ch-p/r-i	
	Z7	-	++	+	-	-	-	-	x	Ch-r/p, Ph-p	Ch → Ph
	Z4	-	++	+	-	xx	-	(x)	x	Ch-g/r/p, Ph-p/r	Ch → afc → Ch, Ch → Ph
	Z3	-	-	++	-	-	-	x	-	Ph-g/p/r	
	Z2	-	-	-	-	x	-	-	-		
	ZJ	-	++	+	-	xx	x	-	x	Ch-s, Ph-p	Ph → fm, Ph → sc
	ZI	-	-	(+)	-	-	x	-	-		
	ZB	-	+	-	-	xx	x	-	-	Ch-r/(p)	
ZA	-	+	(+)	-	xx	xx	-	-	Ch-p-i, Ph-s/(p)	Ch → fm	

Authigenic silicates: An – analcime, Ch – chabazite, Ph – phillipsite, Oth – others (Cl – clinoptilolite, Er – erionite, Kn – kenyaite, Nt – natrolite) [(+)/+/++ signs indicate relative abundance]. Other diagenetic features: fm – Fe/Mn oxides, ch – channels, cc – clay coatings, sc – secondary carbonates [(x)/x/xx signs indicate relative abundance]. Mode of occurrence (for chabazite and phillipsite): g – groundmass, p – pores, s – glass shards, v – volcanic rock fragments, i – infillings, ic – infillings in cracks. Associations: cc – coarse clay coatings, fc – fine clay coatings, afc – authigenic fine clay, fm – Fe/Mn oxides, sc – sparitic carbonates; → sequence (not replacement), + co-occurrence (with no apparent difference in time of development).



Table 3. Main features of zeolite occurrences in thin-sections, for the fluvial deposits of Beds II to IV.

Unit	Sample	— Authigenic silicates —				Other diagenetic features				Associations
		An	Ch	Ph	Oth	fm	ch	cc	sc	
Bed IV	MC24	+	-	++	-	x	-	xx	-	Ph → fm, Ph → fc, fc → Ph, An + Ph
	MC19	++	-	-	-	xx	-	-	xx	
	MC18	++	-	-	-	xx	-	-	xx	
	MC16	++	-	-	-	xx	-	-	x	
	MC14	+	-	-	-	xx	-	-	x	An → sc, sc + An
	MC12	++	-	-	-	xx	x	xx	-	cc + An
	MC11	+	-	-	-	xx	x	(x)	x	
	MC11b	+	-	-	-	xx	(x)	x	xx	sc + An, fc + An
	MC9	+	-	-	-	xx	-	x	x	
	MC8	+	-	-	-	xx	-	-	-	
MC6	+	-	-	-	xx	-	-	-		
Bed III	MC4	-	-	-	-	xx	-	-	-	
	MC3	++	-	-	-	xx	xx	xx	-	fc → An
	MC1	++	-	-	-	xx	xx	xx	-	fc → An
	RB24	+	-	-	-	xx	-	xx	x	cc → An → fc, fc + An (+ sc)
	RB21	+	++	-	Nt	x	xx	xx	-	Ch/Nt → fc, cc → Ch
	RB20	+	++	-	Nt	xx	xx	-	x	An/Ch → Nt
	RB18	-	++	-	-	xx	-	-	xx	Ch + sc
	RB15	-	++	-	-	xx	x	-	-	
	RB14b	+	-	-	-	xx	-	x	xx	An → fc, sc + An
	RB14	+	-	-	-	x	-	xx	xx	An → sc
	RB12	+	-	-	-	xx	-	x	xx	
	RB10	+	-	-	-	x	(x)	xx	x	fc → An, An → sc
	RB8	++	(+)	+	-	xx	x	-	xx	An/Ph → sc, An + Ph
	RB6b	++	-	-	-	x	xx	xx	-	fc → An
RB5	++	-	-	-	xx	xx	x	x	cc/fc → An	
Bed II	RB3	++	-	++	-	xx	-	(x)	-	An + Ph, fc → Ph/An
	RB2	+	-	++	-	xx	x	x	xx	sc → Ph, fc → Ph, Ph → An
	RS39	++	(+)	+	-	-	xx	xx	-	An → Ph
	RS38	++	-	+	-	x	xx	xx	x	cc → An → fc, An → Ph, An/Ph → sc, sc → Ph
	RS35	++	-	++	-	-	xx	xx	x	sc/fc → An, An → Ph, cc → An → fc

Legend – see that for Table 2.

#### General features of zeolite occurrences

Each zeolite mineral has the same crystal morphology throughout the deposits: pseudocubic rhombohedral for chabazite, elongated prismatic with {110} terminations for phillipsite (see Figure 5a), trapezohedral for analcime (see Figure 7d), elongated prismatic with {001} terminations for erionite (see Figure 4b), tabular for clinoptilolite, and lath-shaped with {111} terminations for natrolite (see Figure 6b) (cf. Mumpton and Ormsby, 1976; Gottardi and Galli, 1985). Typical crystal sizes for the most common zeolite minerals are up to 5 µm for chabazite and 15 to 25 µm for analcime and phillipsite. Authigenic K-feldspar was not recognized in thin-sections, and its distribution could not be documented by the available XRD results because abundant detrital feldspar masks its possible presence.

All zeolite minerals are dominated by Na and free of Ca, as determined by EDS analysis. Chabazite is free of K in most intervals (ZA, Z9, Z17, RS7, RS24), except at the top of Bed III (RB15, with a Na/K atomic ratio of ~6/1). All analyzed phillipsite contains significant amounts of K (Na/K ~4/1 to 2/1) (Z3, ZL, RB2,

MC24). Erionite (Na/K ~3/1) and clinoptilolite (Na/K ~10/1) are also K-bearing (RS19, RS21, RS22). In natrolite (RB20, RB21), as well as analcime (RB8, RB15), Na is the only extra-framework cation.

In the following paragraphs, the nature of zeolite occurrences is described for the lake margin and fluvial deposits. The boundary between these facies is the base of Tuff IIB (see Figure 2). For every interval, an overview of the zeolite minerals that are present is first given, followed by a description of their mode of occurrence and the relationship between the various zeolite minerals, and then by information about their relationship with other diagenetic features. For associated occurrences of zeolites and Fe/Mn oxides, only intervals where zeolites are covered by Fe/Mn oxides are reported below. The reverse situation is much more common, throughout Beds I to IV.

#### Zeolites in lake-margin deposits of Bed I

Chabazite is the most abundant zeolite in the Bed I deposits (Table 2; Figure 2). Phillipsite is recognized in many samples as a subordinate phase and occasionally as the dominant zeolite mineral (Z3).

Chabazite occurs, in varying degrees, as (1) the main or sole constituent of altered vitric volcanic rock fragments and glass shards, (2) coatings and infillings of pores, and (3) a major constituent of the groundmass. Occurrences as part of altered rock fragments include chabazite infillings and coatings of vesicles, generally without any glass remaining between these relics (Figure 3a). The vesicles are generally lined by thin clay coatings with high interference colors (smectite), also in fragments or parts of fragments where no zeolites developed. Chabazite in pores is restricted to channels in several intervals, and it is absent in more recently developed cracks. It commonly occurs as complete infillings (rather than coatings), composed of small euhedral to subhedral crystals with a limited degree of intergrowth (ZA, Z9, Z17, ZK) (Figure 3b). In intervals with a high chabazite content outside the pore system (Z4, Z10, Z11, Z15, Z19, Z22, ZK, ZL, Z4), the groundmass has a distinctive greyish color in comparison with intervals with a low chabazite content.

Phillipsite is mainly recognized in pores, commonly occurring in larger numbers of pores than chabazite and

also appearing in intervals that do not contain any chabazite in the pore system. It is also recognized as part of altered volcanic rock fragments that largely consist of xenotopic chabazite. Phillipsite always occurs along the surface of chabazite coatings or aggregates where both minerals occur together (Figure 3c).

Chabazite and phillipsite occurrences are only rarely associated with other diagenetic features. They are impregnated by Fe/Mn oxides in three intervals (ZA, ZJ, ZK), and phillipsite coatings are locally covered by sparitic carbonates (ZJ). Elsewhere, chabazite coatings and infillings contain intercalations of yellowish fine clay with second-order interference colors (Z4, ZK) which are different from the illuvial clay coatings in other parts of the deposits (Figure 3d).

#### *Zeolites in lake-margin deposits of Bed II*

*Deposits below Tuff IIA.* The Bed II deposits below Tuff IIA (see Figure 2) include a central partly diatomaceous interval without any zeolites (RS8 to RS16). Chabazite is by far the most common zeolite outside this interval

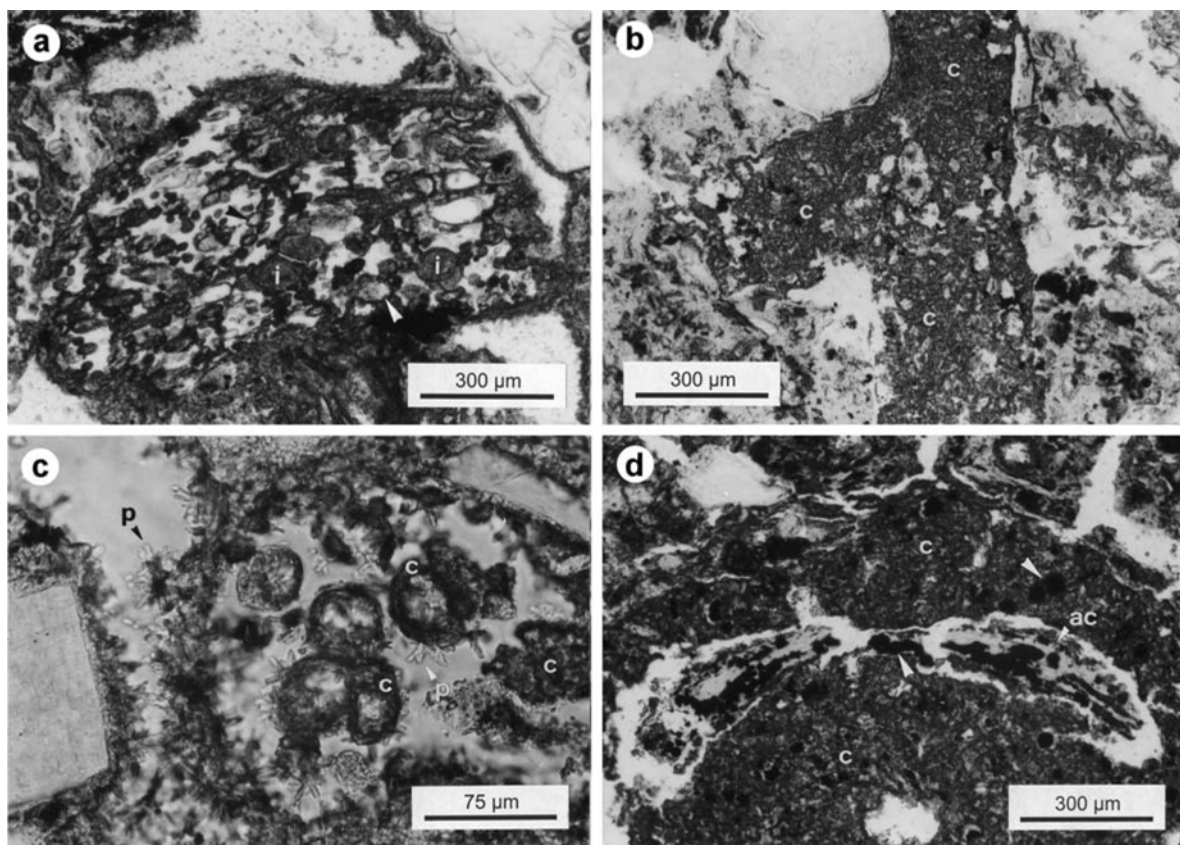


Figure 3. Zeolites in lake-margin deposits of Bed I. (a) Partly altered vitric volcanic rock fragment, with chabazite coatings (arrow) and infillings [i] of vesicles (interval Z7; plain polarized light [PPL]). (b) Complete chabazite [c] infilling of a branching root gallery (Z9; PPL). (c) Phillipsite (elongated prismatic crystals [p], along the sides of pores (left) and covering chabazite [c] infillings and coatings of vesicles in a completely altered vitric volcanic rock fragment (right) (chabazite → phillipsite sequence) (Z3; PPL). (d) Thick chabazite [c] coating, with an intercalation of authigenic clay [ac] (chabazite → authigenic clay → chabazite); both materials, formed in a channel of which only a small central zone remains empty (bottom), are locally impregnated with Fe/Mn oxides (arrows) (ZK; PPL).

(Table 2; Figure 2). Erionite is also recognized, as well as kenyaite ( $\text{NaSi}_{11}\text{O}_{20.5}(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ ). Chabazite only occurs in the intervals with the strongest field indications for subaerial exposure (heterogeneous aspect, dark color) (RS5, RS7, RS17, RS19). It occurs chiefly in pores and only rarely as part of altered volcanic rock fragments. In one interval, vitric fragments are nearly unaltered, with thin clay coatings along the sides of vesicles as the only sign of alteration (RS16). Chabazite is present in many pores in all chabazite-bearing intervals, but not in recent cracks with closely matching sides, which occasionally cross chabazite occurrences. Erionite occurs as crystals that cover chabazite in pores (RS17). Spherulitic kenyaite aggregates are recognized for a few pores with chabazite coatings or infillings (RS5) (Figure 4a).

**Tuff IIA.** Erionite is the only zeolite mineral in Tuff IIA (Figure 4b). It occurs primarily as small crystals (20–35  $\mu\text{m}$ ) in pores, and it is also recognized in vesicles of a few glass fragments. All volcanic glass in this interval is nearly unaltered, with only thin clay coatings around vesicles.

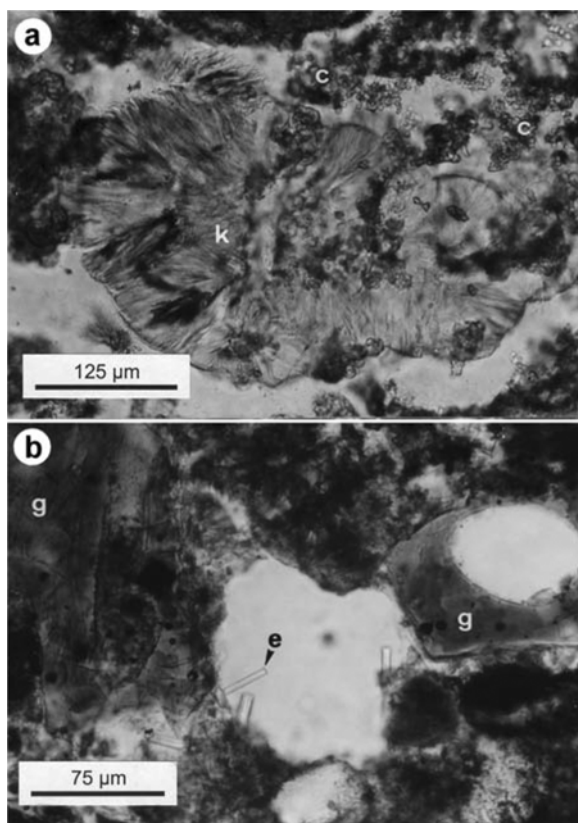


Figure 4. Authigenic silicates in lake-margin deposits of Bed II. (a) Spherulitic kenyaite aggregate [k] in a pore with a chabazite infilling [c] (kenyaite  $\rightarrow$  chabazite sequence) (RS5; PPL). (b) Erionite crystals [e] in pores, in an interval containing nearly unaltered volcanic glass [g] (RS22; PPL).

**Lower augitic sandstone.** The basal part of this interval (RS24) contains chabazite coatings in pores, similar to those in lower parts of Bed II. It also contains clinoptilolite, which occurs as isolated crystals covering chabazite coatings (RS24). A higher interval only contains (abundant) phillipsite, along the sides of pores (RS31).

#### *Zeolites in fluvial deposits of Bed II*

**Tuff IIB.** The most common zeolite in Tuff IIB is analcime, occurring as coatings in pores (Table 3; Figure 2). The interval also contains considerable amounts of phillipsite, which covers any analcime that is present. Chabazite is locally associated with analcime in one interval (RS39). Analcime and phillipsite are commonly covered by sparitic calcite and fine clay coatings (Figure 5a). Analcime also occurs between coarse and fine clay coatings (RS35, RS38), and phillipsite locally covers sparitic calcite (RS38).

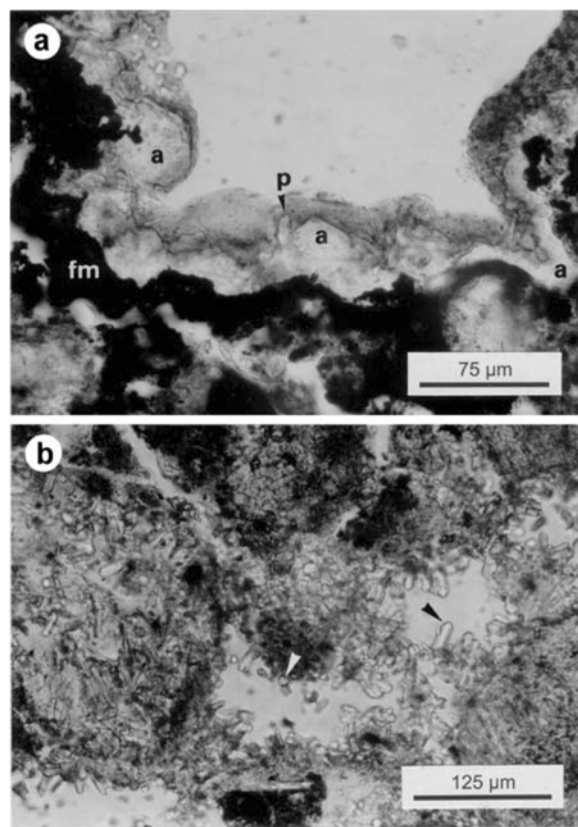


Figure 5. Zeolites in fluvial deposits of Bed II. (a) Analcime coating [a], overgrown by phillipsite crystals [p], followed by a fine clay coating, with strong Fe/Mn oxide impregnation of the sediment below the zeolite coating (fm) (Fe/Mn oxides  $\rightarrow$  analcime  $\rightarrow$  phillipsite  $\rightarrow$  fine clay sequence) (RS38; PPL). (b) Analcime (small equant crystals) (e.g. white arrow) and phillipsite (elongated prismatic crystals) (e.g. black arrow), occurring together in pores (right) and in cavities in an altered volcanic rock fragment (left) (analcime + phillipsite association) (RB3; PPL).



*Top of Bed II.* Phillipsite, occurring as coatings in pores, is the most abundant zeolite mineral in this part of Bed II (RB2, RB3). Analcime occurs together with phillipsite in the upper part of the interval (RB3) (Figure 5b). In lower parts, analcime mostly occurs in dissolution cavities in altered volcanic rock fragments and it locally covers phillipsite in pores (RB2). Both minerals cover fine clay coatings in some pores (RB2, RB3), and phillipsite locally covers sparitic calcite (RB2).

### *Zeolites in fluvial deposits of Bed III*

Analcime is the dominant zeolite in the Bed III deposits, occurring as sub/euhedral crystals and xenotopic isotropic coatings (Table 3; Figure 2). Phillipsite is locally present in lower parts of the interval. Chabazite and minor amounts of natrolite occur in the upper half, above a highly calcareous interval with a high micritic carbonate content of the groundmass and a sparitic carbonate cement (RB14).

The zeolites in Bed III occur exclusively as coatings and infillings of pores. In thin-sections of intervals with

prominent mottling, there is no difference in zeolite content between parts with a high Fe oxide content and zones with Fe oxide depletion (RB15, RB18, MC1, MC3). In some samples with a high secondary carbonate content, analcime only occurs in parts with a non-calcareous groundmass and without carbonates or clay coatings in pores (RB12, RB14). Pores containing isolated analcime crystals include dissolution cavities in altered volcanic rock fragments. Chabazite occurs as relatively coarse-grained optically anisotropic coatings that are generally xenotopic (see Figure 6a), in contrast to the fine-grained aggregates of predominantly subhedral crystals in Beds I and II (see Figure 3b, 3d). Chabazite also occurs around corroded augite grains (RB15, RB18) (Figure 6a). Some grains of this type are surrounded by calcite instead of chabazite (RB18). Phillipsite occurs together with analcime in the only phillipsite-bearing interval (RB8). Natrolite, occurring as relatively large sub/euhedral crystals (50–100  $\mu\text{m}$ ), covers both analcime and chabazite (Figure 6b).

Analcime commonly covers fine clay coatings (RB5, RB6b, RB10, MC1, MC3), and also occurs along the

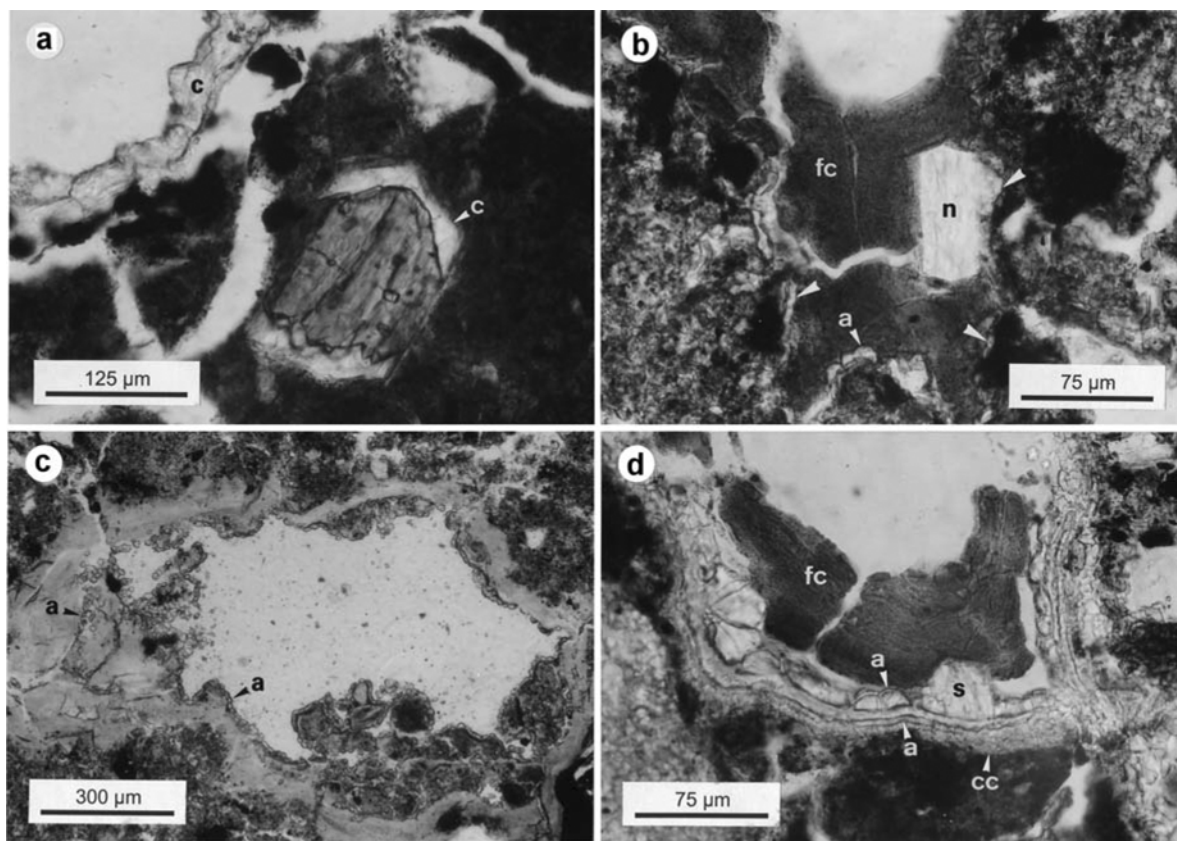


Figure 6. Zeolites in fluvial deposits of Bed III. (a) Chabazite [c] around a corroded augite grain (right) and as a coating around a pore (top left) (RB15; PPL). (b) Subhedral natrolite crystal [n], covered by a fine clay coating [fc] and covering a thin analcime or chabazite coating (arrows) with some subhedral analcime crystals [a] (analcime/chabazite → natrolite → fine clay sequence) (RB21; PPL). (c) Analcime crystals [a] along the surface of a fine clay coating (labeled in the center) and in cracks within the coating (labeled at left) (fine clay → analcime) (MC1; PPL). (d) Coarse clay coating [cc], followed by a thin analcime [a] coating, followed by yellowish fine clay, followed by subhedral analcime [a] and sparitic carbonates [s], followed by orange fine clay (coarse clay → analcime → fine clay → analcime + sparitic calcite → fine clay) (RB24; PPL).

sides of cracks within these coatings (RB6b, MC1, MC3) (Figure 6c). Elsewhere, analcime, chabazite or natrolite are covered by fine clay (RB14b, RB21, RB24) (see Figure 6b). In one interval (RB24), analcime occurs between coarse and fine clay coatings, and it also occurs within the fine clay, partly with associated sparitic calcite and with a pale color of the clay below the zeolite band (Figure 6d). Chabazite covers coarse clay coatings in an interval in which it is covered by fine clay in other pores (RB21). In several samples, analcime, phillipsite or chabazite are covered by sparitic calcite (RB8, RB10, RB14, RB14b), or they occur together with sparitic calcite without a clear difference in time of development (RB18). A sparitic carbonate cement locally encloses a thin analcime coating parallel to the sides of a pore (RB14b).

#### *Zeolites in fluvial deposits of Bed IV*

Analcime is the only zeolite mineral in most parts of Bed IV, occurring in high concentrations in the upper part of this unit (MC12, MC16, MC18, MC19) (Table 3; Figure 2). Phillipsite only occurs at the top of Bed IV (MC24).

Analcime occurs exclusively as coatings of pores, which include packing pores (primary pores), channels and cracks. It generally occurs in large parts of the pore system (Figure 7a), but very seldom as complete infillings of wide pores. Some analcime occurrences are crossed by cracks without zeolites. Nowhere is analcime associated with vitric volcanic rock fragments. At the top of Bed IV (MC24), rock fragments of this type are completely altered to clay, without any associated zeolites (Figure 7b). In the only phillipsite-bearing interval (MC24), most phillipsite occurs as small crystals (10  $\mu\text{m}$ ) in pores, throughout the sample. In this interval, dissolution cavities in volcanic rock fragments and mineral grains contain larger phillipsite crystals (up to 75  $\mu\text{m}$ ); analcime occurs together with these phillipsite crystals, representing all analcime that is recognized for this interval (Figure 7c).

In an interval with a high sand content (MC 9 to MC14), analcime is only present in pores that contain clay coatings or secondary carbonates, occurring within coarse or fine clay coatings (MC11b, MC12) or as crystals that are covered or enclosed by sparitic calcite (MC11b, MC14) (Figure 7d). In the only phillipsite-

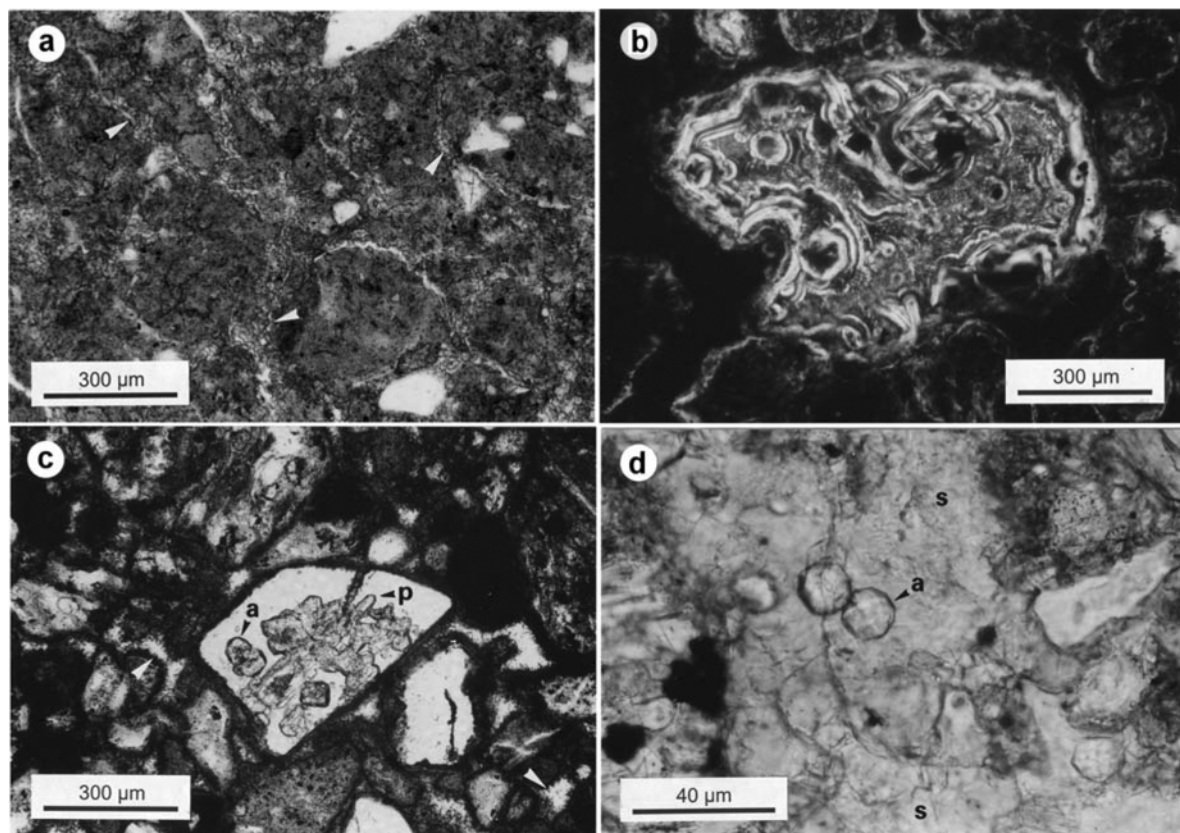


Figure 7. Authigenic silicates in fluvial deposits of Bed IV. (a) Analcime infillings of narrow cracks (arrows) (MC18; PPL). (b) Volcanic glass fragment, completely altered to smectite (MC24; circular polarized light). (c) Phillipsite [p] and analcime [a] in an altered mineral grain (analcime + phillipsite association), in an interval with small phillipsite crystals along the sides of most pores (arrows), covering thin fine clay coatings (fine clay  $\rightarrow$  phillipsite sequence) (MC24; PPL). (d) Euhedral analcime crystals [a], enclosed by a sparitic carbonate cement [s] (analcime + sparitic calcite association) (MC11b; PPL).

bearing interval (MC24), phillipsite covers clay coatings throughout the sample, and it is covered by a thick paler clay coating in one pore. Phillipsite is also covered by Fe/Mn oxides in some pores.

## DISCUSSION

Zeolite formation in lake and soil environments requires conditions with high alkalinity and relatively high salinity, resulting in high Al and Si concentrations and elevated  $(\text{Na}+\text{K}+\text{Ca})/\text{H}^+$  ratios (e.g. Sheppard and Hay, 2001). These conditions are commonly met in geological settings with volcanic activity, as in several rift valley lakes with zeolite-bearing deposits near Olduvai (Hay, 1966, pp. 36–39; Surdam and Eugster, 1976). Zeolite mineralogy is determined by Si/Al ratios and by the relative concentrations of potential extra-framework cations in solution. Regardless of chemical requirements, three main possible mechanisms or contexts of zeolite formation should be considered: (1) zeolite formation pencontemporaneous with sedimentation, by an interaction of allogenic material with lake water (e.g. Hay, 1970, 1976), (2) interaction with pore water during subaerial exposure (e.g. Renault, 1993), during breaks in sedimentation, and (3) processes acting during subaerial exposure after incision of the gorge (e.g. Hay, 1963, 1964). In the following discussion, lake-margin deposits and fluvial deposits are treated separately. Table 4 presents a general summary of the main features of zeolite occurrences in all major intervals, based on more detailed information given in the Results section, including Figure 2, Table 2 and Table 3.

### Lake-margin deposits

Chabazite is the dominant zeolite in the studied lake-margin deposits of Bed I and the lower part of Bed II. In saline alkaline lake environments, this mineral typically forms in outer parts of the lake basin, at lower salinities and alkalinities than in more central parts, where analcime and K-feldspar are the dominant authigenic silicate minerals (e.g. Sheppard and Gude, 1973; Gude and Sheppard, 1988).

Part of the zeolites in the lake-margin deposits formed by interaction of volcanic material with saline alkaline solutions, as recorded by the common occurrence of chabazite as an alteration product of vitric volcanic rock fragments. The first step in their alteration was the development of thin smectite coatings, which were commonly preserved when chabazite formed during continued alteration of the glass. During a final stage, glass dissolution often proceeded without local zeolite formation, as shown by the common absence of glass between isolated chabazite occurrences that represent coatings and infillings of vesicles in the original glass fragments.

Interaction between volcanic material and alkaline solutions can also account for high chabazite concentrations in the groundmass, when glass dissolution and zeolite formation take place in different parts of the sediments instead of representing local replacement reactions. Another possible mechanism for the development of a zeolite-rich groundmass is replacement of fine-grained detrital Al silicates (e.g. Remy and Ferrell, 1989; Renault, 1993). Both types of zeolite formation within the groundmass, in contrast to mineral formation

Table 4. Summary of the main features of zeolite occurrences in the studied deposits.

Unit	Zeolite minerals		Main mode of occurrence	Main sequences and associations*
	Dominant	Others		
<b>Fluvial deposits</b>				
Bed IV	analcime	phillipsite	pores	analcime + illuvial clay or sparitic carbonates phillipsite + analcime illuvial clay → phillipsite
Bed III	analcime	phillipsite, chabazite, natrolite	pores	analcime/chabazite → natrolite various zeolites → illuvial clay or sparitic carbonates illuvial clay → analcime
Bed II	analcime	phillipsite, chabazite	pores	analcime → phillipsite analcime/phillipsite → illuvial clay or sparitic carbonates illuvial clay → analcime/phillipsite sparitic carbonates → phillipsite
<b>Lake-margin deposits</b>				
Bed II	chabazite	erionite, phillipsite, clinoptilolite	pores	chabazite → erionite chabazite → clinoptilolite chabazite → kenyaite
Bed I	chabazite	phillipsite	volcanic debris, groundmass, pores	smectite → chabazite → phillipsite phillipsite → sparitic carbonates chabazite + authigenic clay

\* → and + signs as in Tables 2 and 3 (right column)



in macropores, require continuous contact with saline alkaline solutions that pervade the deposits. It will generally take place in subaqueous settings, or at or near water saturation in subaerial settings, rather than within or above the vadose zone of a soil profile.

Chabazite was formed or redistributed extensively within the pore system during periods of subaerial exposure. It commonly occurs as complete infillings consisting of loosely stacked crystals, rather than dense intergrowths that may have formed by continued growth of coatings along the sides of a pore. The development of loose infillings generally requires conditions resulting in mineral formation in water-filled pores, at or above the groundwater table. The nature of these chabazite occurrences therefore suggests that zeolite formation in pores at this stage took place under conditions with a shallow groundwater table below a subaerially exposed surface.

Zeolites are largely absent in an interval that includes abundant diatom remains (RS10, RS11) and unaltered glass (RS16). Lake-water salinity and alkalinity must have been too low to allow zeolite formation, which is compatible with the persistence of freshwater conditions with relatively low pH due to decaying organic matter in wetlands around springs (Deocampo and Ashley, 1999). Zeolites only occur at a few levels in this part of Bed II, representing thin surface horizons affected by zeolite formation during periods of subaerial exposure with very shallow groundwater depths.

Chabazite in altered volcanic rock fragments may, in principle, have formed at a different stage than chabazite in pores, *e.g.* at an earlier stage by subaqueous diagenesis. If the times of development were different, both periods of zeolite formation were characterized by similar chemical environments, producing the same mineral phase. Phillipsite, which always covers chabazite where both minerals occur together and which occurs in larger numbers of pores than chabazite, mainly formed at a later stage, after further development of the pore system. In contrast to chabazite in this part of the deposits, it never formed under conditions that resulted in the development of loose zeolite infillings. Zeolite formation was only locally followed by a period of frequent water saturation with Fe/Mn oxide redistribution or the development of sparitic calcite infillings.

The overall predominance of chabazite suggests a relatively early stage of inflow water evolution, with relatively low salinity and alkalinity. This is also indicated by the occurrence of associated intercalations of authigenic smectite, which generally forms from less evolved solutions than zeolite minerals. The formation of phillipsite after a period of chabazite formation records a change in chemical environment. This change may, in principle, have taken place during a single period of zeolite development (*e.g.* Brey and Schmincke, 1980), but there are no indications of this in the studied deposits. Phillipsite forms in conditions with a higher pH

(Brey and Schmincke, 1980) or higher  $K^+$  activities (Chipera and Apps, 2001) than chabazite. It can therefore be expected to have formed during drier periods, from more evolved highly alkaline solutions with high relative  $K^+$  concentrations following a stage with formation of Na-dominated authigenic minerals. The formation of erionite and clinoptilolite after chabazite requires a significant increase in Si/Al activity ratios, which can be caused by a decrease in pH (Mariner and Surdam, 1970) or by the removal of Al by zeolite formation (*e.g.* Sheppard and Gude, 1969). An influence of local sediment composition on zeolite mineral assemblages is suggested by aberrant (non-chabazitic) zeolite occurrences in a number of tuff beds (phillipsite predominance in Tuff IC and IF, erionite in Tuff IIA).

#### *Fluvial deposits*

Analcime is the dominant zeolite in the fluvial deposits of Beds II to IV, in agreement with earlier reports (*e.g.* Hay, 1966, 1970). Analcime typically forms at rather high salinity and alkalinity, in more central parts of saline alkaline lake basins than other zeolite minerals (*e.g.* Sheppard and Gude, 1969, 1973; Gude and Sheppard, 1988). In such environments, analcime formation is favored by high  $Na^+/H^+$  ratios, low Si/Al ratios and low  $H_2O$  activities. There are no clear indications that a change in sediment composition contributed to the abrupt shift from chabazite to analcime predominance.

Phillipsite occurs in the lower part of the sequence of fluvial deposits, representing a transition to the zeolite assemblage that is recognized for the lake-margin deposits. The common co-occurrence of phillipsite and analcime (RB3, RB8, MC24), without indications of differences in time of development, shows that they formed in conditions that allow their co-precipitation (see *e.g.* La Iglesia *et al.*, 1991). Chabazite is recognized in thin-sections for the upper part of Bed III, above an interval with a high secondary carbonate content (RB14). The re-appearance of relatively abundant chabazite seems to be related to a temporary change in water chemistry, associated with a period of subaerial exposure that is recorded by that calcareous interval. A change in zeolite mineralogy following a period of exposure with carbonate enrichment is also recorded at the top of Bed IV, where the base of a phillipsite-dominated section coincides with the top of an interval with an upward increase in (nodular) carbonate content. Natrolite, which has an even lower Si/Al ratio and higher extra-framework cation content than analcime (see Table 1), formed under conditions of higher salinity and alkalinity than this more common phase.

Zeolites in the fluvial deposits occur nearly exclusively in pores. In contrast to chabazite in parts of the lake-bed deposits, nowhere do they occur as loose complete infillings of macropores, which would imply a lower degree of water saturation. Zeolites in the fluvial deposits are not associated with volcanic rock fragments,



except locally at the top of Bed IV. Analcime and phillipsite occur in dissolution cavities in some rock fragments, but this is not necessarily related to their dissolution. Similarly, chabazite around corroded augite grains can be infillings of dissolution cavities rather than replacement products. Only the formation of analcime and phillipsite associated exclusively with altered rock fragments at the top of Bed IV (MC24) is clearly related to local dissolution. The presence of analcime as part of the groundmass is not recognized in thin-sections (in contrast to chabazite in Bed I), and XRD results indicate that submicroscopic analcime is not a major constituent. An absence of submicroscopic zeolites would not exclude the possibility that zeolites formed to a large extent by an interaction of saline alkaline pore water with clay minerals or amorphous Al silicates. There are no indications, in any case, that analcime formed by transformation of a zeolite precursor as has been inferred for several other analcime occurrences (e.g. Sheppard and Gude, 1969, 1973; Ratterman and Surdam, 1981).

No clear relationship exists between zeolite content or mineralogy and the presence of indications for soil development or subaerial exposure. Significant changes do occur around some lithological discontinuities, including levels which represent paleosurfaces: (1) the lower boundary of the fluvial deposits marks an abrupt change to an analcime-dominated zeolite assemblage; (2) the common occurrence of phillipsite ends abruptly at the boundary between Beds II and III; (3) a paleosurface level marks the base of a chabazite-rich interval in the middle of Bed III; (4) a significant increase in analcime content occurs above the top of a sandy interval in the middle of Bed IV; and (5) a paleosurface is recognized for the lower boundary of the phillipsite-dominated upper part of Bed IV. These examples show that breaks or major changes in sedimentation have an impact on zeolite mineralogy, but not through zeolite formation in deposits below an exposed surface. Vertical variations compatible with zeolite enrichment by groundwater evaporation along an exposed surface, which was subsequently covered by deposits with a relatively low zeolite content, are only recognized for the top of both Bed III intervals with reddish deposits (RB4 to RB6b, and RB15 to MC4).

Part of the zeolites in the fluvial deposits formed at an early stage, after the development of secondary pores but before the formation of (fine) clay coatings or sparitic carbonates. For one interval, early analcime formation is also suggested by indications that it was partly dissolved before or during a period with secondary carbonate enrichment and clay illuviation (RB12, RB14). In several intervals, zeolites occur between or within other diagenetic features in pores. Analcime locally occurs between a coarse-clay coating, which typically forms at a relatively short distance from the soil surface, and a fine-clay coating, formed at greater depths within the vadose zone. Zeolites occur-

ring within fine-clay coatings show that zeolite formation occasionally continued during periods of fine clay illuviation, under conditions of alternating wetting and drying. Analcime associated with sparitic calcite formed under rather stable conditions with a high degree of water saturation, which is generally required for the development of a sparitic carbonate cement. Iron oxide depletion below intercalations of analcime and sparitic calcite is compatible with this, because it indicates reducing conditions which can be related to water saturation. Conditions required for the development of these associated zeolite and carbonate occurrences are encountered in the lower part of the capillary fringe above the water table, where zeolite enrichment can be strong (Bernhard and Barth-Wirsching, 2002).

Although some zeolites in the fluvial deposits formed at an early stage, most zeolites formed at a late stage, after a period of clay illuviation and locally after the development of sparitic calcite coatings or infillings. It also generally postdates Fe/Mn oxide redistribution under conditions with a fluctuating groundwater table, recorded by the presence of analcime coatings in pores with Fe/Mn oxide impregnation of the sediment along their sides. Zeolite formation after a period of Fe/Mn oxide redistribution is also suggested by the lack of variations in zeolite content with Fe/Mn oxide content in mottled intervals. Other features recording late-stage development include the presence of analcime in cracks that formed within illuvial clay coatings. It is also recorded by the occurrence of analcime in large parts of the pore system, including planar pores formed by shrinkage, instead of being confined to channels as in large parts of the lake-margin deposits. Some of these zeolites could have formed after the deposits became exposed to the atmosphere along the sides of the gorge. However, there are various indications that zeolites did not form extensively after incision of the gorge, which was eroded to its present level prior to deposition of the Naisiusiu Beds (Hay, 1976) (62 ky BP; Skinner *et al.*, 2003). Indications against zeolite formation after exposure along the sides of the gorge include the absence of late-stage zeolites in all intervals in which zeolites are covered by clay coatings or secondary carbonates and the mentioned changes in zeolite content or mineralogy around lithological discontinuities.

## CONCLUSIONS

The occurrence of zeolites in the Olduvai Basin is largely related to the presence of volcanic rocks and debris within the catchment. Their presence mainly contributes to zeolite formation through the effect of their alteration on lake-water and pore-water composition (e.g. Jones *et al.*, 1977). Weathering of volcanic rocks can also supply detrital clays that can interact with saline alkaline lake or soil water to form zeolites at a later stage. Although pseudomorphic replacement of

vitric volcanic debris is common in some of the deposits, volcanic material contributes to zeolite formation only to a limited extent as a constituent that is susceptible to *in situ* alteration to zeolites. As a result, zeolites formed in large quantities outside tuff layers and within pores in tuffaceous and non-tuffaceous deposits, which is ultimately related to high element mobilities in alkaline environments. The same type of zeolite distribution can be expected for other zeolite-bearing deposits with an important volcanic component.

Some of the zeolites may have formed in a subaqueous setting, but they certainly formed extensively during periods of subaerial exposure, resulting in their common occurrence in pores. The recognition of paleosurfaces that were exposed during periods of zeolite formation is difficult. A detailed study of vertical trends would be needed, but their interpretation will be complicated by the superposition of zeolite occurrences that formed during successive stages of subaerial exposure. In addition, studies of vertical variations might essentially produce a record of groundwater levels during periods of zeolite formation (English, 2001; Bernhard and Barth-Wirsching, 2002).

Establishing the timing of zeolite formation must be done with care for deposits with intervals showing indications of subaerial exposure and for deposits susceptible to zeolite enrichment or redistribution in present-day exposures. The present study illustrates the use of several criteria to obtain information about this aspect of zeolite formation, such as the relationship between zeolite occurrences and illuvial clay coatings or sparitic carbonate infillings.

Variations in zeolite mineralogy reflect changes in water composition. Within the study area, the water had a relatively low salinity and alkalinity during deposition and early diagenesis of the lake-margin deposits of Bed I and the lower part of Bed II, replaced by pore water with higher K/Na ratios during later stages of diagenesis. In the younger fluvial deposits, zeolites formed under conditions with more highly saline, Na-rich solutions. This type of sequence, whereby an analcime-dominated facies is succeeded by a facies dominated by other zeolite minerals, is more commonly recognized as a lateral trend. Its occurrence at Olduvai is related to a fairly abrupt basin-wide change in depositional environments rather than to a gradual change in patterns of variation in water composition.

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