Paleolakes of Eastern Africa: Zeolites, Clay Minerals, and Climate

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Scanning electron microscope image of phillipsite (long) and chabazite (blocky) crystals from an altered tuff from the Olduvai paleolake. Image is 30 microns across. PHOTO: L. MCHENRY.

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The eastern branch of the East African Rift System hosts many shallow modern lakes and paleolakes, which can be sensitive recorders of changing climate conditions (complicated by tectonics) during the past few million years. However, many of such lakes are saline–alkaline (salty and high pH), and these conditions do not easily preserve pollen and other biologically derived paleoclimate indicators. Fortunately, some preserved minerals that formed in these extreme environments reflect subtle shifts in lake water chemistry (controlled by changes in climate conditions) and therefore provide a continuous record of local and regional climate change. We present two different mineral proxies (zeolites and clays) from two different paleolake basins (Olduvai Gorge, Tanzania, and Chew Bahir, Ethiopia) as examples.

KEYWORDS: zeolites; clay minerals; paleolake; climate; eastern Africa

INTRODUCTION AND BACKGROUND

The eastern branch of the East African Rift System (EARS), which bisects eastern Africa from Ethiopia south through Kenya and into Tanzania, has hosted plentiful lakes through the Pliocene to the present (FIG. 1), varying from fresh to highly saline–alkaline (high pH and very salty) (e.g., Trauth et al. 2007). Paleolakes, which are lakes that existed in the past but are currently dry, preserve a record of past climate and tectonic changes that can help reconstruct how the environment evolved during the past few million years (Trauth et al. 2007; Campisano et al. 2017). In eastern Africa, this record is of particular interest because it coincides with local fossil and stone tool evidence for hominin evolution (e.g., Campisano et al. 2017). Studying these paleolake deposits can thus provide insight into the environments in which hominins lived and help evaluate hypotheses in which climate dynamics and inferred habitat transformations may have affected their physical and cultural evolution (e.g., Campisano et al. 2017).

The paleolakes of the eastern branch of the EARS document dramatic shifts in climate during the Quaternary, indicated by intervals of deep freshwater lakes and shallow lakes with higher alkalinity (pH > 9) and salinity (e.g., Lyons et al. 2015). Shallow soda lakes in the region typically have pH ranges of 10–10.5, and salinity from 5% to saturation (Grant and Jones 2000). Some changes are likely due to tectonics (forming basins for lakes to fill), because faulting, uplift, and volcanism can affect basin geometry, orographic effects, and the interconnectivity of lake systems over time (e.g., Trauth et al. 2007; Fischer et al. 2020). Rainfall in eastern Africa is heavily influenced by Indian Ocean monsoons, which tend to vary in intensity on orbital timescales (e.g., Wang et al. 2017). Orbital precession, modulated by eccentricity, controls the pacing, extent, and intensity of monsoonal moisture (Trauth et al. 2007). Other changes could relate to local, regional, or even global climate at times when orbitally controlled insolation is less pronounced (Trauth et al. 2007).

Paleolakes can preserve many different lines of evidence for lake conditions and past climate. Phytoliths, diatoms, pollen, sponge spicules, plant waxes, and aquatic fossils can all provide a direct record of organisms that resided in and near a lake, and changes in their makeup can tell us about paleoecology. However, saline–alkaline paleolakes are more difficult to study. First, fewer organisms make these lakes their homes, which limits their abundance and diversity in these deposits. Second, saline–alkaline lake water and groundwater are hostile to many materials, and many of these proxies (e.g., pollen) are not preserved (e.g., Deocampo et al. 2009). In these types of deposits, alternative methods must be employed to continuously reconstruct past environments. One proxy that can help reconstruct paleolake environments even under harsh conditions is the record of authigenic minerals that form within a lake and its sediments (as opposed to detrital minerals, which form elsewhere and are transported in). Zeolites, carbonates, clay minerals, and even authigenic K-feldspar and albite can form in lake sediments under saline–alkaline conditions, and the specific minerals formed provide insight into the conditions at the time of formation (e.g., Hay and Kyser 2001; Velde and Meunier 2008). Changes in the assemblages of these minerals over time can help define both one-time and cyclical changes in the environment (e.g., Deocampo et al. 2017).

Zeolites

Zeolites are a group of porous framework aluminosilicate (tectosilicate) minerals, used widely in industry for their cation exchange properties. They are compositionally complex minerals that form extensive solid solutions, with the dominant cation indicated by a suffix (e.g., phillipsite-Na, phillipsite-K), although when a mineral is not specifically identified on compositional grounds, the name for the

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interact with groundwater after deposition, and thus the zeolite signal might lag conditions within the lake itself or be overprinted by later alteration (e.g., Hay and Kyser 2001). See Table 1 for a list of zeolites common in the EARS.

In the EARS, the presence and composition of zeolites in paleolakes have been extensively used to identify intervals of exceptional aridity. The zeolite analcime has been used as an indicator of more arid conditions in records from across the region, including Chew Bahir, Ethiopia (Arnold et al. 2021; Gebregiorgis et al. 2021), the Pleistocene Naivasha Basin, Kenya (Trauth et al. 2001), and the Pliocene–Pleistocene Chemeron Formation of the Baringo Basin, Kenya (Minkara 2017). Analcime indicates more saline conditions because it is favored by a higher Na/K ratio, typical of more saline conditions overall, though analcime can also form at the expense of other zeolites over time or if conditions change. Fluctuations in salinity (and thus Na/K ratios) can result in fluctuations in phillipsite and analcime in saline–alkaline deposits (e.g., Chemeron Formation; Minkara 2017). Trauth et al. (2001) used a succession of zeolites as indicators of changing alkalinity (pH) in the Late Pleistocene Naivasha Basin, with analcime indicating the highest alkalinity followed by clinoptilolite, phillipsite (pH ~9), chabazite, and finally smectite clays with decreasing pH.

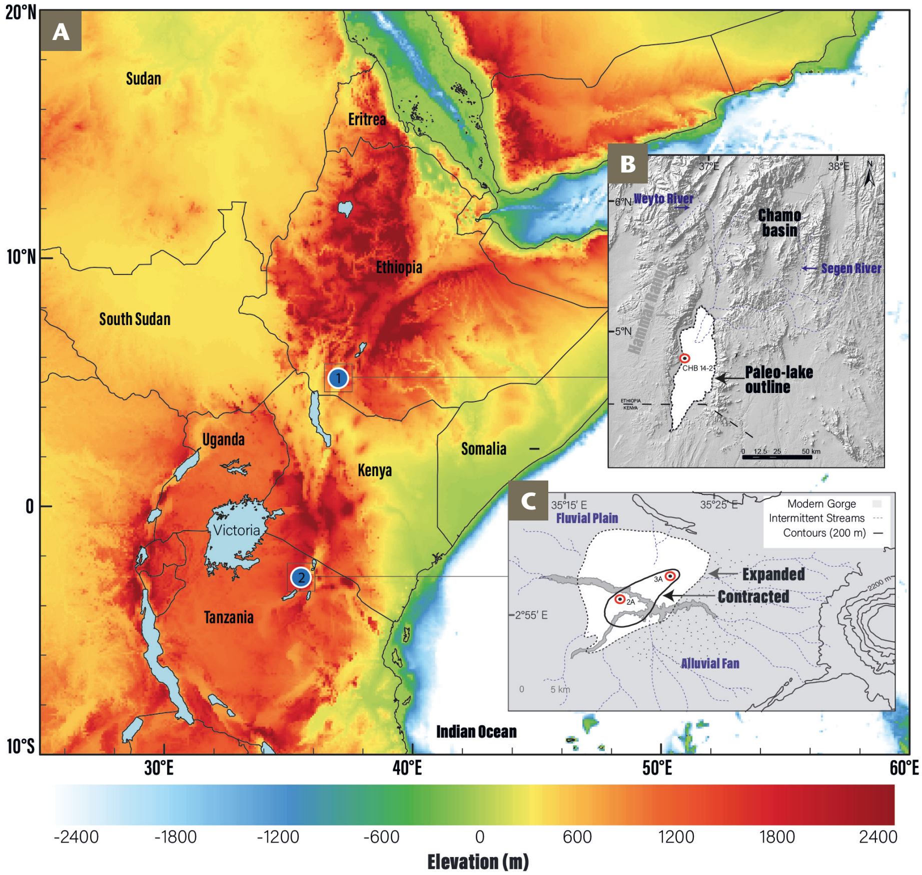

Figure 1 (**A**) Map of eastern Africa showing the positions of Chew Bahir and Olduvai. (**B**) Chew Bahir Basin (CHB) in southern Ethiopia, showing the coring sites mentioned in the text. (**C**) Olduvai Gorge (after Hay (1976)) with the extent of Pleistocene paleolake Olduvai as updated by Stanistreet et al. (2020a).

series (e.g., phillipsite) can be used (Coombs et al. 1997). While natural zeolites form in many environments, they form in the greatest concentrations in saline–alkaline lakes, especially where volcanic ash is abundant (e.g., Hay and Sheppard 2001). Extensive volcanism in the EARS provides this starting material. Volcanic glass and minerals alter into zeolites and clays in these closed-basin lakes, and the exact zeolites formed depend on both the original composition of the volcanic ash (e.g., rhyolitic versus basaltic) and the conditions within the lake and its sediments, including the pH, salinity, activity of water and aqueous silica, and relative abundances of alkali (Na^+, K^+) and alkaline earth (Ca^{2+}, Mg^{2+}) cations (Hay and Sheppard 2001). During wetter intervals, closed-basin lakes tend to be more dilute and may not form zeolites; while during drier intervals, the remaining fluids are more saline and the pH is higher, thereby providing the conditions needed for zeolite formation. Particularly saline–alkaline conditions can result in the zeolite mineral analcime, or even authigenic K-feldspar or albite. These mineralogical differences will manifest both over time (e.g., between different layers in a paleolake core, deposited under changing conditions at the same position) and space (e.g., between the margins and center of a paleolake deposit). One caveat when using zeolites as proxies for lake conditions is that these sediments continue to

Clay Minerals

Clay minerals are hydrous phyllosilicates (layered silicates) that typically have a fine grain size (Moore and Reynolds 1997; Velde and Meunier 2008). We differentiate between clay minerals and the clay size fraction (<2.0 µm), which can also contain other (fine-grained) minerals such as quartz, carbonates, or zeolites (Moore and Reynolds 1997). Common clay minerals found in eastern Africa paleolake basins are kaolinite, illite, and smectite group minerals, with montmorillonite being the most common in that group (Table 2) (Deocampo et al. 2009; Foerster et al. 2018). Phyllosilicate structures consist of two types of layers, referred to as tetrahedral and octahedral sheets, based on the number of oxygens coordinated with different cations (Velde and Meunier 2008). These two-dimensional

Table 1 COMMON ZEOLITES IN EASTERN AFRICAN SALINE-ALKALINE PALEOLAKES

Mineral series	Example Formula	DEC*	Environment
Analcime	$Na(AlSi_2O_6)\cdot H_2O$	Na, Minor K	High salinity (Na^+ > K^+)
Chabazite	$Ca_2[Al_4Si_8O_{24}]\cdot 13H_2O$	Ca, Na, K	Less alkaline, high Ca^{2+}
Clinoptilolite	$Na_6(Si_{30}Al_6)O_{72}\cdot 20H_2O$	Na, K, Ca	High Si activity
Erionite	$K_{10}[Si_{26}Al_{10}O_{72}]\cdot 30H_2O$	K, Na, Ca	Glass alteration
Heulandite	$(Ca,Na,K)_5(Si_{27}Al_9)O_{72}\cdot 26H_2O$	Ca, Na, K, Ba, Sr	
Mordenite	$(Na_2,Ca,K_2)_4(Al_8Si_{40})O_{96}\cdot 28H_2O$	Na, Ca, K	
Phillipsite	$K_6(Si_{10}Al_6)O_{32}\cdot 12H_2O$	K, Na, Ca	High K^+

* DEC = Dominant extraframework cations

sheets can be packed into different combinations to form layers. The way in which these sheets are organized into layers determines the layer charge, which helps determine the capacity of the mineral to accept specific cations. Each "layer" in illite and smectite consists of a single octahedral sheet sandwiched between two tetrahedral sheets. These layers stack to form the overall clay structure, differing largely in what occupies the interlayer space (K, in the case of illite). The spacing between these layers is a major distinguishing feature in the X-ray diffraction (XRD) patterns of clay minerals. The precise identification of clay minerals, especially smectite, is challenging in part because of the overlap of very similar peaks in the diagnostic diffraction patterns, such that sample pre-treatment is required to distinguish the overlapping reflections (e.g., Fig. 5). Typically for the XRD analysis of clay minerals, three diffractograms are measured following air-drying, ethylene glycol solvation, and heating of samples, which results in a diagnostic shift of the smectite peak, whereas the illite peak remains the same under all sample pre-treatment variants. Another diagnostic tool for clay mineral identification is the 060 reflection, which can help determine whether the octahedral layer is occupied by three divalent cations (e.g., Mg^{2+} in trioctahedral clays) or two trivalent cations (e.g., Al^{3+} in dioctahedral clays) (e.g., Fig. 6; Moore and Reynolds 1997).

Most clay minerals are weathering products, which means they are of detrital origin, such that the clay mineral composition within deposited sediments in terrestrial basins typically reflects the mineralogy of the source catchment. Under certain conditions, so-called *authigenic* clay minerals can also form as direct precipitates from lake water or at low temperatures via the transformation of precursor minerals. Such starting or *precursor* material can be derived from weathered volcanic material (e.g., tuff, lava), which is abundant in the EARS. A common example of such an alteration product is low-temperature authigenic illite. The conditions of the available water in the depositing environment (e.g., pH, salinity), the availability of precursor materials, and the saturation of the water with specific cations such as Mg, K, and Fe determines the mineral suite that can form through authigenic processes. Clay minerals rich in Al, or zeolites rich in Ca or K, have been shown to produce Mg-rich authigenic clay minerals in many eastern African alkaline, saline lakes (e.g., Moore and Reynolds 1997; Deocampo et al. 2009). During wetter intervals, associated with freshwater conditions in closed-lake basins, heavily weathered silicates like smectite or kaolinite dominate the mineral suite, and are typically rich in Al. Dry-climate intervals, with a reduced moisture influx and correspondingly concentrated saline and alkaline brines, are rich in authigenic clay minerals like illite. In closed-basin lake deposits not overly diluted by detrital or biogenic sediments, authigenic clay minerals formed under such conditions allow us to reconstruct the prevailing climatic conditions during the time of deposition (e.g., Deocampo 2009, 2017; Gebregiorgis et al. 2021). For example, in the saline, alkaline, and silica-rich waters of many eastern African lakes, the crystal chemistry of authigenic minerals is shown to be influenced by prevailing climate conditions where authigenic clay minerals typically become enriched in Mg in their octahedral layers relative to Al during periods of intensifying brines (Foerster et al. 2018; Arnold et al. 2021). Similarly, as clay minerals form in isotopic equilibrium with ambient water at the time of crystallization, the oxygen isotopic signature of authigenic clay minerals can help reconstruct the isotopic composition of paleolake waters and provide a record of the paleosalinity (Gebregiorgis et al. 2020).

Table 2 COMMON CLAY MINERALS IN EASTERN AFRICAN SALINE-ALKALINE PALEOLAKES

Clay mineral	General formula	Adsorbed or absorbed cations	Environment
Kaolinite	$Al_2Si_2O_5(OH)_4$		Less alkaline, fresh water lake
Montmorillonite	$(Na, Ca)_{0.33}$ $(Al Mg)_2$ (Si_4O_{10}) $(OH)_2$ nH_2O	Hydrated exchangeable cations	Low salinity
Illite	$(K,H)Al_2$ $(Si,Al)_4O_{10}(OH)_2$ XH_2O	K	High salinity

CASE STUDIES: PALEOLAKE OLDUVAI AND CHEW BAHIR

Case Study: Paleolake Olduvai

The Olduvai Basin in northern Tanzania contains paleolake sediments and tuffs deposited in a closed-basin lake during the Pleistocene. The seven Olduvai Beds known from outcrops are subdivided, from base to top, into Beds I–IV, Masek, Ndutu, and Naisiusiu (Hay 1976), and extend from 2.03 Ma to the Holocene (Deino et al. 2021). Outcrops expose clay and zeolite-rich lacustrine sediments in Olduvai Bed I and lower Bed II, between ~1.92 and 1.7 Ma (Hay and Kyser 2001), interfingering with lake margin sediments that contain archeological sites. In 2014, the Olduvai Gorge Coring Project (OGCP) retrieved sediment cores from near the anticipated lake center, more than doubling the thickness of the lake record known from outcrops, down to ~2.24 Ma (Deino et al. 2021). The older lake intervals, known only from cores and assigned to the recently defined Naibor Soit Formation (Stanistreet et al. 2020a), appear to be fresher than the well-studied saline–alkaline paleolake of Beds I and II, as revealed by zeolites and other proxies (McHenry et al. 2020).

The authigenic mineralogy of paleolake Olduvai based on outcrop exposures has been studied extensively and used to reconstruct the changing lake conditions. Zeolites have long been identified as major minerals at Olduvai, and Hay and Kyser (2001) recognized Mg-rich smectite; illite; calcite; dolomite; analcime, phillipsite, chabazite, clinoptilolite, and erionite zeolites; K-feldspar; chert; and pyrite among its authigenic minerals in the Pleistocene Bed I–II lake interval. The volcanoes Ngorongoro, Olmoti, and potentially Loolmalasin of the neighboring Ngorongoro Volcanic Highlands provided volcanic ash to the basin during this interval, facilitating the production of zeolites. Deocampo et al. used the composition of ultrafine clays (2009) and bulk samples (2017) in this interval to track changes in the lake chemistry, with higher Mg contents indicating more alkaline conditions. While volcanic ash deposited and altered within the saline–alkaline lake may consist primarily of zeolite (often phillipsite), lake claystones also contain zeolites (Hay 1976; McHenry et al. 2020).

The lacustrine intervals of OGCP Core 2A, recovered from near the depocenter of the Olduvai Bed I/II paleolake, were sampled at 32-cm intervals for a variety of paleoenvironmental proxies, including with XRD. Zeolites and other minerals were identified using bulk powder XRD, with results reported by McHenry et al. (2020). Overall trends in the mineral assemblage are shown in Fig. 2. Analcime

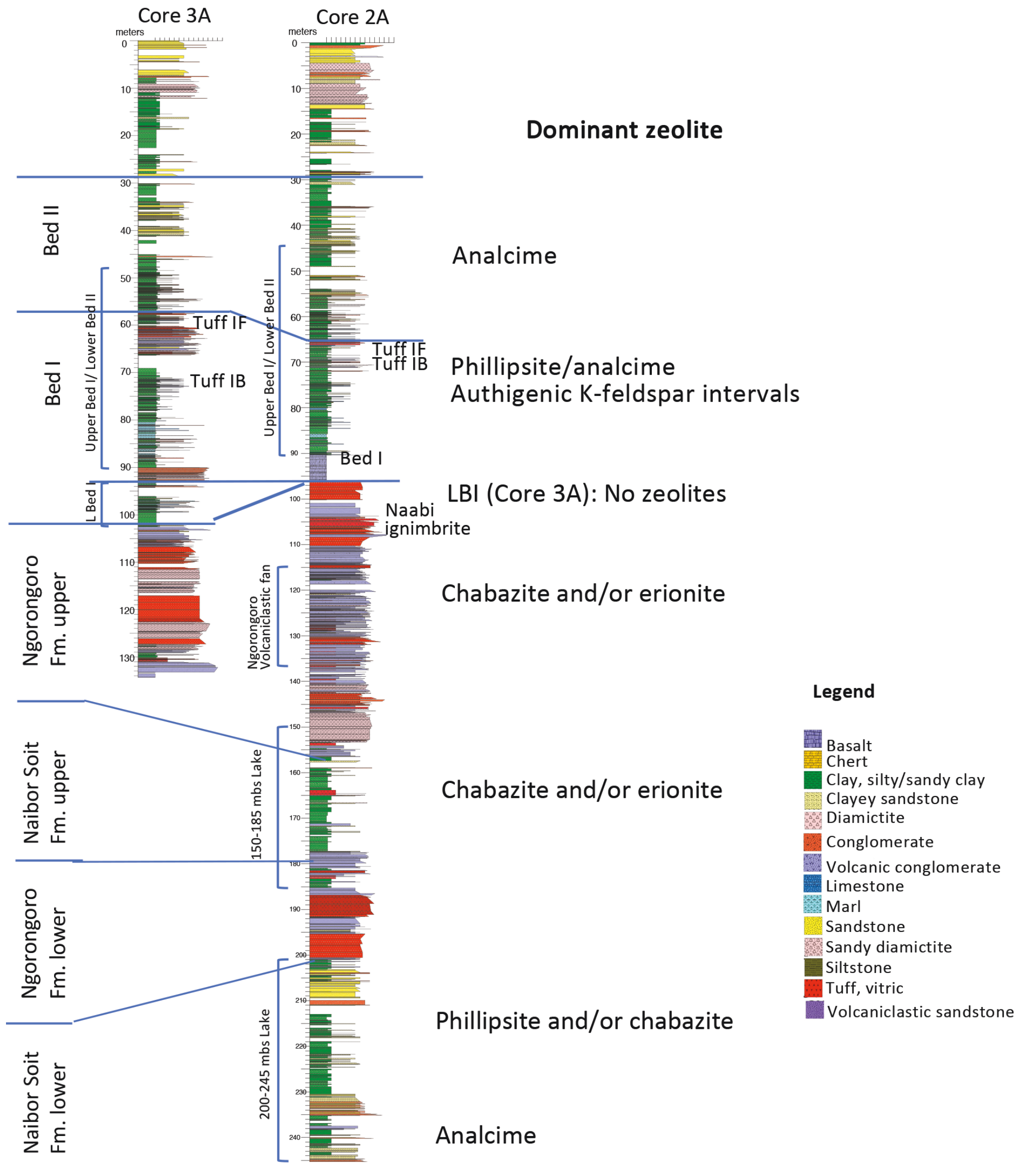

Figure 2 Stratigraphic sections of Olduvai Gorge Coring Project cores 2A and 3A, highlighting the dominant zeolites as identified by X-ray diffraction for each interval. Modified from McHenry et al. (2020).

is the dominant zeolite in the oldest lake sediments from the core, shifting abruptly to phillipsite and chabazite at 2.199 (+0.016/−0.013) Ma (dates based on the core age model of Deino et al. 2021). Lacustrine deposition was at least locally disrupted by the eruption and emplacement of a volcaniclastic fan from the neighboring Ngorongoro Volcano (2.16–2.14 Ma), then resumed from 2.14 to 2.09 Ma. Zeolites in this interval of fluviolacustrine sediments featured chabazite and erionite, which form under less saline–alkaline conditions than analcime or phillipsite, consistent with relatively fresher conditions. This is also the only interval in the core that preserves phytoliths (silica particles formed within plants), another indicator of fresher conditions (Rodríguez-Cintas et al. 2020). This paleolake was once again displaced by another, thicker fan of volcaniclastic materials. Tuffs within this fan preserve some fresh volcanic glass, which was altered to zeolite (principally chabazite and erionite) in some samples.

A disconformity separates the top of this fan from the overlying Bed I basalt (identified both in cores and outcrops) and Upper Bed I deposits in Core 2A, but a different core from the Olduvai Basin (Core 3A) records fresher conditions for this Lower Bed I interval (~1.90–2.00 Ma), with claystone but no zeolites. The next section, Bed I/II, correlates to the well-studied Bed I/II lake record from outcrops. Directly above the Bed I basalt lies a short interval of lacustrine claystone lacking zeolites, consistent with continued fresher conditions, ending at 1.870 (+0.033/−0.037) Ma. Above this interval, as expected based on previous outcrop studies (e.g., Hay and Kyser 2001; Deocampo et al. 2009), the authigenic minerals vary, indicating different (and likely cyclical) levels of saline–alkaline conditions (Deocampo et al. 2017). Within this section, prolonged, highly arid conditions are marked by authigenic K-feldspar (which replaced phillipsite and/or other zeolites), whereas less arid conditions are marked by phillipsite but no K-feldspar. Moderately arid intervals have both phillipsite and K-feldspar. Almost all samples from this interval contain zeolite (usually phillipsite) and/or authigenic K-feldspar, indicating that, while conditions were variable, saline–alkaline conditions dominated. These interpretations are summarized in Table 3. One potential complication to this interpretation is mineral overprinting, when earlier-formed minerals are replaced as conditions change in the sediment. This can be assessed using scanning electron microscopy.

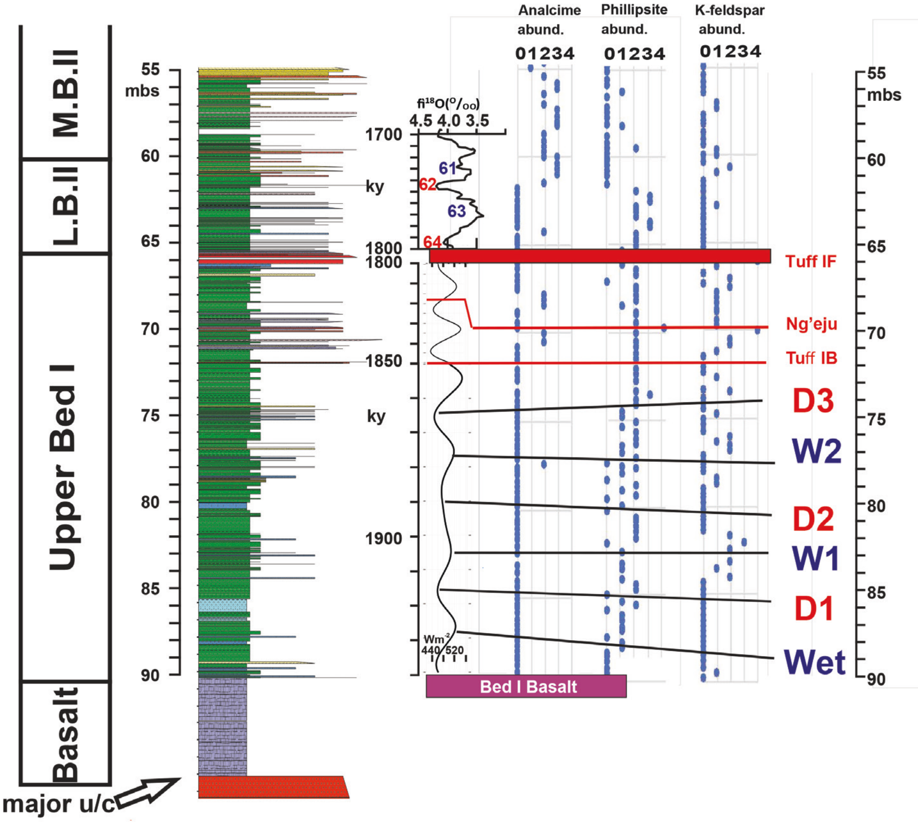

Figure 3 Olduvai Upper Bed I and Bed II stratigraphic sections, with ages (extrapolated from Deino et al. 2021), identified tuffs, and relative abundances (04) of analcime, phillipsite, and K-feldspar. See Fig. 2 legend. Trends in zeolite and K-feldspar abundances are related to wet and dry intervals (W and D, respectively) identified based on other core climate indicators, including biomarkers (Colcord et al. 2019) and paleosalinity (Stanistreet et al. 2020b). Insolation curve from Stanistreet et al. (2020b) and references therein, showing precession-dominated cycles below Tuff IF and obliquity-dominated cycles above (Marine Isotope Stages (MIS) 61-64). Dates (in ka) derived from the Deino et al. (2021) age model. Modified from McHenry et al. (2020).

At 62 m below the surface in Core 2A (1.667 +0.064/−0.068 Ma, within Olduvai Bed II), analcime replaces phillipsite as the dominant zeolite, indicating an increase in the Na/K ratio (likely as a result of increasing salinity). Authigenic K-feldspar is also much less common above this level, consistent with lower K, likely related to a change in the detrital sediment source.

To demonstrate that these alternating intervals of zeolite and K-feldspar in Olduvai Bed I/II show changes in aridity versus humidity, the mineral-based record can be compared against other proxies from the same core. This pattern is consistent with the core scan X-ray fluorescence (XRF) record presented by Stanistreet et al. (2020b), in which Mg-rich intervals indicate more arid conditions while higher Al indicates more dilute fluids. Colcord et al. (2019) used biomarkers to define wetter and drier episodes for Core 2A within Upper Bed I, defining two wet (W1 and W2) and two dry (D1 and D2) episodes. Stanistreet et al. (2020b) used higher Ti concentrations in core-scan XRF data as a proxy for wetter conditions during this same interval and identified the same wet and dry episodes, adding a third dry episode (D3) below Tuff IF at the boundary between Beds I and II. The positions of these five episodes, relative to the zeolite and K-feldspar trends, are indicated in Fig. 3.

Table 3 BED I PALEOLAKE CONDITIONS, BASED ON ZEOLITES AND AUTHIGENIC K-FELDSPAR

Observation	Interpretation
K-feldspar (no zeolite)	Driest
K-feldspar and phillipsite	Dry
Phillipsite (and not K-feldspar)	Intermediate
No zeolite or K-feldspar	Wet

A caveat associated with using zeolites as proxies for short-duration climate intervals is that zeolites continue to form in the sediments after deposition. Hay and Kyser (2001) noticed a difference in oxygen isotopes for different authigenic minerals (K-feldspar and chert), indicating that not all formed at the same time. Saline–alkaline lake fluids can infiltrate downward into underlying sediment, and can potentially overprint the earlier-formed record. Hay and Kyser (2001) attributed the zeolites of the underlying volcaniclastic fan to the downward flow of these lake-associated fluids. Larsen (2008) found similar mineral overprints in his study of the Lake Tecopa beds in California, USA.

Case Study: Chew Bahir

Chew Bahir site. The Chew Bahir Basin (CHB), at the southern end of the Main Ethiopian Rift (4.1–6.3° N, 36.5–38.1° E), is a deep, tectonically bound basin that today holds an extensive saline mudflat (~30 km wide and ~100 km long) and is located ~90 km east of the key paleoanthropological site Omo-Kibish (Foerster et al. 2012; Fischer et al. 2020; Gebregiorgis et al. 2021). Chew Bahir is a closed drainage basin but held an up to ~45-m-deep extensive paleolake during pronounced wet phases such as the last precession-driven African Humid Period (~15–5 ky BP; Fig. 4), when paleolake Chew Bahir overflowed into Lake Turkana. The southern Ethiopian Rift Abaya and Chamo lakes and paleolake Chew Bahir were likely connected hydrologically during such wet intervals based on paleoshorelines and lake balance modeling (Fischer et al. 2020). Otherwise, the CHB is a terminal sink for weathering products from its 32,400-km^2 catchment, which is dominated by Miocene basalts in the east and Late Proterozoic gneisses in the west, including the Hammar Range (Foerster et al. 2012). The Hammar Range, separating the CHB from the Omo-Turkana Basin to the southwest, is a major source of detrital deposits along the basin's western margin, as extensive alluvial fans draining the graben shoulders are periodically activated during strong rain events and transport weathering products into the basin (Foerster et al. 2012). Other sources of the fluvial deposits in the CHB are the perennial Weyto and Segen rivers, which drain the northeastern and northwestern parts of the catchment, an area rich in younger volcanic material (Foerster et al. 2018; Gebregiorgis et al. 2021).

Beneath the modern playa surface, the CHB contains at least 3 km of sedimentary infill that provides an archive of global to regional and local environmental fluctuations at different timescales. Short sediment cores along a northwest–southeast transect across the basin (<18.8 m; ~45 ky

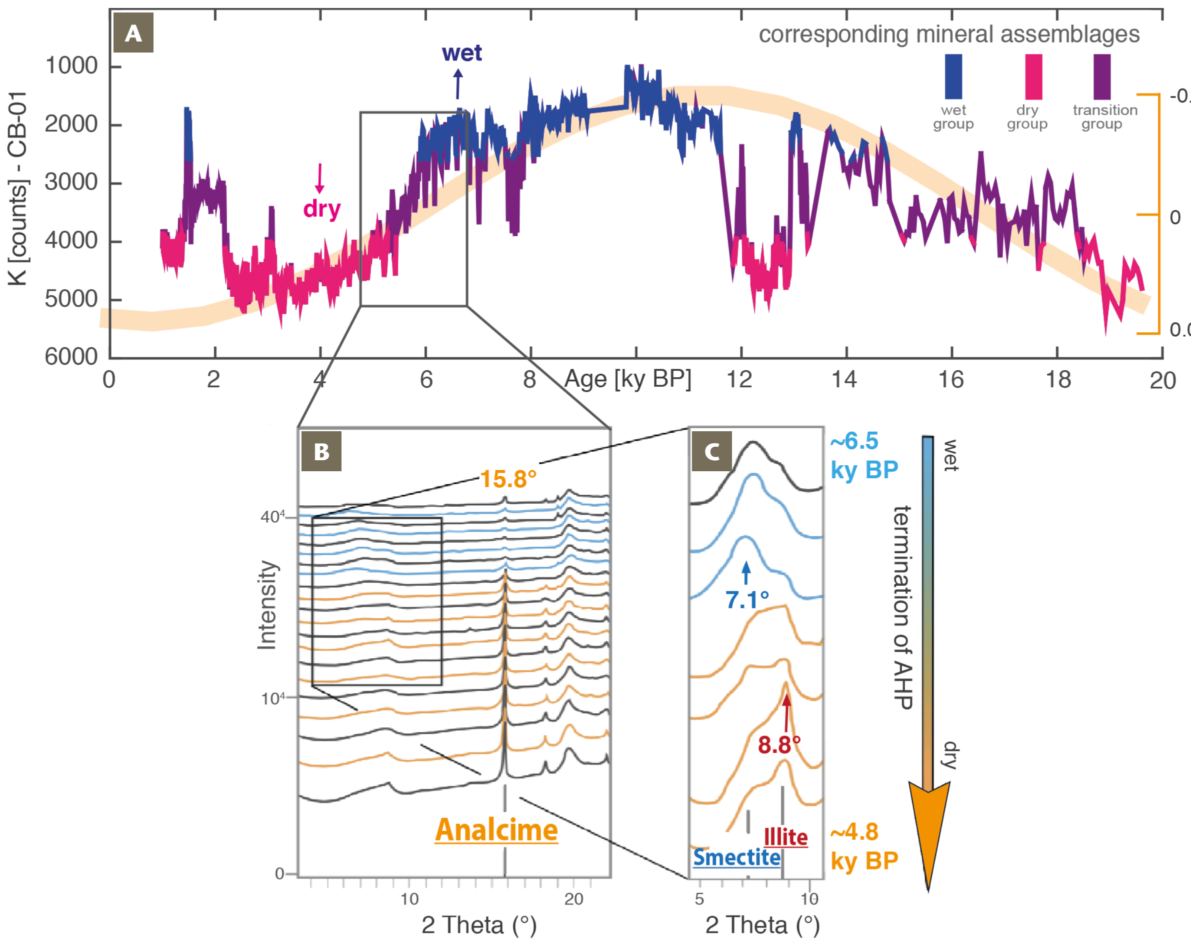

FIGURE 4 (**A**) Aridity proxy K for Chew Bahir. Variations of potassium (K) content in sediment core CB-01 (last 20 ky) on a reverse y-axis. MODIFIED AFTER FOERSTER ET AL. (2012). The most likely process responsible for the link between the climate and potassium concentrations in lake sediments of the CHB is authigenic mineral alteration (illitization) in clay minerals during periods of declining water level. (**B**) X-ray diffraction pattern (2 theta scale) of the corresponding section in CB-02 samples showing the transformation of mineral assemblages at the termination of the African Humid Period. MODIFIED AFTER SCHULZE (2016). (**C**) The gradual wet–dry transition is marked by the illitization of smectites and the formation of authigenic zeolites (mostly analcime, diagnostic peak at 15.8° 2Θ). Clay minerals are increasingly altered by progressive K-fixation into low-temperature authigenic illite (diagnostic peak at 8.8° 2Θ) at the expense of smectites (diagnostic peak at 7.1° 2Θ). AFTER FOERSTER ET AL. (2018).

BP; Foerster et al. 2012), a core from the center of the basin (~41 m; 116 ky BP; Foerster et al. 2022), and duplicate long-cores from the western shore of the basin (~293 m; covering the last ~620 ky; e.g., Arnold et al. 2021; Foerster et al. 2022) have been studied. The results indicate that, in addition to fluvial-deltaic and lacustrine processes, the composition of the deposited sediments is significantly controlled by post-sedimentary processes, including authigenic mineral alteration. Determining the extent of mineral alteration is an important prerequisite for interpreting micro-X-ray fluorescence datasets, but, foremost, the authigenic products themselves provide direct paleohydrological data (Foerster et al. 2018).

Potential of analyzing Chew Bahir's authigenic mineral suite. Results from studies of the Chew Bahir cores show that sedimentary deposits are composed of a variety of lacustrine and silty clays (e.g., Foerster et al. 2012, 2022). Because clay minerals react to changes in hydrochemical conditions (e.g., Moore and Reynolds 1997; Velde and Meunier 2008; Deocampo et al. 2009) by adjusting their crystallographic composition, the Chew Bahir cores are perfectly suited to study authigenic phases and their evolution. Essentially, the mineralogy of the authigenic products, including clay minerals and zeolites (e.g., Hay and Kyser 2001; Deocampo et al. 2009), is a valuable and sensitive climate proxy for fluctuations in the water chemistry of paleolakes in closed basins, such as Chew Bahir or Olduvai (e.g., Moore and Reynolds 1997; Deocampo et al. 2009; Foerster et al. 2018). Analyses of XRD patterns of bulk samples and clay separates down individual cores (i.e., with time) document clearly defined variations between characteristic mineral groups downcore: a dry-climate group, a wet-climate group, and a transition group (FIGS. 4 and 5). The marked shifts in the mineral assemblages are strongly controlled by an authigenic overprint.

Climate-characteristic mineral assemblages in Chew Bahir. Samples of the **wet-climate group** are characterized by Al-rich montmorillonite and kaolinite and lack analcime (FIG. 5). The clay minerals are likely the product of intense silicate hydrolysis under humid climate conditions in a freshwater environment, with low salinity and low alkalinity. Under these deep-lake conditions, Al was preferred over Mg in the octahedral layer of the clays. The dominant clays in the wet-climate group are Al-rich montmorillonite, as determined by their 060 reflection XRD patterns (FIG. 6). The **transitional group** comprises mainly intermediate clay minerals that show various levels of authigenic alteration in both smectite-to-illite transformation and Al-to-Mg substitution in the octahedral layer (FIG. 6). The **dry-climate group** is dominated by illite and abundant analcime. The illite identified in the dry-climate group is the result of enhanced K uptake in smectite structures, a process described as (low-temperature) illitization or "reversed weathering" (Deocampo

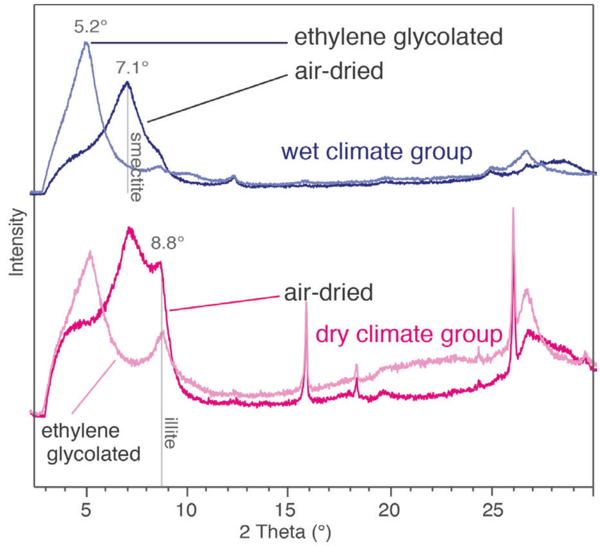

FIGURE 5 Characteristic X-ray diffraction (XRD) patterns of <2 µm clay separates representative of the dry-climate group (red/pink) compared with wet-climate groups (blue) in Chew Bahir. MODIFIED AFTER FOERSTER ET AL. (2018). To distinguish potentially overlapping diagnostic peaks, the diffraction patterns of core CB-01 provide supporting evidence for authigenic illitization during episodes of higher alkalinity and salinity in the closed-basin paleolake. The oriented clay mineral samples were measured in the air-dried (N) and ethylene glycol (EG) solvated states to distinguish overlapping reflections. Smectites expand under glycol treatment to 5.2° 2Θ, whereas the illitic component remains unaltered with a diagnostic illite reflection at 8.8° 2Θ sharply evident in all dry-climate group samples.

et al. 2009). This process is significantly controlled by paleohydrochemistry driving the illitization of smectite during periods of increased evaporation. The mineral assemblage for the dry-climate group also shows Al-to-Mg substitution in the clay octahedral layers and a discrete trioctahedral phase, which demonstrates the authigenic nature of the observed changes (FIG. 6). Interestingly, these Al-to-Mg substitutions in the octahedral sheet also cause an increase in the octahedral layer charge (Al^{3+} is exchanged for Mg^{2+}) (Hay and Kyser 2001; Deocampo et al. 2009). This increasing layer charge likely fuels the progressive uptake of K^+ observed in the illitization process (Deocampo et al. 2009, 2017). This provides the opportunity to link mineralogy with geochemistry (Foerster et al. 2018; Arnold et al. 2021; Gebregiorgis et al. 2021).

Mineral alteration pattern during the African Humid Period Mid-Holocene wet–dry transition. Using the Mid-Holocene termination of the African Humid Period as an example of a major wet–dry transition in the eastern African climate, the degree of authigenic transformation in the Chew Bahir clay minerals during this interval demonstrates that mineralogy changes are a robust proxy for different hydrochemical environments (Foerster et al. 2018; FIG. 4). While the Chew Bahir K record shows lower values during the prevailing humid conditions around 7.15 ka, the increase in K content in the sediment mirrors the gradual eastern-African aridification trend during the Holocene reaching dry conditions by ~5 ky BP (Foerster et al. 2012). The corresponding shift documented in the mineral composition shows the advancing smectite-to-illite transformation associated with the increased K-uptake in smectite (Foerster et al. 2018; FIGS. 4 and 5).

Mineral alteration during the last 620 ky. The model of authigenic illitization and observed changes in octahedral composition controlled by hydrochemistry can be successfully applied to the Chew Bahir long core, covering the last ~620 ky (Arnold et al. 2021). Advanced hyperspectral analyses (0.25–17-µm wavelength range) show absorption features consistent with increasing Al-to-Mg substitution in clay minerals during arid episodes. The corresponding increase in the potassium concentrations during these drier phases during the last 620 ky matches the model of K-uptake through authigenic illitization and is in good agreement with the inverse relationship of identified smectite abundances and K concentrations (Arnold et al. 2021). The absorption band ratio at 1.16 µm confirms analcime occurrences during the driest intervals in the record (Arnold et al. 2021; Foerster et al. 2012, 2022).

A major challenge remaining in authigenic clay mineral studies is defining and understanding the hydrochemical "thresholds" that lead to the formation of specific clay mineral phases. Additionally, the specific precursor material has not yet been definitively identified, and the detrital versus authigenic origin of the clay minerals can only be assumed based on the Mg versus Al patterns observed in the 060 XRD reflections. A modern analog study helped constrain the transport processes, sedimentation, and later alteration in the CHB catchment (Gebregiorgis et al. 2021); however, distinguishing between detrital and authigenic phases has been a matter of debate for decades and will require further evidence (Foerster et al. 2018). A major caveat in authigenic clay mineral studies is that sample preparation and individual phase interpretation are time consuming, and therefore high-resolution datasets are not yet available.

SUMMARY AND CONCLUSIONS

Link to Hominins

To understand transformations in hominin habitats over time, it is important to understand changes in the hydrology and climate. On evolutionary timescales, mineral proxy records can contribute to a robust and well-preserved reconstruction of past environmental conditions, paralleling potential key transitions and events in human evolution. On sub-millennial timescales, mineralogical proxies

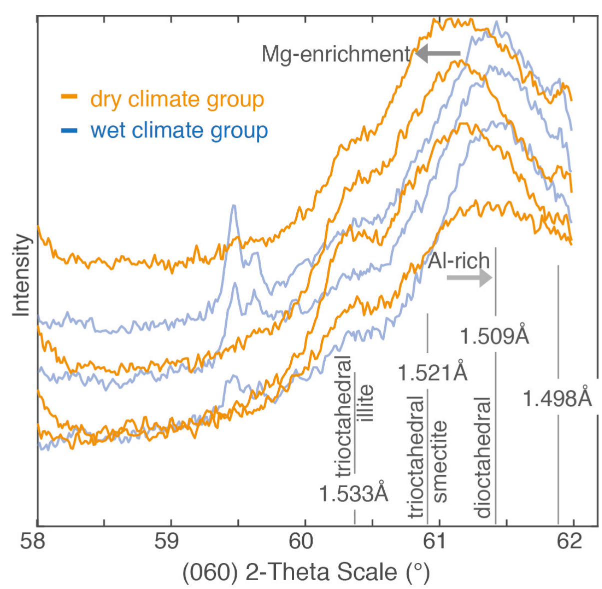

FIGURE 6 The octahedral composition of the CHB clay minerals, determined by XRD analyses of powdered and randomly oriented clay aggregates, showing diagnostic patterns for samples of the wet- and dry-climate groups. With a decreased moisture influx, a change in paleohydrological conditions is assumed (increased salinity and alkalinity). The octahedral occupancy responds via Mg-enrichment and the development of a discrete trioctahedral phase. Samples of the wet-climate group reflect dioctahedral Al-rich phases. MODIFIED AFTER FOERSTER ET AL. (2018).

such as zeolites and authigenic clays can help constrain environmental threshold conditions and the magnitude of specific climate events. Determining the degree of alteration, especially in clay minerals, can enable the reconstruction of even subtle shifts in the paleohydrochemistry and related hydroclimatic variations. Where the resolution of the record allows, changes on timescales of human generations can be reconstructed, offering a unique opportunity to directly compare climate and archeological records from the same region.

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