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Orbital control of Pleistocene euxinia in Lake Magadi, Kenya

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ABSTRACT

Lake Magadi is an internally drained, saline and alkaline terminal sump in the southern Kenya Rift. Geochemistry of samples from an ~200 m core representing the past ~1 m.y. of the lake's history shows some of the highest concentrations of transition metals and metalloids ever reported from lacustrine sediment, including redox-sensitive elements molybdenum, arsenic, and vanadium. Elevated concentrations of these elements represent times when the lake's hypolimnion was euxinic—that is, anoxic, saline, and sulfide-rich. Euxinia was common after ca. 700 ka, and after that tended to occur during intervals of high orbital eccentricity. These were likely times when high-frequency hydrologic changes favored repeated episodes of euxinia and sulfide precipitation. High-amplitude environmental fluctuations at peak eccentricity likely impacted water balance in terrestrial habitats and resource availability for early hominins. These are associated with important events in human evolution, including the first appearance of Middle Stone Age technology between ca. 500 and 320 ka in the southern Kenya Rift.

INTRODUCTION

The Hominin Sites and Paleolakes Drilling Project (HSPDP, https://hspdp.asu.edu/) drilled cores in several rift basins of eastern Africa to obtain long, continuous paleoenvironmental records close to important fossil and archaeological sites (Cohen et al., 2016; Campisano et al., 2017). Lake Magadi (Kenya; Fig. 1) is within 100 km of several important sites for human origins research, including Olduvai Gorge, Laetoli, and Peninj in Tanzania, with Olorgesailie (Kenya) <20 km distant. Monsoon intensity fluctuations due to orbital and other factors are hypothesized to have influenced early hominin habitat structure, selective pressures, and speciation (Potts and Faith, 2015). Results from core HSPDP-MAG14-2A, Olorgesailie outcrops, and core ODP-OLO12-1A (Olorgesailie Drilling Project, https://humanorigins.si.edu/research/east-african-research-projects/olorgesailie-drilling-project) in the Koora Graben (Fig. 1) suggest that environmental variability, especially the intensity of arid episodes, between ca. 500 and 300 ka played a role in mammal species turnover and the first appearance of Middle Stone Age technology (Owen et al., 2018a, 2019; Potts et al., 2018, 2020). Paleolimnological records from the regional drainage sump can offer unique perspectives on environmental change and the timing and drivers of human evolution.

GEOLOGIC SETTING

Lake Magadi occupies a set of subparallel grabens in the rift between metamorphic highlands to the east and west. Magadi Trachyte (ca. 1.4–0.8 Ma) covers much of the rift floor, cut by rift-parallel faulting. Pliocene-Pleistocene volcanos are found throughout the region, mostly trachyandesitic to basaltic with a few carbonatites (Baker and Mitchell, 1976).

Lake Magadi is a saline, alkaline pan fed by hydrothermal groundwater and ephemeral streams (Jones et al., 1977). It was part of a large Pleistocene paleolake extending south to Lake Natron in Tanzania (Hillaire-Marcel and Casanova, 1987). Inflow waters are Na-CO_3 brines, with evaporation producing some of the most concentrated alkaline fluids on Earth (Deocampo and Jones, 2014). With pH >10, these fluids commonly produce authigenic silicates such as zeolites and magadiite (Na-silicate) (Eugster, 1967). Despite hypersaline modern conditions, some Middle to Late Pleistocene deposits represent much fresher conditions, including diatomaceous mud with fish fossils (Owen et al., 2018b).

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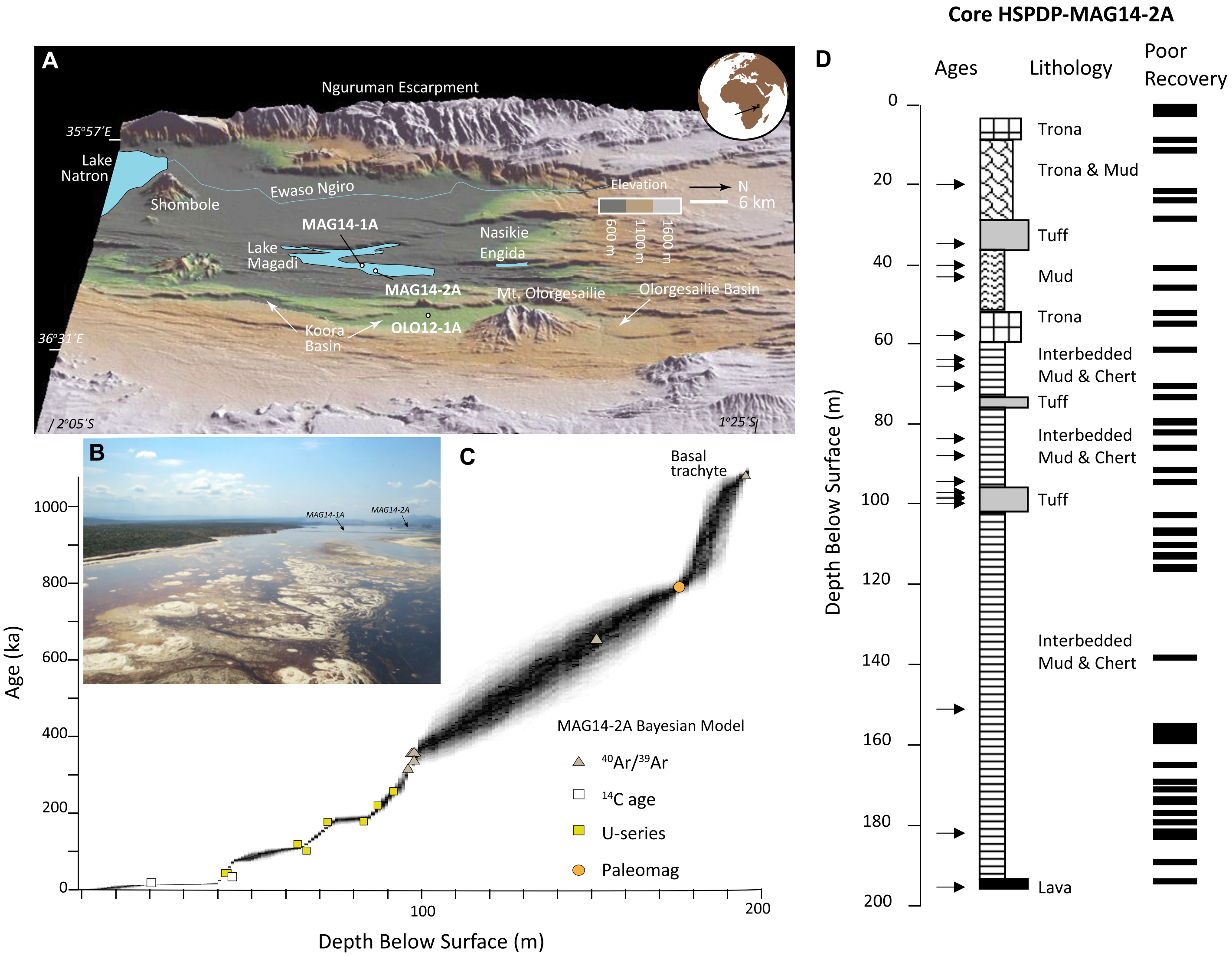

Figure 1. Location and stratigraphy of core HSPDP-MAG14-2A in the Kenyan Rift. (A) Topography of the southern Kenya Rift, view toward the west (shaded topography from GeomappApp.org). (B) View north over Lake Magadi, Kenya (June 2019) showing trona rafts and seasonally flooded lake. The width of Lake Magadi at the location of Core HSPDP-MAG14-1A is ~2.6 km. (C) Bayesian chronological model for core HSPDP-MAG14-2A. See Owen et al. (2018a) for details of geochronology. (D) Simplified lithological log.

METHODS

Core HSPDP-MAG14-2A was drilled to a depth of 194 m and halted in basal trachyte. Lithologies including decimeter-scale interbedded resistant chert and soft muds made drilling difficult; total recovery was ~60% (Campisano et al., 2017). A Bayesian geochronology was based on radiocarbon, $^{40}Ar/^{39}Ar$, paleomagnetic, and U-series dates using Bacon version 2.2 (Owen et al., 2018a). We collected 344 samples at a spacing of ~30 cm from intact core segments at the National Lacustrine Core Facility (Minneapolis, Minnesota, USA) and analyzed them by inductively coupled plasma–mass spectrometry (ICP-MS) following a four-acid digestion by Actlabs (Toronto, Canada; Hu and Qi, 2014). Mineralogy was determined with a Panalytical X-ray diffractometer, analyzing randomly oriented powders from 5 to 65° 2θ at 45 mV and 40 mA (Rabideaux, 2018).

RESULTS

The top ~60 m of core is dominated by trona and trona-bearing zeolitic mud (Cohen et al., 2016). The remainder of the core is mostly laminated to massive zeolitic mud interbedded with chert. Some intervals contain silt- to sand-sized euhedral cubic pyrite crystals.

Sediments older than ca. 700 ka have a Zr/TiO_2 ratio of ~100, whereas younger sediments have a ratio of ~2200, with increased variability in bedded trona in the upper part of the core (Fig. 2). Zr/TiO_2 ratios reflect source-rock geochemistry and are generally unaffected by weathering, so this implies little change in the composition of detrital sources for the basin after the shift ca. 700 ka. Many samples have Mo (to 1500 mg/kg), As (to 200 mg/kg), and V (to 450 mg/kg) concentrations among the highest ever reported in lacustrine sediments (e.g., Owen et al., 2018b). These transition metals and metalloids are commonly associated with euxinic sulfide deposits such as pyrite that scavenge them from saline bottom waters (Vorlicek et al., 2004; Thiam et al., 2014). Variable concentrations are found throughout the clays and silts, which are generally dark colored and reduced; high concentrations are found preferentially in lithologies containing coarse-grained pyrite (Fig. 2; Table S1 in the Supplemental Material[1]). La/Lu in the core increases from the start of the record until ca. 600 ka, after which La/Lu strongly correlates with Mo concentration, particularly during peak eccentricity intervals (Table S3), with a possible long-term declining trend.

[1]Supplemental Material. Comparison of Lake Magadi euxinia with global paleoclimate and orbital parameters, photography of selected core intervals, geochemical data, and statistical analyses. Please visit https://doi.org/10.1130/GEOL.S.15832119 to access the supplemental material, and contact editing@geosociety.org with any questions.

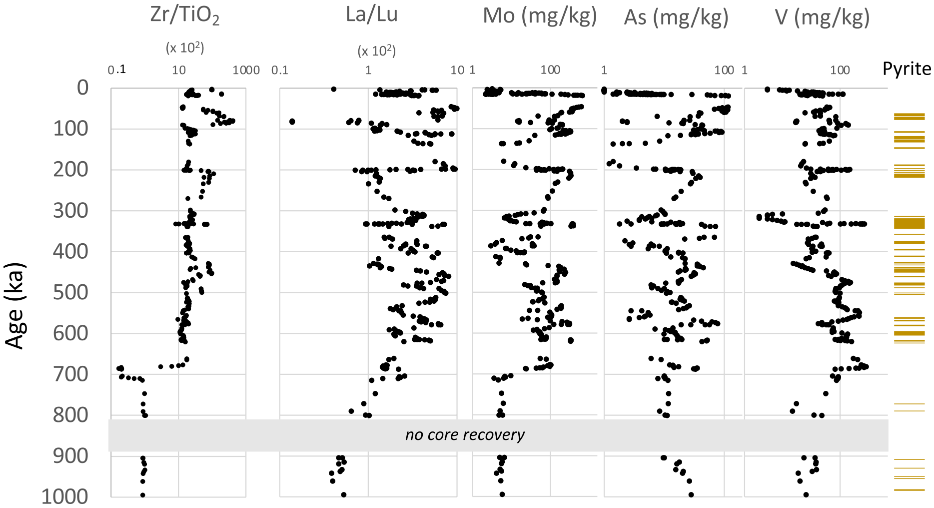

Figure 2. Trace metal geochemistry of core HSPDP-MAG14-2A in the Kenyan Rift, calculated as running five-point averages. Shift in Zr/TiO_2 ratios suggests basin reorganization at ca. 700 ka, and otherwise fairly constant source-area geochemistry. La/Lu ratios suggest gradual increase in anoxia until ca. 600 ka, after which it is cyclical, correlating with euxinia indicators molybdenum, arsenic, and vanadium.

ally meromixis may occur, restoring stratification, perhaps with a freshwater cap.

A range of environmental conditions is represented geochemically (Fig. 3): well-mixed, well-stratified, and euxinia. Euxinia is likely triggered during negative-water-balance episodes; complete desiccation is not implied, however, because sulfide precipitation persists. This is consistent with a lack of paleosols in the core (Muiruri et al., 2021), though some cherts show evidence of subaerial exposure (Leet et al., 2021). Hypolimnic euxinia could persist into episodes of lake-level rise, given that dense bottom waters lie beneath fresher surface waters—perhaps even until thorough mixing occurs. Stratification may be enhanced by lake deepening, but it is not required; e.g., shallow-water anoxia (<0.1 mg/L O_2) is observed at nearby Nasikie Engida (Fig. 1A) with <2 m water depth (De Cort et al., 2019).

Geochemical cyclicity is observed after ca. 820 ka (Fig. 4). Intervals in which Mo concentration is more than 1σ above the mean co-occur with maximum eccentricity over the past ~700 k.y., suggesting sensitivity due to hydrologic closure. Before ca. 700 ka, the geochemical record was likely not sensitive to paleohydrology and the lake may have been hydrologically open. Nearly constant Zr/TiO_2 before and after ca. 700 ka suggests a shift in detrital source at that time, likely related to volcanic, tectonic, or geomorphic events (e.g., stream capture or fault movements).

Correlation between La/Lu and Mo concentration after ca. 600 ka (Fig. 2) suggests that light rare earth element (LREE) enrichment was highest during euxinia. This is consistent with marine observations where anoxic brines become LREE enriched due to redox cycling of Mn- and Fe-oxides (Bau et al., 1997). Late Pleistocene Lake Magadi cherts (Kerrich et al., 2002) have La/Lu an order of magnitude lower, suggesting they formed in less euxinic conditions, perhaps even in oxygenated waters. The high La/Lu and Mo concentration values in the uppermost part of the core dominated by evaporite trona reflect the most recent euxinia in the lake over the past ~100 k.y., possibly related to basin tectonics rather than climatic forcing (Owen et al., 2019).

Molybdenum concentration and eccentricity have no correlation over the data set as a whole, but significant correlations ($p < 0.01$) are found in 50 k.y. and 100 k.y. windows across most of the data set (Table S2). Euxinia tends to peak during eccentricity maxima, associated with eccentricity driven aspects of global paleoclimate records, including sapropel and benthic foraminiferal $\delta^{18}O$ records from the eastern Mediterranean Sea (Emeis et al., 2000; Konijnendijk et al., 2014) and the record of glacial terminations over the past 700 k.y. (Fig. 4). Euxinia as indicated by peak Mo concentrations was

DISCUSSION

Hyperaccumulation of molybdenum, arsenic, and vanadium has not previously been observed in East Africa, though high levels are reported in Lake Kivu hot springs (between Congo and Rwanda) (Degens and Kulbicki, 1973). Owen et al. (2018b) rarely found Mo concentrations above typical ICP-MS detection limits (2 mg/kg) among hundreds of samples across the region. Molybdenum, arsenic, and vanadium accumulation generally requires euxinia: anoxic, sulfide-rich brine. High salinity can occur due to saline hydrothermal input, evaporative concentration, or both; an anoxic hypolimnion in Lake Magadi implies persistent chemostratification. Shallow saline lakes may be anoxic because dense brines resist wind shear, have low oxygen solubility, and rapidly consume oxygen when warmed (Deocampo and Jones, 2014; De Cort et al., 2019). Therefore, it is not unexpected that mixing and oxygenation occur only during flooding events (Talling, 1992). This is also supported by bioturbated magadiite beds (ca. 25–9 ka) overlain by muds, reflecting freshening, lake-level rise, and oxygenation (Buatois et al., 2020). If lake-level rise persists, eventu-

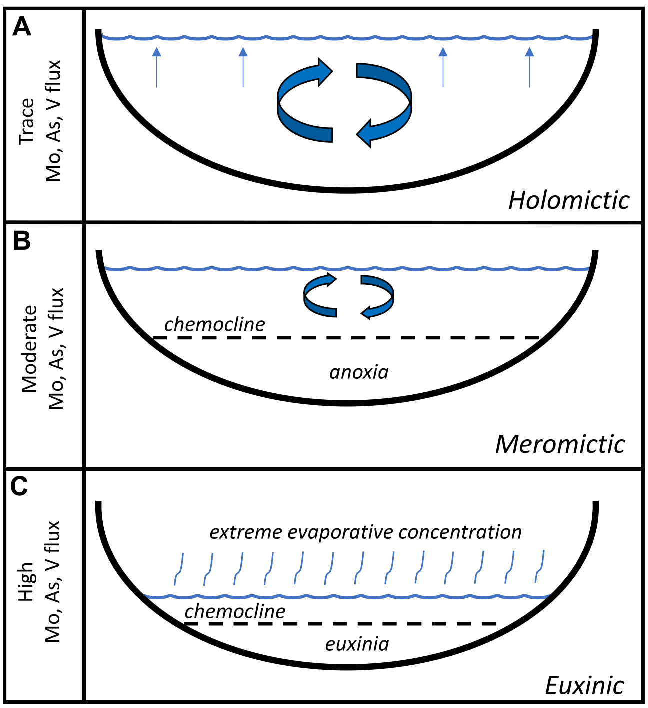

Figure 3. Model of euxinia indicator accumulation in Lake Magadi, Kenya. (A) Well-mixed waters preserve only traces of molybdenum, arsenic, and vanadium especially during lake-level rise because these elements sorb or precipitate easily. (B) Stratified waters accumulate significant concentrations as sustained anoxia mobilizes these elements into aqueous phase. (C) Hyperaccumulation in sulfide phases (i.e., pyrite) as extreme evaporative concentration and anoxia combine to raise concentrations in anoxic bottom waters.

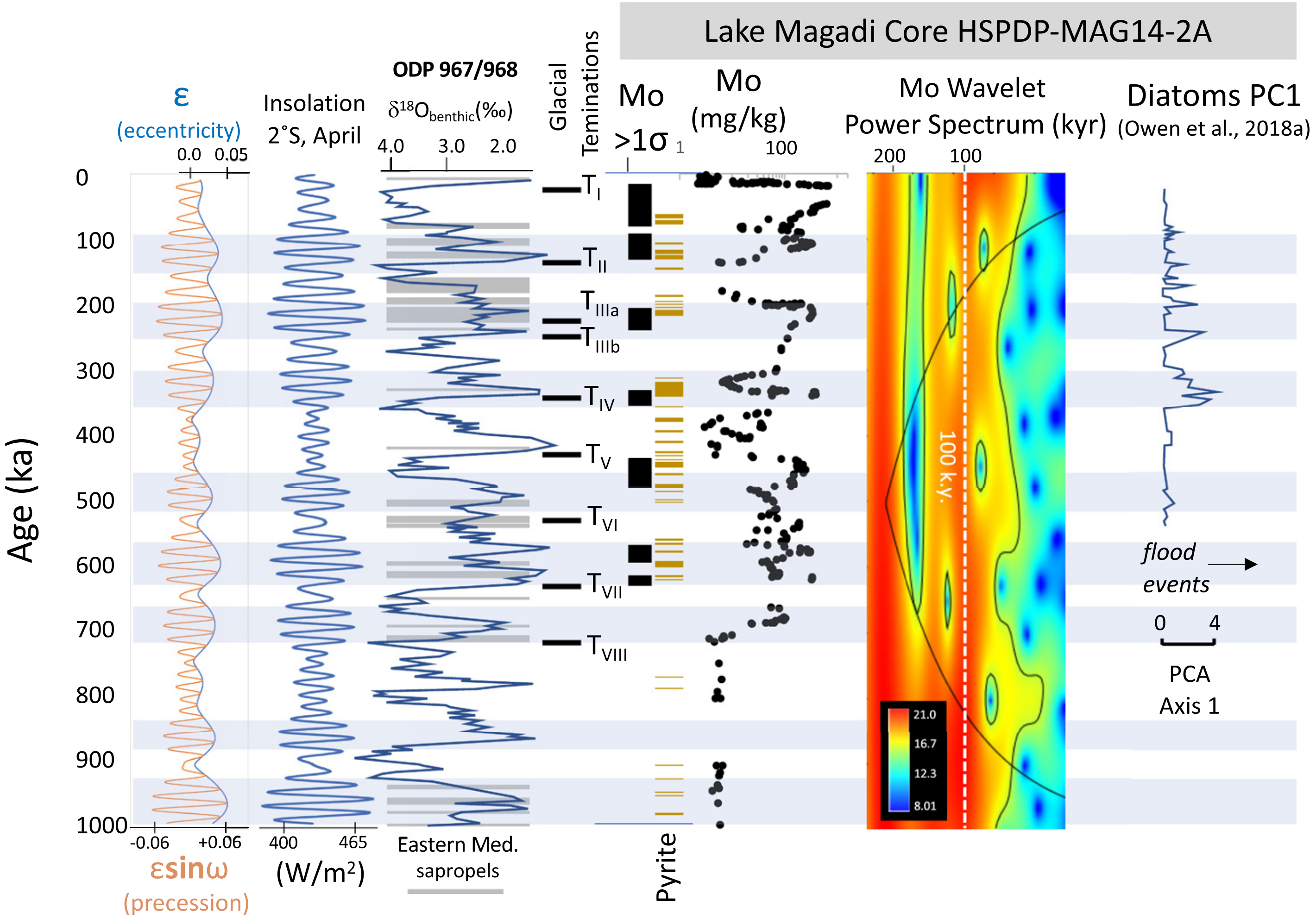

Figure 4. Paleoclimate context of Lake Magadi (Kenya) euxinia. Mo concentration shows 100 k.y. cyclicity after ca. 820 ka, with peaks occurring in high-eccentricity intervals, associated with last eight glacial terminations, and Mediterranean (Med.) benthic foraminiferal (ODP—Ocean Drilling Program) and sapropel records (Emeis et al., 2000; Konijnendijk et al., 2014). Diatom assemblages (PC1—first principal component) suggesting flood events occur more frequently during interglacial compared to glacial intervals (Owen et al., 2018a). Insolation curve is from Laskar et al. (2004). Mo wavelet shows power in 100 k.y. band, with cone of influence and $p = 0.05$ significance contour indicated by black lines. Light shaded bars indicate intervals of high eccentricity. Orbital eccentricity (ε) and precession (εsinω) follow Laskar et al. (2004), where ω is the angle between the axes of perihelion and vernal equinox.

high at all glacial terminations or shortly thereafter, except at termination V, which fell during an eccentricity minimum when precession forcing was weakest (Fig. S1 in the Supplemental Material). Significant cyclicity in the 100 k.y. band is observed for the record from ca. 820 ka to ca. 200 ka (Fig. 4).

High-frequency hydroclimatic changes are known from across eastern Africa during this time interval. At nearby Olorgesailie, shifts between lacustrine and subaerial conditions occur throughout the record over thousands of years (Owen et al., 2008; Deocampo et al., 2010). High-frequency episodic desiccation was shown in the Koora Graben core, ~11 km east of Lake Magadi (Potts et al., 2020). High-frequency change is also known from Lake Malawi ~2000 km to the south (Lyons et al., 2015; Ivory et al., 2016) and Chew Bahir (Ethiopia) ~700 km to the north (Foerster et al., 2018).

Diatom flora in the upper part of the core show high-frequency flood events (Owen et al., 2018a, 2019), and pollen taxa show frequent expansion and contraction of *Podocarpus* forests (Muiruri et al., 2021). These are not represented geochemically, likely because dense, euxinic waters can persist long beyond the onset of euxinia, extending even into early diagenesis (Domagalski et al., 1990), and so may not be specifically tied to surface hydrology on short time scales. Absent an oxidizing event such as lake overturning, euxinia indicators could then be time averaged, smoothing the signal. Accumulation may continue even as a freshwater cap develops, only subsiding upon depletion of the brine or mixing of the water column.

Cyclicity of 100 k.y. in the euxinia signal therefore suggests that intervals of high eccentricity were times when episodes of euxinia were favored, driven by intervals of negative water balance, even as lake level rose and fell. In the diatomaceous upper part of the core, Owen et al. (2018a) found high-frequency pulses of freshwater benthic taxa representing flood events. While they occurred at higher frequencies and are not restricted to high-eccentricity times, they occurred more often during high-eccentricity intervals and correlate with diatom-inferred lake transgressions in the Koora Graben core (Fig. 4; Potts et al., 2020).

Euxinia indicators, then, are associated with both aridity and flooding—high-amplitude salinity events occurring over precessional or other high-frequency time scales, even though the signal may be smoothed out. The greater amplitude of such events during eccentricity maxima argues for an orbital source of the variability (i.e., precession), given that the amplitude of precession was itself modulated by eccentricity over the Pleistocene (Berger and Loutre, 1994). When the amplitude of precession is weakest during low eccentricity (e.g., ca. 400 ka), Mo concentration is correspondingly low, suggesting a breakdown in euxinia (Fig. 4). High Mo at the beginning of this low-eccentricity interval may represent a lag after the eccentricity peak ca. 495 ka.

High-amplitude (i.e., precession-scale) environmental fluctuations undoubtedly had a profound impact on moisture availability and vegetation over evolutionary time scales (Potts, 2013). This likely influenced habitats for early hominins and other vertebrates, vertebrate faunal turnover, expansion of early hominin material transport range, and the development of Middle Stone Age technologies (Potts et al., 2018, 2020).

CONCLUSIONS

Drilling in the Lake Magadi basin and geochemical analyses have yielded lake sediments with some of the highest molybdenum, arsenic, and vanadium concentrations ever reported. These indicate euxinia—strong stratification with anoxic, sulfidic, and saline hypolimnic waters—beginning at ca. 700 ka. Before then, the basin likely was not sensitive to orbitally induced changes in regional hydrology and perhaps was not even hydrologically closed. At ca. 700 ka, a significant event occurred that changed the sediment source and made the lake hydrologically sensitive. Rare earth element data suggest a gradual increase in anoxia from ca. ca. 700 to 450 ka, after which eccentricity-scale variability dominated. Peaks in euxinia indicators (molybdenum, arsenic, and vanadium) tended to occur during intervals of high eccentricity and are associated with most glacial terminations over the past 700 k.y.

The Lake Magadi geochemical record adds to the body of evidence emphasizing the importance of eccentricity modulation of precession in Pleistocene records of hydroclimate in eastern Africa. It also provides a clear indicator of intense droughts in the region during glacial maxima since ca. 700 ka, superimposed on a long-term increase in aridity known from other proxy records. Euxinia episodes in Lake Magadi are consistent with environmental fluctuations hypothesized to play a role in vertebrate and human evolution and the emergence of the Middle Stone Age in East Africa.

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