

“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 a ~200-m core representing the past ~1 Myr of the lake's history show some of the highest concentrations of transition metals and metalloids ever reported from lacustrine sediment, including redox-sensitive elements Mo, As, and V. Elevated concentrations of these elements represent times when the lake's hypolimnion was euxinic – that is, anoxic, saline, and sulfide-rich. Euxinia was common over the past ~700 ka, tending 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 about 500 and 320 ka in the southern Kenya Rift.

INTRODUCTION

The Hominin Sites and Paleolakes Drilling Project (HSPDP) 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 (Figure 1) is within 100 km of several important sites for human origins research, including Olduvai Gorge, Laetoli, and Peninj, with Olorgesailie <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 in the Koora Graben (Figure 1), suggest that environmental variability, especially the intensity of arid episodes, between ~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 (~1.4-0.8 Ma) covers much of the rift floor, cut by rift-parallel faulting. Plio-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 ephemeral lake fed by hydrothermal groundwater and ephemeral streams (Jones et al., 1977). It was part of a large Pleistocene paleolake extending

south to Lake Natron (Hillaire-Marcel and Casanova, 1987). Inflow waters are Na-CO₃ brines, with evaporation producing some of the most concentrated alkaline fluids on earth (Deocampo and Jones, 2014). With pH>10, authigenic silicates such as zeolites and magadiite (Na-silicate) are common (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).

METHODS

Core HSPDP-MAG14-2A was drilled to a depth of 194 m and halted in basal trachyte. Lithologies including dm-scale interbedded resistant chert and soft muds made drilling difficult; total recovery was approximately 60% (Campisano et al., 2017). A Bayesian geochronology was based on radiocarbon, ⁴⁰Ar/³⁹Ar, paleomagnetic, and U-series dates using Bacon v.2.2 (Owen et al., 2018a). 344 samples were collected every ~30 cm from intact core segments at the National Lacustrine Core Facility, and analyzed by ICP-MS following a four-acid digestion by ACTLABS (Toronto; Hu and Qi, 2014). Mineralogy was determined with a Panalytical XRD, analyzing randomly oriented powders from 5–65° 2θ at 45mV and 40mA (Rabideaux, 2018).

RESULTS

The top ~60 m of core are 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 ~700 ka have $\text{Zr/TiO}_2 = \sim 100$, whereas younger sediments have ~2200, with increased variability in bedded trona in the upper part of the core (Figure 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 ~700 ka. Many samples have Mo (up to 1500 mg/kg), As (up to 200 mg/kg), and V (up 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 often 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 of Mo, As, and V 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 (Figure 2; Sup. Table 1). La/Lu in the core increases from the start of the record at ~1 Ma to ~600 ka, after which La/Lu strongly correlates with Mo, particularly during peak eccentricity intervals (Sup. Tab. 3), with a possible long-term declining trend.

DISCUSSION

Very high concentrations of Mo, As, and V have not previously been observed in East Africa, though high levels are reported in Lake Kivu hot springs (Degens and Kulbicki, 1973). Owen et al. (2018b) found Mo concentrations above typical ICP-MS detection limits (2 mg/kg) to be rare among hundreds of samples across the region. High Mo, As, and V generally require 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 O₂ 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 only occur during flooding events (Talling, 1992). Freshening, lake level rise, and oxygenation are also supported by bioturbated magadiite beds (~25-9 ka) overlain by muds (Buatois et al., 2020). If lake level rise persists, eventually meromixis may occur, restoring stratification, perhaps with a freshwater cap.

A range of environmental conditions is represented geochemically: well-mixed, well-stratified, and euxinia (Figure 3). 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, as 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; for example, shallow water anoxia (<0.1mg/L O₂) is observed at nearby Nasikie Engida with <2 m water depth (De Cort et al., 2019).

Geochemical cyclicity is observed after ~820 ka (Figure 4). Intervals in which Mo >1 σ above the mean co-occur with maximum eccentricity over the past ~700 ka, suggesting sensitivity due to hydrologic closure. Before ~700 ka, the geochemical record was likely not sensitive to paleohydrology and the lake may have been hydrologically open. Nearly constant Zr/TiO₂ before and after ~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 after ~600 ka 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 Magadi cherts (Kerrick et al., 2002) have an order of magnitude lower La/Lu, suggesting they formed in less euxinic conditions, perhaps even in oxygenated waters. The high La/Lu and Mo values in the uppermost part of the core dominated by evaporite trona reflect the most recent euxinia in the lake over the past ~100kyr, possibly related to basin tectonics rather than climatic forcing (Owen et al., 2019).

Mo and eccentricity have no correlation over the dataset as a whole, but significant correlations ($p < 0.01$) were found in 50 kyr and 100 kyr windows across most of the dataset (Supp. Table 2). Euxinia tends to peak during eccentricity maxima, associated with eccentricity-driven aspects of global paleoclimate records, including sapropel and benthic foraminiferal $\delta^{18}\text{O}$ records from the eastern Mediterranean (Emeis et al., 2000; Konijnendijk et al., 2014), and the record of glacial terminations over the past 700 ka (Figure 4). Euxinia as indicated by peak Mo concentrations was high at all glacial terminations or shortly thereafter, except Term. V, which fell during an eccentricity minimum when precession forcing was weakest (Supp. Figure 1). Significant cyclicity in the 100 kyr band is observed for the record from ~820 ka to ~200 ka (Figure 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

Magadi (Potts et al., 2020). High-frequency change is also known from Lake Malawi to the south (Lyons et al., 2015; Ivory et al., 2016) and Chew Bahir 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.

100 kyr cyclicity 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. (2018) 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 they correlate with diatom-inferred lake transgressions in the Koora core (Figure 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 timescales, even though the signal may be smoothed out. The greater amplitude of such events during eccentricity maxima argue for an orbital source of the variability (i.e. precession), as the amplitude of precession is itself modulated by eccentricity over the Pleistocene (Berger and Loutre, 1994). When the

amplitude of precession was weakest during low eccentricity (e.g. ~400 ka), Mo is correspondingly low, suggesting breakdown in euxinia (Figure 4). High Mo at the beginning of this low eccentricity interval may represent a lag after the eccentricity peak ~495 ka.

High amplitude (i.e. precession-scale) environmental fluctuations undoubtedly had a profound impact on moisture availability and vegetation over evolutionary timescales (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 Mo, As, and V concentrations ever reported. These indicate euxinia, strong stratification with anoxic, sulfidic, and saline hypolimnetic waters, beginning at ~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 ~700 ka, a significant event occurred that changed the sediment source and made the lake hydrologically sensitive. REE data suggest a gradual increase in anoxia from ~700–450 ka, after which eccentricity-scale variability dominates. Peaks in euxinia indicators (Mo, As, V) tended to occur during intervals of high eccentricity and are associated with most glacial terminations over the past 700 ka.

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 ~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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FIGURE CAPTIONS

Figure 1. Location and stratigraphy of Core MAG14-2A. A: Topography of the south Kenya Rift, view toward the west (GeomappApp.org). B: View north over Lake Magadi (June 2019) showing trona rafts and seasonally flooded lake. C: Bayesian chronological model for Core MAG14-2A. See Owen et al., 2018a. D. Simplified lithological log.

212

213 Figure 2. Trace metal geochemistry of core MAG14-2A, calculated as running 5-point averages.

214 A shift in Zr/TiO₂ ratios suggests basin reorganization at ~700 kyr, and otherwise fairly constant

215 source area geochemistry. La/Lu ratios suggest a gradual increase in anoxia up until ~600 kyr,

216 after which it is cyclical, correlating with euxinia indicators Mo, As, and V.

217

218 Figure 3. Model of euxinia indicator accumulation in Lake Magadi. (A) Well-mixed waters

219 preserve only traces of Mo, As, and V especially during lake level rise, as these elements sorb or

220 precipitate easily. (B) stratified waters accumulate significant concentrations as sustained

221 anoxia mobilizes these elements into the aqueous phase. (C) hyperaccumulation in sulfide

222 phases (i.e. pyrite) as extreme evaporative concentration and anoxia combine to raise

223 concentrations in anoxic bottom waters.

224

225 Figure 4. Paleoclimate context of Lake Magadi euxinia. Mo shows 100 kyr cyclicity after ~820 ka,

226 with peaks occurring in high eccentricity intervals, associated with the last eight glacial

227 terminations, and the Mediterranean benthic foraminiferal and sapropel records (Emeis et al.,

228 2000; Konijnendijk et al., 2014). Diatom assemblages suggesting flood events are found at a

229 much higher frequency, and may occur more frequently during interglacials, though not

230 exclusively (Owen et al., 2018a). Insolation curve from Laskar et al. (2004). Mo wavelet shows

231 power in the 100 kyr band, with cone of influence and p=0.05 significance contour indicated by

232 black lines.

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Figure 1

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Core HSPDP-MAG14-2A

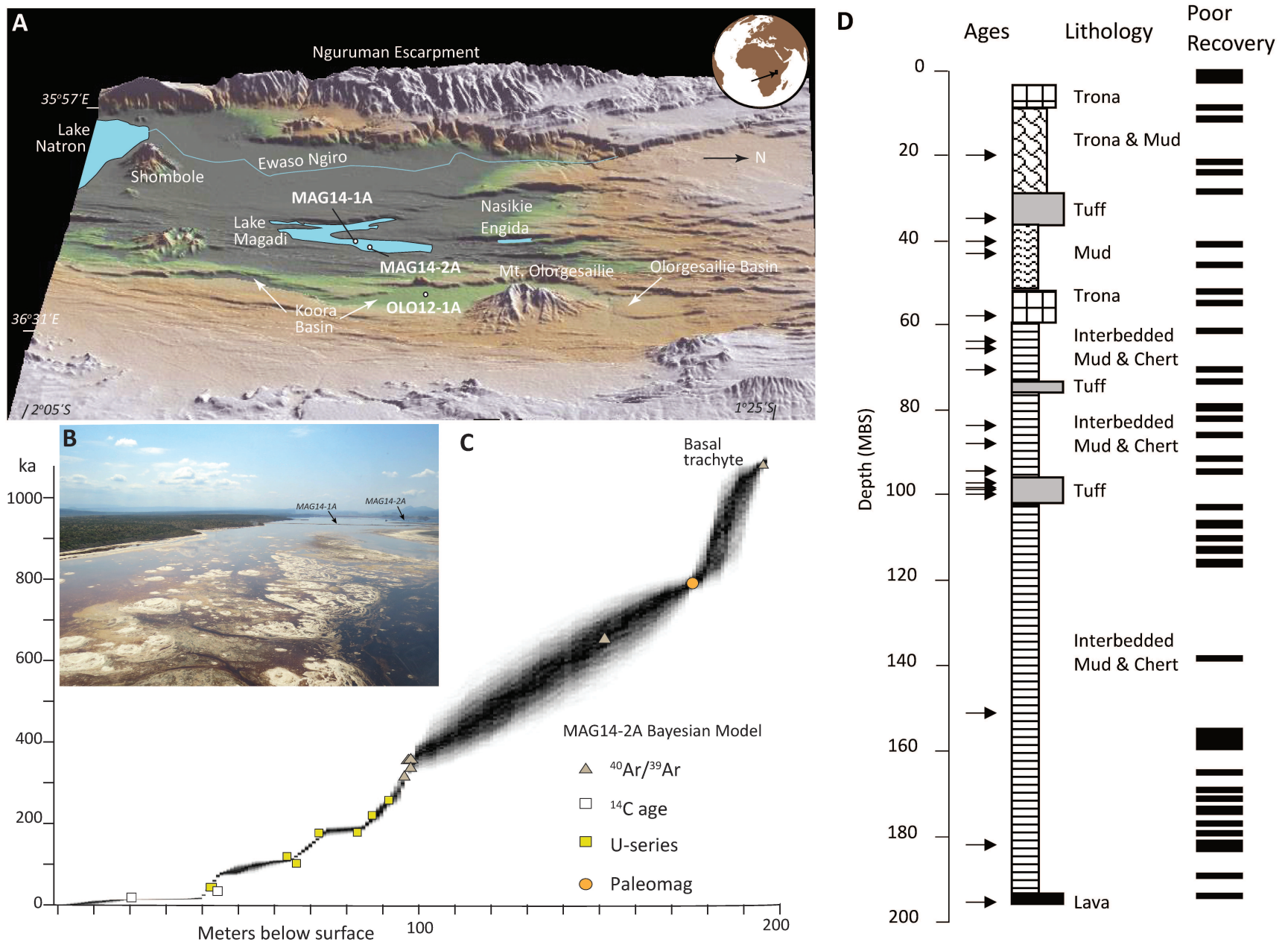


Figure 2
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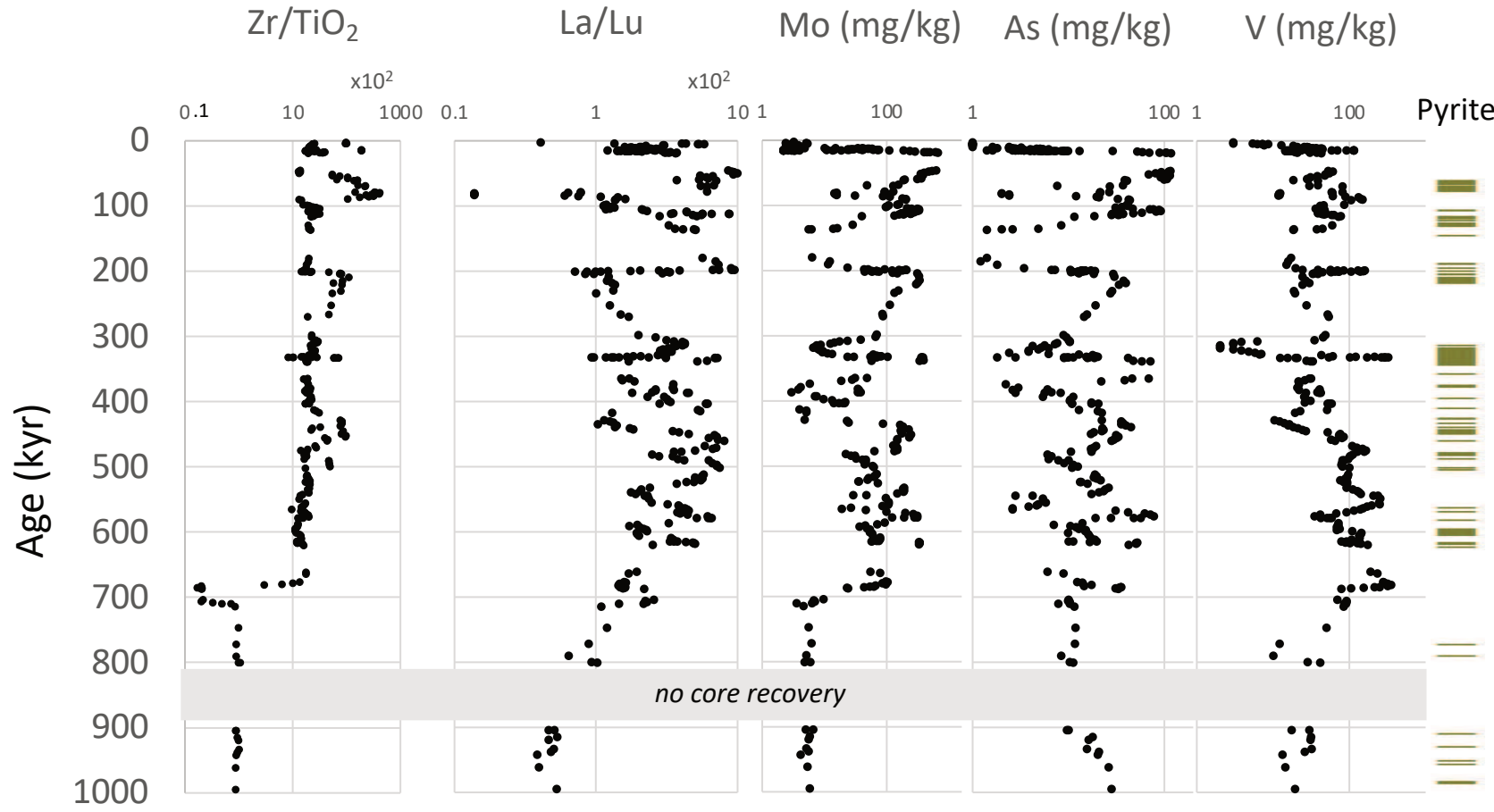


Figure 3
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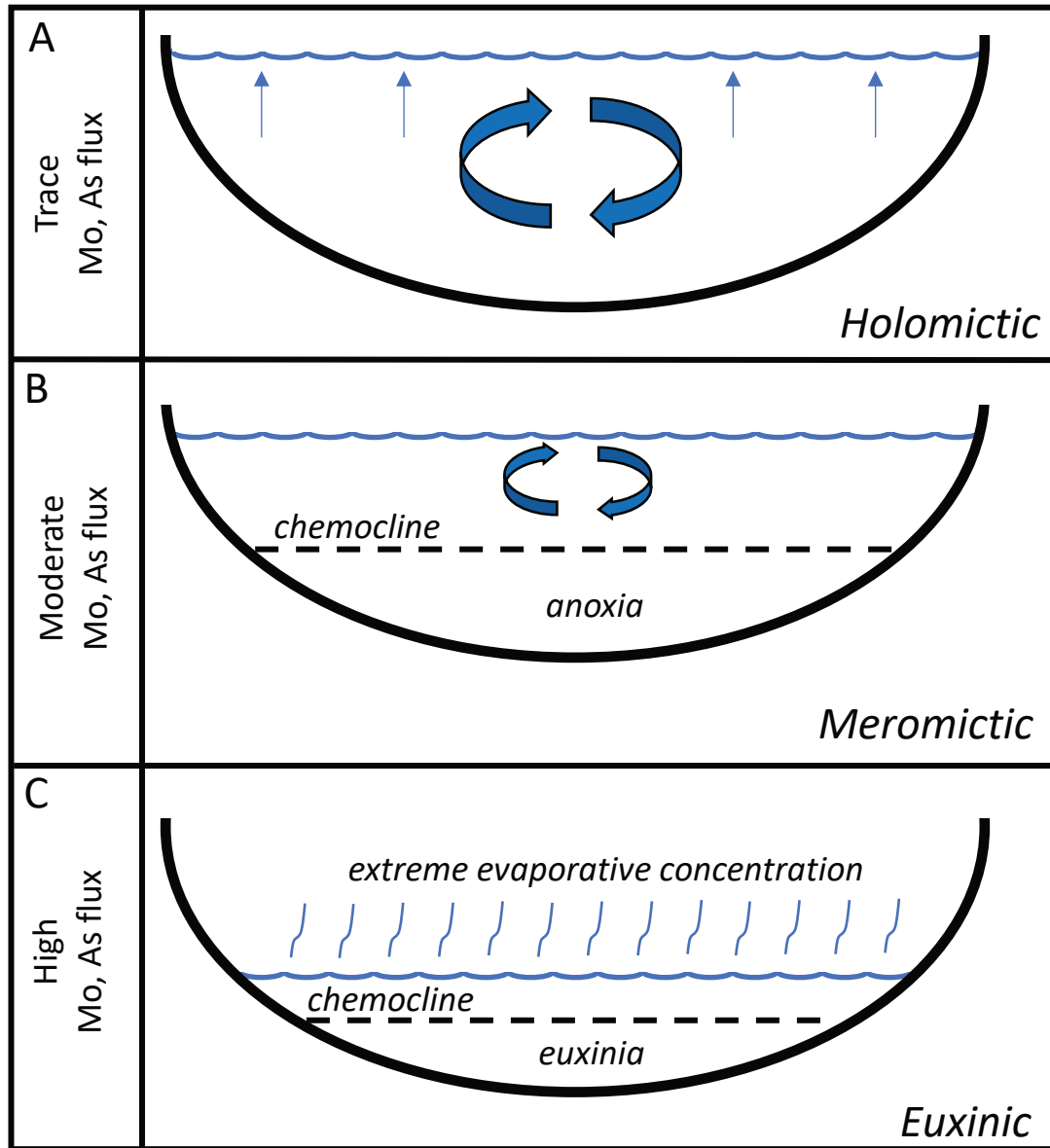


Figure 4
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