



Climate change and productivity variations recorded by sedimentary sulfur in Lake Edward, Uganda/D. R. Congo

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ABSTRACT

We investigate changes in the sulfur geochemistry of sediment cores from Lake Edward, Uganda/Congo to constrain the effects of recent climate changes in the region on the partitioning and isotopic composition of reduced sedimentary sulfur. We measured the concentration and isotopic composition of kerogen sulfur, chromium-reducible, and acid-volatile sulfides, as well as the abundance and partitioning of sedimentary phosphorus and iron, and the abundance and isotopic composition of organic carbon and nitrogen. Results indicate an approximately 150% increase in sulfur concentrations in sediments from Lake Edward over the past 200 years, during which time rainfall in the basin increased and the salinity of the lake fell. Increased sulfur concentrations are largely accounted for by increasing concentrations of kerogen sulfur, which is likely caused by environmentally-driven changes in organic matter quality and concentration, including increased anoxia and nutrient supply to the lake during wet intervals. The isotopic compositions of sedimentary sulfur pools support our interpretation that organic sulfur is derived primarily from sulfurization reactions in the sediment rather than primary bio-sulfur, and gradual isotopic enrichment of the $\delta^{34}\text{S}$ of sedimentary pyrite and kerogen sulfur could result from decreased lake salinity and sulfate availability during the past 200 years. These results highlight the importance of understanding environmentally-mediated changes in organic sulfur accumulation in interpreting the sulfur geochemistry of sediments and sedimentary rocks.

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1. Introduction

The abundance, partitioning, and isotopic composition of sulfur in sedimentary rocks has provided fundamentally important insight into long-term changes in the salinity and biogeochemistry of the world's oceans (Gautier, 1986; Dean and Arthur, 1989; Canfield et al., 2000; Habicht et al., 2002). Sulfur sequestration in marine sediments played a critical role in the evolution of the Earth's biogeochemical cycles of carbon and oxygen (Garrels and Lerman, 1981; Berner, 1987; Canfield et al., 2000), and sulfur cycling strongly influences phosphorus cycling, primary productivity, and alkalinity generation in lakes (Caraco et al., 1989; Giblin et al., 1990). Recent work has shown that the sulfur geochemistry of lacustrine sediments may be a potent indicator of late Pleistocene and Holocene climate variations (e.g. Mayer and Schwark, 1999; Mora and Hinnov, 2005). Yet, although sulfur is a ubiquitous constituent of lacustrine sediments and sedimentary rocks, sulfur geochemistry remains an under-utilized proxy in paleolimnological studies. A number of key questions remain unresolved, for example: Does the abundance and partitioning of sulfur in sediments respond primarily to variations in lake salinity? Or do changes in sedimentary sulfur in

lakes respond primarily to variations in lacustrine carbon cycling, productivity, and stratification?

Dissimilatory bacterial sulfate reduction (BSR) is the primary source of sulfur to both marine and lacustrine sediments, and the sulfide produced by BSR has three major sinks. First, dissolved sulfide can react with ferrous iron in anoxic lake sediments to form iron monosulfides and disulfides (e.g., pyrite; Berner, 1970; Goldhaber and Kaplan, 1974; Raiswell and Berner, 1985). Second, sulfide can react with sedimentary organic matter (Canfield et al., 1998a; Werne et al., 2003), and plays a key role in organic matter diagenesis and preservation (Sinninghe-Damsté and de Leeuw, 1990; Werne et al., 2004). Third, the sulfide produced by BSR can be oxidized back to sulfate or reactive intermediates such as polysulfides or thiosulfate either abiotically or by photo- and chemotrophic microbes, which produces (partially) oxidized sulfur for additional dissimilatory reduction steps (Jørgensen et al., 1979; Roden and Tuttle, 1993). The concentration of sedimentary sulfur in sediments and its partitioning between these sinks is dependent on a host of environmental variables, including sulfate concentrations, iron availability, redox conditions, and organic matter quantity and quality (Raiswell and Berner, 1985; Raiswell et al., 1988; Canfield, 1989; Mossmann et al., 1991; Lyons and Berner, 1992; Zaback and Pratt, 1992; Anderson and Pratt, 1995; Henneke et al., 1997; Lyons, 1997; Passier et al., 1997; Filley et al., 2002; Werne et al., 2004). The complexity of the sulfur cycle, combined with the heterogeneity of lakes and the paucity of studies of

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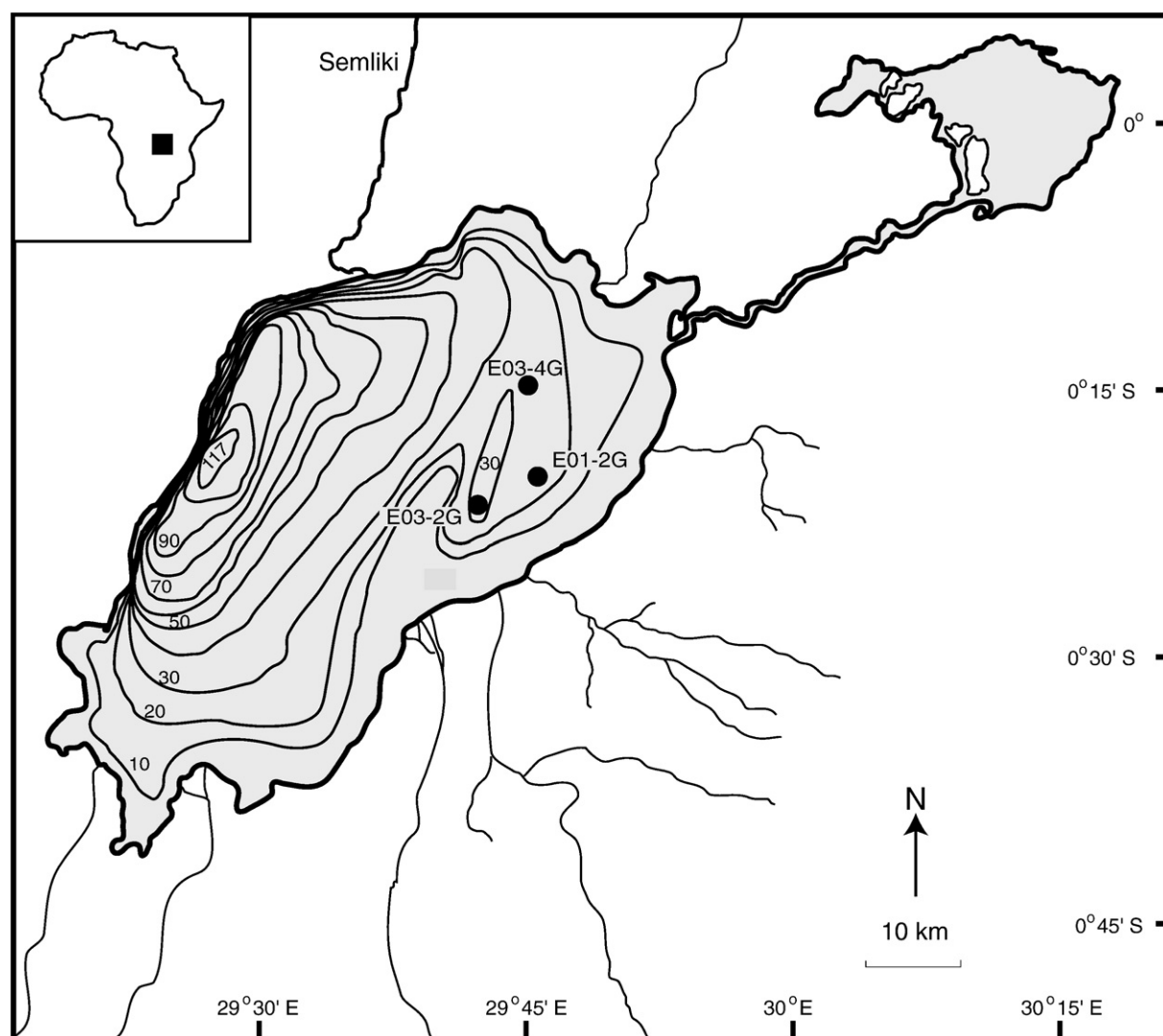


Fig. 1. Site map showing the bathymetry of Lake Edward, the location of major inflowing and outflowing rivers, and the location for cores analyzed in this study. Bathymetric contours are given in 10 meter intervals. The inset at upper left indicates the location of Lake Edward within Africa.

the behavior of sulfur in freshwater systems, severely limits our ability to utilize and interpret sedimentary sulfur geochemistry in lakes as an indicator of past hydrologic or biogeochemical processes.

Here we present analyses of the sulfur geochemistry of sediment cores from Lake Edward, Uganda/Democratic Republic of the Congo (DRC). Previous studies suggest that sedimentary sulfur concentrations in Lake Edward can be interpreted to reflect changes in precipitation during the Holocene (Beuning and Russell, 2004). Lake Edward's salinity has varied considerably during the last ~150 years in response to large-scale, high-amplitude climate variations observed across much of East Africa (Russell et al., 2007). This salinity history, documented by recent studies (Russell et al., 2007; Bessems et al., 2008), provides a natural laboratory in which we can test the effects of changes in lake salinity on sulfur biogeochemistry. We investigated changes in the abundance, partitioning, and isotopic composition of sedimentary sulfur in Lake Edward, and find that sedimentary sulfur concentrations respond to environmental- and climate-driven changes in the quality of sedimentary organic matter during this period of changing limnological conditions. These results highlight the importance of understanding the partitioning of sedimentary sulfur into organic and inorganic pools and the processes controlling the formation of sedimentary organic sulfur in lake sediments.

2. Study site

Lake Edward lies along the border between Uganda and the DRC in the western arm of the East African rift valley (Fig. 1). The lake occupies a half-graben and has a maximum depth of 117 m just east of the western shoreline (Lehman, 2002). Lake Edward is connected to the shallow, dilute, and hypereutrophic Lake George, which drains into Edward via the Kazinga Channel. Principal inflows to Lake Edward derive from the Rwenzori Mountains to the north, the Kigezi highlands

Table 1

Mean chemical composition (μM) of surface waters of Lake Edward based upon the average of samples collected in 2000–2003 (Russell and Johnson, 2006) and recently published sources (Lehman, 2002).

| Component | Concentration (μM) |
|------------------|---------------------------------|
| Na | 3770 |
| K | 1780 |
| Mg | 1660 |
| Ca | 335 |
| HCO ₃ | 7660 |
| Cl | 690 |
| SO ₄ | 250 |

to the east, and the Virunga volcanoes to the south. The lake is presently open, draining north to Lake Albert via the Semliki River, but loses approximately 50% of its water income to evaporation (Russell and Johnson, 2006).

Lake Edward is anoxic below ca. 30 m water depth to its maximum depth of 117 m, but is only weakly thermally stratified. Sporadic measurements of Lake Edward's water chemistry are available starting in 1953, and indicate an average surface salinity of 0.7 ppt and pH of ~8.9 (Lehman, 2002). The chemical composition of Lake Edward is dominated by Na^+ , followed by K^+ and Mg^{2+} , with HCO_3^- as the dominant anion (Table 1). Modern SO_4^{2-} concentrations in the surface mixed layer average ~250 μM (range of 242–256 μM). The lake is presently mesotrophic.

3. Methods

3.1. Sample collection

Gravity core E03-2G was collected from 30 m water depth in May 2003 using a MUCK gravity corer fitted with a 2.75-in. polycarbonate tube. The core site is in a part of the lake that experiences intermittent anoxia (Lærdal et al., 2002). Visual field inspection suggested that the core recovered an intact sediment/water interface. The core was sealed immediately after recovery, and transported to the University of Minnesota, where it was immediately split and sampled in a nitrogen-filled glove bag to avoid oxidation of unstable iron monosulfides. The core was sampled in continuous 2 cm intervals except for the uppermost centimeter, which was sampled in a 1 cm interval. Sampling avoided sediment smeared against the wall of the core liner. Samples were sealed in Quorpak™ vials in the glove bag, then immediately frozen at -40°C before being freeze-dried.

3.2. Bulk geochemical analysis

Freeze-dried samples were homogenized, and divided for various analyses. Total carbon (TC), total inorganic carbon (TIC), and total sulfur (TS) content were measured using UIC Inc. carbon and sulfur coulometers. Total organic carbon (TOC) was determined by the difference of TC and TIC, and CaCO_3 concentration was calculated stoichiometrically from TIC assuming all TIC was present as CaCO_3 . The Mg content of authigenic calcite was analyzed using X-ray diffraction as outlined in Goldsmith and Graf (1958). Core E03-2G has not been directly dated, but correlation of the % Mg in calcite stratigraphy to a nearby core, E03-1G that was dated using ^{210}Pb and AMS ^{14}C (Russell and Johnson, 2007) allows us to assign E03-2G approximate ages assuming that the core top dates to 2003. Biogenic

opal content was analyzed using wet chemical digestion followed by spectrophotometric analysis (Mortlock et al., 1989) using a modified procedure outlined in Russell and Johnson (2005). To determine the isotopic composition and abundance of organic carbon and nitrogen, approximately 1 cm^3 of sediment was fumigated in HCl to remove carbonate using a protocol modified from Hedges and Stern (1984), and analyzed using a Costech elemental analyzer interfaced with a Finnegan Delta Plus XP isotope ratio mass spectrometer at the Large Lakes Observatory, University of Minnesota Duluth. Additional gravity cores collected in 2001 and 2003 (E01-1G and E03-4G) were analyzed for their carbon and total sulfur concentrations using UIC coulometers for comparison to E03-2G.

3.3. Phosphorus speciation

0.1 g dried, homogenized sediment was weighed into 50 ml Falcon tubes, and analyzed for concentration of phosphorus species (oxide-associated, authigenic, detrital, and organic) following a method modified from the SEDEX procedure (Ruttenberg, 1992). Matrix matched calibration standards were prepared for each set of samples, and standards and samples were analyzed via flow injection analysis on a Lachat QuikChem FIA + 8000 series. The concentration of each sample was found using a standard area-concentration curve and values were corrected by subtracting the average blank values within each subset. Sample sets with the external standard concentration error under 10% were considered acceptable.

3.4. Sulfur speciation and isotopic composition

We utilized a sequential extraction scheme modified from Werne et al. (2003) to determine the concentration and isotopic composition of acid-volatile sulfides (AVS, composed of unstable iron mono- and polysulfide minerals), chromium-reducible sulfides (CRS, composed of pyrite and elemental sulfur), and organic or kerogen-bound sulfur (KS). Briefly, the concentration of AVS was determined by reacting sediment with 6N HCl. Chromium reduction followed the protocol outlined in Canfield et al. (1986) to determine % CRS. In both AVS and CRS determinations, the evolved H_2S was driven via N_2 carrier gas into 30 ml of 3% Ag nitrate with 10% NH_4OH and trapped as Ag_2S for gravimetric quantification (Newton et al., 1995). Elemental sulfur concentrations are typically very low in lake sediments (Loshner and Kelts, 1990) as well as marine systems (Goldhaber and Kaplan, 1974), so here we assume that CRS is composed of iron sulfide, primarily pyrite. The residues after chromium reduction were washed three times with distilled, deionized water, filtered and dried in a dessicator. Splits of the filtered residues

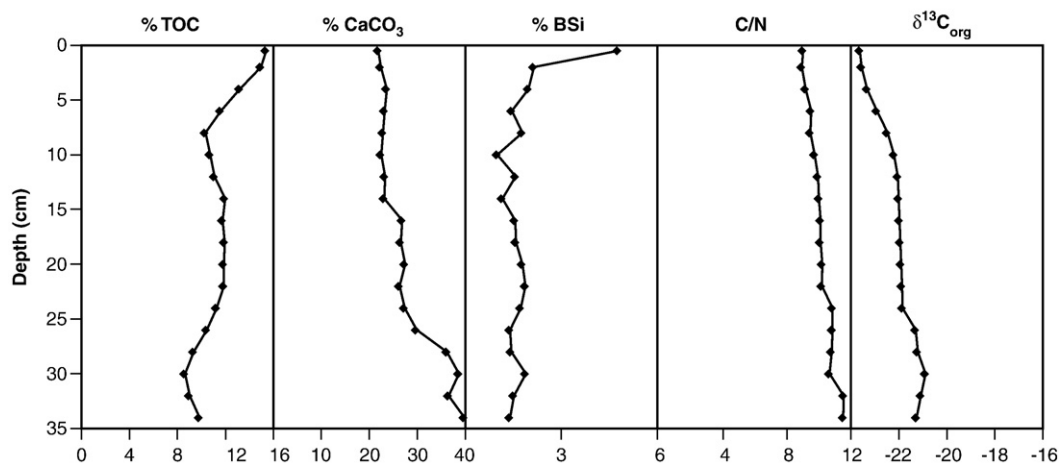


Fig. 2. Total organic carbon (% TOC), calcium carbonate (% CaCO_3), and biogenic silica (% BSi) concentrations, the atomic organic carbon to nitrogen ratio (C/N), and the carbon isotopic composition of bulk organic matter ($\delta^{13}\text{C}_{\text{org}}$) in E03-2G plotted versus depth.

were analyzed using UIC Sulfur Coulometer to determine total organic sulfur concentration (i.e., kerogen sulfur, KS).

Isotopic compositions of AVS and CRS were measured on the Ag_2S precipitates liberated during acid distillation and chromium reduction, and the isotopic composition of kerogen sulfur was determined using rinsed, filtered residue splits. The various extracted sulfur species and filtered residues were placed in tin boats with V_2O_5 catalyst and analyzed for their sulfur isotope compositions by combustion in a continuous flow elemental analyzer connected to a Finnigan 252 stable isotope ratio monitoring mass spectrometer at the Indiana University Bloomington Stable Isotope Research Facility (IUB-SIRF). Sulfur isotope compositions are expressed as permil (‰) deviations from V-CDT using the conventional delta notation. Measurements were directly calibrated against multiple laboratory standards, including NBS-127 (+20.00‰ V-CDT). Standard deviation was better than 0.5‰.

3.5. Fe analysis

Concentrations of pyrite Fe were calculated stoichiometrically assuming all S extracted by the chromium reduction method exists as FeS_2 . The reactive iron content of the sediments was measured by acid digestion of dry sediment in 12N HCl at 100 °C for 1 minute, followed by spectrophotometric determination of Fe concentrations using Ferrozine (Stookey, 1970; Raiswell et al., 1988). Reactive iron has traditionally been operationally defined by this analysis (Berner, 1970; Raiswell et al., 1988); however, studies have shown that this method may overestimate the reactive iron reservoir by solubilizing Fe silicates that are reactive only on much longer timescales (Raiswell et al., 1994).

4. Results

Total organic carbon concentrations (% TOC) in E03-2G range from 8.6 to 15.4% (Fig. 2). % TOC generally increases toward present (the top of the core), with two minima centered at 8 and 30 cm depth. Calcium carbonate concentrations (% CaCO_3) range from 21.9 to 39.8%, and generally decrease toward present. Biogenic silica concentrations (% BSi) are less than 5% throughout the core, and are less than 2% except in the uppermost 2 cm of the sediment (Fig. 2). The decrease in % BSi

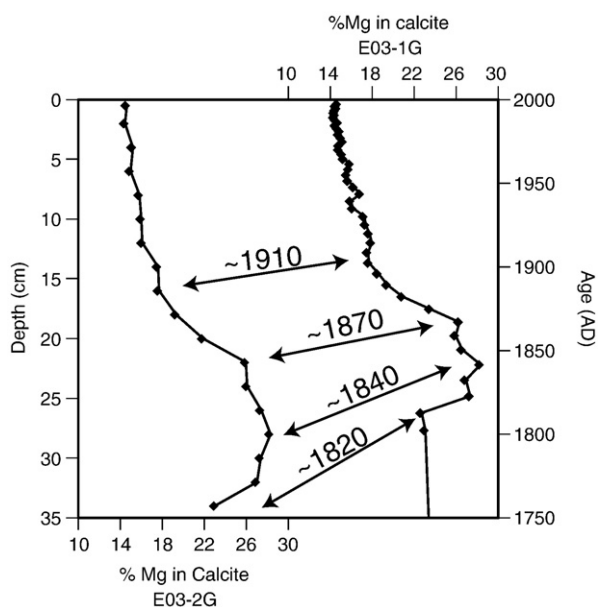


Fig. 3. % Mg in calcite from core E03-2G, plotted together with % Mg in calcite values from another gravity core, E03-1G, dated using ^{210}Pb and ^{14}C (Russell and Johnson, 2007). Stratigraphic tie lines indicate rough ages for E03-2G in years AD.

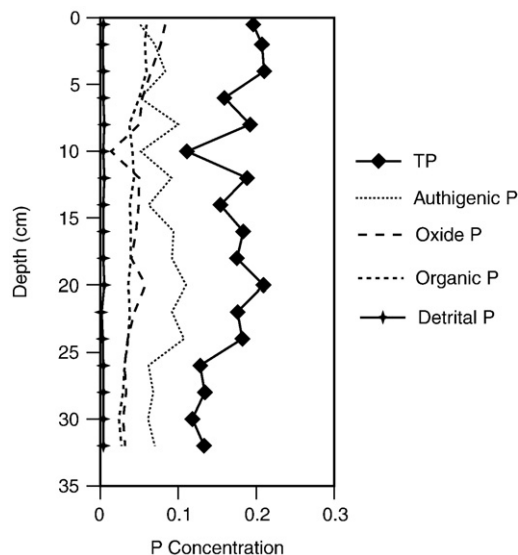


Fig. 4. Total, authigenic, oxide, organic, and detrital phosphorus concentrations in E03-2G plotted against depth. The key at right identifies the phosphorus fraction indicated by different dashed and filled lines with symbols.

below surface sediments likely reflects opal diagenesis in the alkaline waters of Lake Edward. The C/N ratio of organic matter in E03-2G averages 10.14, and gradually decreases from 11.5 at the base of the core to ~9 at the core top. $\delta^{13}\text{C}_{\text{org}}$ values average -22.05‰ , and decrease from values of -21‰ at the base of the core to -23.5‰ toward present (Fig. 2).

% Mg in calcite values range from 14.5 to 28.3%, similar to values previously reported from late Holocene-aged muds from Lake Edward (Russell and Johnson, 2007). Trends in % Mg in calcite in E03-2G are very similar to trends in a nearby core (E03-1G), dated via ^{210}Pb (Fig. 3). We have not developed a precise age model based upon these stratigraphic ties, but these data constrain the timing of the deposition of sediments in E03-2G to within the last ca. 200 years (Fig. 3).

Total sedimentary phosphorus (TP) concentrations in E03-2G range from 0.11 to 0.21% of the sediment, and generally increase in concentration towards the present (Fig. 4). Detrital phosphorus concentrations are minimal throughout the sediment core, indicating that the majority of the TP is composed of reactive phosphorus. Organic and oxide-bound phosphorus concentrations are roughly equal, averaging 0.045 and 0.04% of the sediment, respectively, and

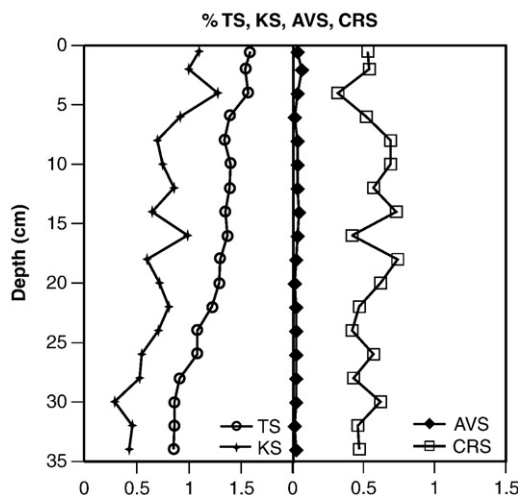


Fig. 5. Total sulfur (% TS), kerogen sulfur (% KS), acid-volatile sulfur (% AVS), and chromium-reducible sulfur (% CRS) concentrations versus depth in core E03-2G. Note rising concentrations of % TS and % KS, in contrast to % AVS and % CRS.

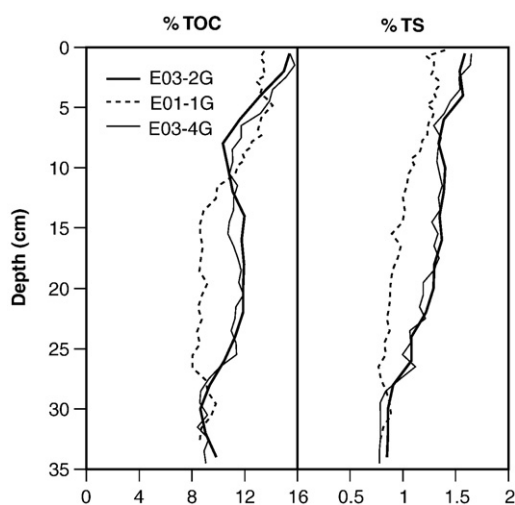


Fig. 6. % TOC and % TS for cores E03-2G, E01-1G, and E03-4G, all from the eastern side of Lake Edward, plotted versus depth.

both of these highly reactive phosphorus phases increase towards the present. Authigenic phosphorus, P contained in authigenic minerals including carbonates and apatite, comprises 0.051 to 0.11% of the sediment and the majority of the phosphorus pool.

Total sulfur concentrations (% TS) range from 0.85 to 1.59%, and increase in a nearly linear fashion from the bottom of the core toward present (Fig. 5). Similar trends in % TS and % TOC are observed in gravity cores (E01-2G and E03-4G) recovered from sites at similar depths in Lake Edward but situated about 7 and 12 km from E03-2G, indicating that results reported for E03-2G are representative of sedimentary trends for much of the shallow, eastern part of Lake Edward (Fig. 6). Acid-volatile sulfides (AVS) comprise less than 0.1% of the sediment at all depths, and exhibit a very small and statistically insignificant increase in surface sediment (Fig. 5). Chromium-reducible sulfide concentrations vary between 0.31 and 0.72% and exhibit no consistent trend with depth. Kerogen-bound sulfur

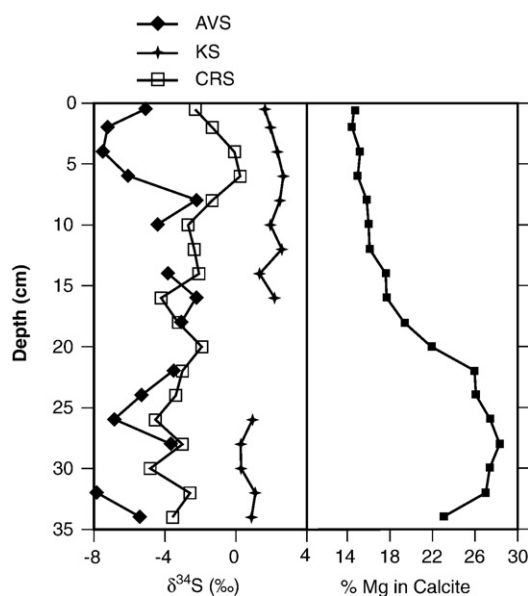


Fig. 7. The isotopic composition of sedimentary acid-volatile sulfides ($\delta^{34}\text{S}_{\text{AVS}}$), chromium-reducible sulfur ($\delta^{34}\text{S}_{\text{CRS}}$), and kerogen sulfur ($\delta^{34}\text{S}_{\text{KS}}$) in core E03-2G. Note the gradual isotopic enrichment in $\delta^{34}\text{S}_{\text{CRS}}$ and $\delta^{34}\text{S}_{\text{KS}}$ towards the top of the core, in contrast with decreased % Mg in calcite that indicates lower salinity.

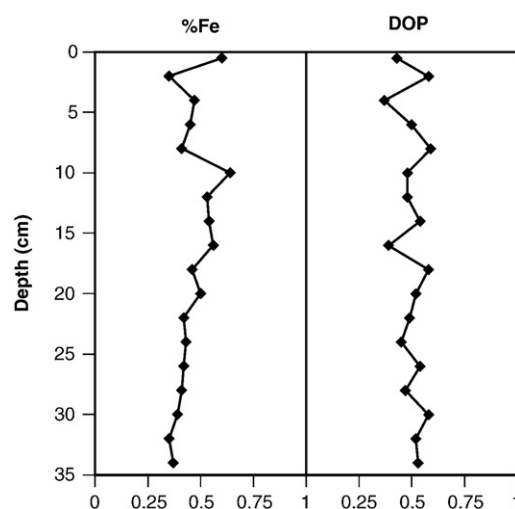


Fig. 8. % reactive iron (% Fe) and the degree of pyritization values (DOP) plotted versus depth for core E03-2G.

concentrations (% KS) range from 0.37% at the base of the core to 1.22% near the core top, and generally increase from the base of the core toward the present.

The sulfur isotope composition of AVS ($\delta^{34}\text{S}_{\text{AVS}}$) averages -4.90‰ (range from -7.8 to -2.17), $\delta^{34}\text{S}_{\text{CRS}}$ averages -2.58‰ (range from -4.84 to $+0.23\text{‰}$), and $\delta^{34}\text{S}_{\text{KS}}$ averages $+1.60\text{‰}$ (range from $+0.27$ to $+2.66\text{‰}$; Fig. 7). Both $\delta^{34}\text{S}_{\text{CRS}}$ and $\delta^{34}\text{S}_{\text{KS}}$ become progressively ^{34}S -enriched toward the present, albeit with considerable scatter. Such a pattern is consistent with diagenetic formation of sulfides and organic sulfur in diffusion-limited sediments (Jørgensen et al., 1979; Donahue et al., 2008).

Reactive iron concentrations (% Fe) average 0.46%, and exhibit a weak trend of increasing values toward present (Fig. 8). Degree of pyritization values (DOP), calculated as the ratio of iron bound in pyrite relative to the sum of reactive and pyrite-bound Fe (Berner, 1970), ranges from 0.39 to 0.59, and averages 0.5. DOP does not exhibit significant trends with depth.

5. Discussion

5.1. General C–S–Fe systematics

In unpolluted lakes, almost all sulfur is delivered as sulfate derived from weathering and oxidation reactions in the lake's catchment (Goldhaber and Kaplan, 1974; Kilham, 1984; Cook and Kelly, 1992). Some of this sulfate undergoes assimilatory sulfate reduction by phytoplankton during photosynthesis, primarily to form proteins as well as sulfolipids, polysaccharides, and sulfate esters (Abrol and Ahmad, 2003; Mora and Hinnov, 2005). Although sedimentation of this organic matter delivers some sulfur to bottom sediments, *in-situ* bacterial reduction of dissolved sulfate is the primary source of reduced sulfur to marine and lacustrine sediments. Sulfate that diffuses into the sediments is utilized by sulfate-reducing bacteria to oxidize organic matter under anoxic conditions, producing hydrogen sulfide (Goldhaber and Kaplan, 1974; Canfield and Des Marais, 1991; Canfield, 2001a). Much of the sulfide produced by BSR is re-oxidized to sulfate (Jørgensen, 1982; Zopfi et al., 2004), but a fraction of it is buried in sediments either through reaction with iron to form unstable iron monosulfides and/or pyrite (Berner, 1970; Raiswell and Berner, 1985), or through the formation of organic sulfur compounds (Canfield et al., 1998a; Werne et al., 2000). Numerous studies have demonstrated that reduced sulfur is bound to lipids and carbohydrates to form organic sulfur provided that anoxic conditions persist to prevent sulfide oxidation, reactive Fe supply is limited, and that a suitable, functionalized organic substrate is

available (Wakeham et al., 1995; Sinninghe-Damsté et al., 1998; Mora and Hinnov, 2005). Reactive Fe availability is traditionally thought to be particularly important to the incorporation of sulfide into organic matter (Canfield, 1989; Canfield et al., 1996) because iron sulfide precipitation is kinetically favored relative to organic matter sulfurization (Gransch and Posthuma, 1974; Pyzik and Sommer, 1981; Hartgers et al., 1997); however, various studies have documented the simultaneous formation of organic sulfur and iron sulfides (e.g. Urban et al., 1999; Filley et al., 2002). This indicates that the concentration and quality of organic matter, i.e. the extent of functionalized, reactive compounds, could play an equally important role as reactive Fe availability in regulating S burial in sediments.

Sulfate concentrations in freshwater lakes are typically low, limiting the diffusion of sulfate into lake sediments and restricting the zone of active bacterial sulfate reduction to the uppermost centimeters of the sediment column (Fenchel et al., 1998; Molongoski and Klug, 1998). However, despite low concentrations of dissolved sulfate, sulfate reduction rates in freshwater lakes can often approach rates similar to those reported in marine sediments (Sinke et al., 1992; Roden and Tuttle, 1993) due to high rates of sulfide oxidation and intense recycling of sulfate in surface pore waters (Jørgensen, 1982). Rates of iron supply to lake sediments are typically thought to be high, at least compared to offshore marine environments, yet organic sulfur compounds are often the most abundant pool of sedimentary sulfur in lake sediments (Nriagu and Soon, 1985; Landers and Mitchell, 1988; Losher and Kelts, 1990; Kleeberg, 1997; Mora and Hinnov, 2005). These findings suggest that sedimentary organic sulfur could play an important role in paleolimnological studies, given a proper theoretical framework for its interpretation.

5.2. Sedimentary sulfur and paleosalinity

High sulfate concentrations in seawater result in relatively high concentrations of reduced sulfur, primarily in the form of pyrite, provided that sedimentary organic carbon concentrations are high enough to stimulate BSR (Berner, 1970; Raiswell and Berner, 1985; Lin and Morse, 1991; Lyons and Berner, 1992). In contrast, lakes have relatively high organic carbon concentrations (Kelts, 1988; Talbot, 1988), but relatively low aqueous sulfate concentrations limit rates of BSR and result in low reduced sulfur concentrations in lacustrine relative to marine sediments (Berner and Raiswell, 1984; Raiswell and Berner, 1985; Davison, 1988).

Due to this difference between marine and freshwater sulfate availability, various proxies for paleosalinity have been proposed based upon concentrations of sedimentary sulfur, although each can be affected by a variety of environmental factors other than salinity. Berner and Raiswell (1984) suggested that sedimentary sulfur concentrations could be used to diagnose whether ancient sedimentary rocks were formed in marine or freshwater environments. TOC/TS ratios have been suggested as a proxy for salinity (Berner and Raiswell, 1984; Davison, 1988), as have TOC/ S_{pyrite} ratios to avoid biasing sedimentary C/S ratios by the presence of forms of sulfur such as evaporite minerals (Davison et al., 1985; Davison, 1988). However, these proxies will behave poorly in TOC- or Fe-limited settings (Dean and Arthur, 1989; Lyons and Berner, 1992; Canfield et al., 1996). Ratios of $S_{\text{pyrite}}/\text{AVS}$ may also be a function of salinity, as increasing HS^- concentrations in sulfate-rich environments may help to drive the conversion of iron monosulfides to pyrite (Berner et al., 1979; Davison et al., 1985). However, pyrite formation is no longer thought to be a simple reaction of dissolved sulfide with ferrous iron, and likely involves catalysis by microbes as well as unstable sulfur species (c.f. Schoonen, 2004).

Each of these hypotheses is founded in theoretical considerations and may work well in certain marine environments where we have a well-developed understanding of sulfur geochemistry. However, the

proper interpretation of sedimentary sulfur concentrations and ratios in freshwater systems remains largely untested due to a lack of data.

5.3. Sedimentary sulfur in Lake Edward: paleosalinity effects?

% TS values in early Holocene sediments from Lake Edward are as high as 4.7%, extremely high relative to typical lacustrine values (Berner and Raiswell, 1984; Nriagu and Soon, 1985; Davison, 1988) and other freshwater African rift lakes (Talbot et al., 2006). % TS in our more recent sediments in E03-2G average only 1.2%. However, from these studies it is clear that sedimentary sulfur concentrations observed in Lake Edward equal or even exceed those typically observed in recent marine sediments, although dissolved SO_4^{2-} in Lake Edward is about two orders of magnitude lower than in seawater. Moreover, TOC/TS, TOC/ S_{pyrite} , and FeS_2/FeS ratios in E03-2G are all much closer to ratios thought to be typical of marine rather than lacustrine systems (e.g. Davison, 1988; Table 2). These data clearly urge caution in interpreting sedimentary sulfur concentrations and ratios to infer the paleosalinity of depositional environments, both in recent sediments and in the rock record.

Beuning and Russell (2004) assumed that the majority of the total sulfur in early Holocene sediments was bound as pyrite, and suggested that concentrations of reactive Fe limit total sedimentary sulfur concentrations in Lake Edward. They further hypothesized that TS concentrations should rise during wetter conditions when rates of Fe supply to the lake will be highest, as has been observed in other lakes (e.g. Mora and Hinnov, 2005). River-borne particulate iron hydroxides are the most important source of Fe to sediments (Millero et al., 1995), and their flux can be limited by low precipitation rates (Losher and Kelts, 1990; Friese et al., 1998; Mora et al., 2002; Mora and Hinnov, 2005) or by sedimentation of particulate iron in nearshore environments, starving offshore environments in large lakes and euxinic marine systems of reactive Fe (Lyons and Berner, 1992; Canfield et al., 1996). Unfortunately, Beuning and Russell (2004) did not measure reactive Fe concentrations, so their hypotheses concerning the C–S–Fe geochemistry of Lake Edward could not be directly tested.

Several aspects of our new data indicate Fe-limited pyrite formation in Lake Edward. % TOC values in these sediments average 11.4%, much too high to limit rates of sulfate reduction, and the concentration of S_{pyrite} is decoupled from % TOC ($r^2 = 0.0032$) indicating TOC concentrations do not control pyrite concentrations and S burial. Acid-volatile Fe monosulfides are virtually absent from these sediments, indicating an excess of sulfide relative to reactive Fe (Berner et al., 1979). Pyrite formation is believed to be kinetically favored relative to the sulfurization of organic matter given adequate reactive iron (Gransch and Posthuma, 1974), so the abundance of organic sulfur in Edward suggests that the supply of reactive iron limits inorganic sulfur burial in Lake Edward. Finally, the degree of pyritization (DOP), a measure of the extent of reactive Fe transformation to pyrite (Berner, 1970), averages 50% in E03-2G. These DOP values are within the range of values reported for Fe-limited settings in the Black Sea (Lyons and Berner, 1992), particularly given that our procedure for measuring Fe typically overestimates reactive Fe

Table 2

TOC/TS, TOC/ S_{pyrite} , and FeS_2/FeS ratios from Lake Edward, normal marine systems, and 'typical' freshwater environments.

| | Lake Edward | Normal marine | Freshwater |
|---------------------------|-------------|---------------|------------|
| TOC/TS | 9.31 | 0.5–5 | 40–120 |
| TOC/ S_{pyrite} | 22.46 | 0.5–5 | 170–6000 |
| FeS_2/FeS | 24.42 | 0.2–100 | 0.5–5 |

Values from marine and freshwater systems are from Davison (1988). TOC/TS, S_{pyrite} and FeS_2/FeS for Lake Edward represent averages from E03-2G calculated assuming that CRS and AVS values represent pyrite and iron monosulfide concentrations, respectively.

concentrations due to Fe loss from silicates (Raiswell et al., 1994; Canfield et al., 1996).

Given this evidence, it is tempting to suggest that trends in S_{pyrite} , and perhaps TS, in Lake Edward could serve as a proxy for rainfall due to runoff-mediated effects on reactive Fe delivery to lake sediments. Increased % TS towards the present in E03-2G coincides with changes in the Mg/Ca ratio in authigenic calcite, which records decreased precipitation from the late 19th into the early 20th century (Russell et al., 2007), as occurred across much of East Africa (Nicholson, 1998; Verschuren et al., 2000; Bessems et al., 2008). However, % CRS values do not increase toward the present; rather, the rise in % TS is largely accounted for by rising concentrations of organic sulfur. Thus, despite evidence for Fe-limited pyrite formation, sedimentary Fe concentrations do not appear to be the mechanism linking changes in sulfur concentrations to climate in Lake Edward.

Climate-driven transitions between pyrite-dominated and organic sulfur dominated S burial have been previously identified in the Bogota basin as a response to late Pleistocene climate cycles, where high FeS concentrations during wet phases alternate with high KS concentrations during dry phases. Mora et al. (2002) interpreted these transitions to reflect changes in Fe supply to the basin, with high Fe supply and high FeS concentrations marking wet intervals. However, Fe–S concentrations ranged from 0 to 0.1% in the Bogota Basin and varied between ~0 and ~95% of the total sedimentary sulfur (Mora et al., 2002). This behavior is fundamentally different from our record, in which % CRS is relatively abundant and invariant during an interval of rising % KS and increasing rainfall. This behavior suggests that another mechanism, related to shifting concentrations of organic sulfur causes the observed shifts in sedimentary sulfur speciation in Lake Edward.

5.4. $\delta^{34}\text{S}$ variations in Lake Edward: salinity and primary productivity

The isotopic composition of sedimentary sulfur can provide important information on paleoenvironments and biogeochemical processes (Canfield, 2001a). Kinetic fractionation effects cause the sulfide produced by BSR to be significantly ^{34}S -depleted relative to coexisting sulfate (Harrison and Thode, 1958; Goldhaber and Kaplan, 1974; Habicht and Canfield, 1997). Large kinetic fractionation can also occur during sulfide oxidation (Canfield, 2001a) as well as thiosulfate disproportionation (Canfield et al., 1998b). There is very little fractionation associated with pyrite formation (Price and Shieh, 1979; Wilkin and Barnes, 1996), so the $\delta^{34}\text{S}$ of pyrite can be interpreted

in terms of the environmental factors affecting the formation of reduced sulfide.

$\delta^{34}\text{S}$ values of both pyrite and organic sulfur in E03-2G are more ^{34}S -enriched in surface sediments than near the base of the core. This trend could simply reflect sulfur diagenesis in surface sediments, with increasing incorporation of isotopically depleted reduced sulfur with depth. However, this process should also cause increasing sulfur concentrations with depth, in contrast to what we observe. Furthermore, the observed trend is opposite to that typically observed in sediments due to diffusion-limited BSR (Jorgensen et al., 1979; Donahue et al., 2008). Changes in $\delta^{34}\text{S}$ in recent sediments from Lake Edward could also result from a new sulfur source such as biomass or fossil fuel burning, however, such “anthropogenic” sulfur contamination typically is associated with ^{34}S -depleted isotopic compositions (Nriagu and Soon, 1985; Macko and Ostrom, 1994). Moreover, atmospheric sources of sulfate in Lake Edward are a tiny fraction of total sulfur inputs (Lehman, 2002), so an incredibly ^{34}S -enriched sulfur isotope composition of the new S source would be required to explain the observed variations in our core.

Alternatively, the isotopic composition of sedimentary sulfur in Lake Edward could result from changing sulfate concentrations in the lake, providing a powerful new tool to investigate paleoclimate and lacustrine paleosalinity. Canfield, (2001b) and Habicht et al., (2002) have shown that fractionation during BSR is a non-linear function of aqueous sulfate concentrations, with fractionation increasing dramatically at aqueous sulfate concentrations of 200 μM and greater. Sulfate concentrations in Lake Edward today are ~250 μM (Table 1), so elevated sulfate concentrations during intervals of evaporative concentration and drought, such as those present in the late 19th century and represented by the base of E03-2G, could lead to larger isotopic fractionation during BSR and more ^{34}S -depleted sulfur isotope values in pyrite in Edward sediments. In this scenario, trends toward heavier $\delta^{34}\text{S}$ values of both pyrite and organic sulfur over the length of the E03-2G core reflect decreased kinetic isotope fractionation in response to falling sulfate concentrations as Lake Edward freshened over the past century. While these results suggest that $\delta^{34}\text{S}$ can provide important insight into lacustrine paleohydrology and paleosalinity, this process should also result in decreasing concentrations of sulfur towards the present in our sediment core, in contrast to what we observe. Thus, while changes in salinity might influence the isotopic composition of sedimentary sulfur in Lake Edward, they cannot completely explain the observed variations in sedimentary sulfur concentrations.

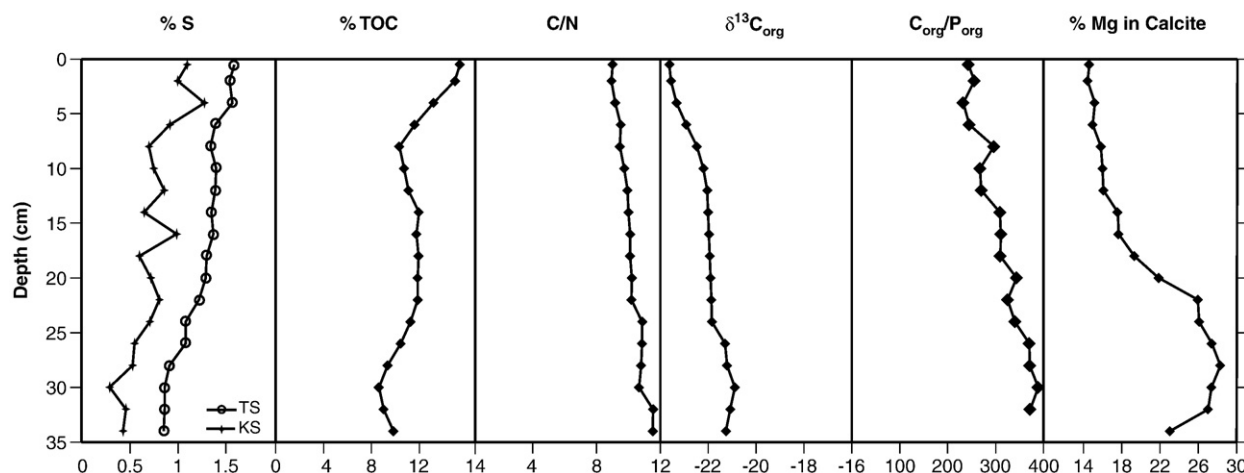


Fig. 9. % TS, % KS, and % TOC together with various indicators of the quality of organic matter present in E03-2G and % Mg in calcite, an indicator of salinity. Note that trends in C/N, $\delta^{13}\text{C}_{\text{org}}$, and $\text{C}_{\text{org}}/\text{P}_{\text{org}}$ are all compatible with increasing concentrations of reactive organic matter in E03-2G towards the present.

5.5. Environmental effects on the formation of kerogen sulfur

The formation of organic sulfur compounds is known to be an effective mechanism for sulfur burial in lake sediments (Nriagu and Soon, 1985; Losher and Kelts, 1990; Kleeberg, 1997; Mora and Hinnov, 2005). Organic sulfur is comprised of both compounds originally present in sedimentary organic matter, as well as organic sulfur compounds formed via diagenesis in the sediment. Atomic C_{org}/S averages ~ 100 in live phytoplankton (Zehnder and Zinder, 1980; Baker et al., 1989), yet C_{org}/S_{org} in E03-2G sediments averages 18.6, indicating that the bulk of the organic sulfur in the sediments was formed by diagenetic reactions between bacterially reduced sulfur and sedimentary organic matter. Moreover, formation of acid-volatile sulfide followed by pyrite is kinetically favored relative to the sulfurization of organic matter during diagenesis (Gransch and Posthuma, 1974; Hartgers et al., 1997), resulting in AVS minerals that are ^{34}S -depleted relative to pyrite, and pyrite that is ^{34}S -depleted relative to organic sulfur compounds when all three products are formed from a pool of sedimentary sulfide (Werne et al., 2004, 2003). In E03-2G, $\delta^{34}S$ of AVS averages -4.90% , $\delta^{34}S$ of pyrite averages -2.58% , and $\delta^{34}S$ of KS averages $+1.60\%$, following the trends that one would predict as iron and organic matter react with a pool of bacterially reduced sulfide.

Given this evidence for the formation of both pyrite and sedimentary organic sulfur, as well as increasing concentrations of kerogen sulfur during an interval of increasing precipitation and decreasing lake salinity, it is critical that we understand the environmental controls on organic matter sulfurization in lake sediments. Studies of lacustrine sediment have documented the co-occurrence of high concentrations of iron sulfides and organic sulfur, even in the presence of excess reactive Fe (Bates et al., 1995; Urban et al., 1999; Mora et al., 2002), similar to our observations in Lake Edward. The abundance of highly functionalized organic matter in lacustrine relative to normal marine systems strongly suggests that organic matter will compete with Fe for available sulfide, in contrast to normal marine systems where reactive iron is the strongly favored substrate for bacterially reduced sulfur (Canfield, 1989; Canfield et al., 1996).

We argue that trends in % KS in Lake Edward are driven by changes in the abundance of highly functionalized organic matter that reacts with reduced sulfide to form kerogen sulfur. Concentrations of KS in our record are highly correlated to % TOC ($r = 0.82$), and increasing concentrations of TOC and KS toward the present are accompanied by a 2.5‰ decrease in $\delta^{13}C_{org}$, decreases in the organic C/N ratio, and a decrease in C_{org}/P_{org} (Fig. 9). These trends could be influenced by a variety of processes. Changes in the atmospheric composition of carbon dioxide (the Suess effect; Keeling, 1979) can account for $\sim 1.5\%$ of this decrease. However, the Suess effect does not explain changes in C/N nor C_{org}/P_{org} , which, together with the observed depletion in $\delta^{13}C_{org}$ are consistent with increased inputs of high-quality aquatic organic matter relative to oxidized terrigenous organic matter to the sediments in an environment dominated by C_4 vegetation (Meyers and Ishiwatary, 1993; Meyers and Teranes, 2001; Talbot et al., 2006). Increasing concentrations of organic and reactive phosphorus (Fig. 4) further support this interpretation. The $\sim 4.2\%$ difference in $\delta^{34}S$ values between KS and CRS observed in Lake Edward is much smaller than the 10‰ offsets typically observed in marine sediments (Werne et al., 2003). This supports the hypothesis that reduced sulfur is reacting with iron and organic matter in a much more simultaneous fashion in lacustrine than in marine systems, and also points to the short distance over which diffusive effects on apparent S-isotope fractionation are operating (Donahue et al., 2008). Thus, rising concentrations of reactive organic matter supplied to the E03-2G site likely promoted increased burial of kerogen sulfur as rainfall increased and lake levels rose in Lake Edward.

Several additional processes within the coupled C–S–Fe–P system could interact with increasing concentrations of functionalized organic matter to stimulate the increase in kerogen sulfur. Filley et al. (2002) suggested that rapid inputs of reactive iron to Mud Lake, USA, may promote organic matter sulfurization through the formation of intermediate sulfur compounds, such as polysulfides, that are highly reactive with organic matter. This mechanism seems unlikely to fully explain the trends in % KS in Lake Edward, as neither Fe nor CRS concentrations are correlated to KS in our sediment core. We have not determined the precise forms of organic sulfur present in Lake Edward, so the reactions forming KS in our sediments are unknown. However, the general scenario proposed by Filley et al. (2002), that the rapid recycling of sulfur between sulfate reducers and sulfide oxidizers in a fluctuating environment produces reduced reactive sulfur that simultaneously binds with iron and organic matter seems plausible for Lake Edward, given the evidence for fluctuating lake levels and the abundance of organic carbon, iron, phosphorus, and various pools of sulfur in our sediments.

Within this scenario, changes in precipitation affect a suite of environmental parameters that regulate sedimentary sulfur burial in Lake Edward, mediated by changes in organic matter quality and concentration. For instance, drought could result in less frequent anoxia, decreased phosphorus supply and aquatic primary productivity, and increasing concentrations of terrigenous organic matter due to decreased lake level, all of which reduce the concentration of highly functionalized organic matter. Moreover, higher rates of bacterial sulfide oxidation could occur at the E03-2G core site as a result of less frequent anoxia, causing depleted $\delta^{34}S$ of sedimentary sulfides. Rising water levels could promote the production and preservation of reactive TOC through increased delivery of phosphorus and more frequent anoxia—the latter of which further increases P supply to the water column through the dissolution of oxide-P (Caraco et al., 1989). Increased TOC loading due to increased nutrient supply during wet intervals could also stimulate higher rates of sulfate reduction, particularly if changes in TOC quantity are coupled with changes in TOC composition. While the interactions between these variables cannot presently be disentangled, abundant, more reactive TOC could rapidly form organic sulfur compounds and cause KS concentrations to rise. Combined with our $\delta^{34}S$ data, these findings suggest that changes in lacustrine productivity and carbon burial more directly affect sedimentary sulfur concentrations in Lake Edward than salinity.

6. Summary and conclusions

The concentration and isotopic composition of reduced sulfur species in marine and lacustrine rocks have traditionally been interpreted to reflect variations in the salinity of depositional environments (i.e. sulfate availability), organic carbon concentrations (which may limit sulfate reduction), or changes in the availability of reactive iron related to surface runoff and erosion. We document ^{34}S -enrichment of sedimentary sulfur and increases in sedimentary sulfur concentrations in Lake Edward, Uganda/Congo, during an interval in which rainfall increased and the lake became less salty. Although the observed isotopic enrichment could be interpreted to reflect decreased sulfate supply related to decreasing lake salinity, the increase in sulfur concentrations is largely accounted for by rising kerogen sulfur concentrations rather than increased in FeS abundance. These changes thus cannot be explained by runoff-driven changes in Fe supply to the lake basin. Rather, our data indicate that factors influencing organic sulfur burial, such as organic matter quality and concentration, can exert considerably more influence on sedimentary sulfur concentrations than do salinity and aqueous sulfate concentrations. Future studies should account for the effects of environmentally-mediated changes in organic matter quality when interpreting changes in sulfur concentrations through time.

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