Chloride budgets in transient lakes: Lakes Baringo, Naivasha, and Turkana'

Abstract-Lakes Baringo, Naivasha, and Turkana, East Africa, are being filled with sediment at a rapid rate. A finite-difference numerical model that includes diffusion and advection terms can describe the chemical evolution of chloride in lake water or pore water in these or other shoaling lakes. For the cases of Baringo and Turkana this model suggests chloride accumulation times on the order of 100-200 and 3,000-5,000 yr. Stable isotopic studies of waters from the East African Rift show that these three lakes are highly evaporated and that Lake Naivasha is the source of water of the 01 Oserian geothermal field.

Closed-basin lakes have a tendency to become more saline with time unless they undergo increases in volume. Numerous studies have documented significant salt loss from closed-basin lakes resulting from diffusion and pore-water burial (e.g. Lerman and Jones 1973; Yuretich and Cerling 1983; Spencer et al. 1985). Lerman and Jones (1973) have shown that the chemistry of many closed-basin lakes can be modeled by a burial-diffusion model that is derived from Fick's laws of diffusion. Thus, the composition of interstitial water can be derived from

$$
\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial z^2} - U \frac{\partial C_i}{\partial z}
$$
 (1)

where C_i is the concentration of species i at some depth z at time t, D_i is the diffusion coefficient in the sediment, and U is the sedimentation rate. Taking z to be zero gives the composition of the lake water.

This expression can be solved analytically by assuming that the depth of the lake remains constant. One result of this assumption is that lakes with a modestly high sedimentation rate (1 mm yr^{-1}) or higher) can reach a steady state composition in a few thousand or tens of thousands of years (Lerman and Jones 1973). However, the assumption of constant depth of a lake is probably only reasonable in cases of very low rates of sedimentation or very high rates of basin subsidence. The range in measured sedimentation rates in lakes is from 4 cm yr^{-1} to 0.01 cm yr^{-1} or less (Krishnaswami and La1 1978). In many cases of high sedimentation rates it is probably not valid to assume a constant lake depth or volume because the lake eventually becomes filled with sediment. Therefore, no adequate model exists for the accumulation of salts in hydrologically closed lakes with high sedimentation rates.

In this study we discuss a numerical scheme to examine the chemical evolution of closed-basin lakes with high sedimentation rates. This model allows the depth of the lake to change with time and allows for a difference between the diffusion coefficients for compacted sediment and the newly deposited uncompacted sediment. We use this model to examine the history of two closed-basin lakes in the East African Rift, Baring0 which is fresh and Turkana which is brackish.

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We consider a hydrologically closed basin with an existing sediment column of arbitrary thickness. The ion of interest has a diffusion coefficient of $D_{i,o}$ in the old sediment. With each time step, an increment of new sediment with a diffusion coefficient $D_{i,n}$ for species *i* is added to the bottom of the lake column and the depth of the lake, $H(t)$, decreases at the same rate as the new sediment accumulates (Fig. 1). Ions are added at the top of the lake column by a production term β . The lake column has a diffusion coefficient $D_{i,j}$, the value of which is set very high and corresponds to an eddy

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Fig. 1. Model for chloride accumulation in a transient lake that fills with sediment. Three diffusion coefficients are specified for species i: $D_{i,j}$, $D_{i,n}$, and $D_{i,o}$ which correspond to an eddy diffusion coefficient in the lake, a diffusion coefficient for newly deposited sediment, and a diffusion coefficient for compacted sediment. $H(t)$ represents the depth of the lake, which changes as a result of sedimentation at rate $U(t)$. $\beta(t)$ is the production term for the ion of interest and represents the river input normalized to the surface area of the lake.

diffusion coefficient. The numerical procedure used is a finite-difference scheme that uses backward differences in time and central differences in space and is similar to that used by Solomon (1985) and Solomon and Cerling (unpubl.) to examine the diffusion of soil gas under a continually changing snow pack. It can be expressed as

$$
\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial z^2} + \beta.
$$
 (2)

Boundary conditions must be established for the solution region: if no droplet formation and aerosol loss take place (Langbein 1961) the upper boundary condition is one of no flux; that is

$$
\frac{\partial C_i}{\partial z} = 0 \quad \text{at} \quad z = 0. \tag{3}
$$

The lower boundary can also be considered to be one of no flux if an impermeable boundary is assumed to be below the old sediments.

Comparing this model to the analytical solution of Lerman and Jones (1973) is only possible for either low sedimentation rates or during the early history of a lake when the fixed depth of the Lerman-Jones model and the varying depth of our model are similar. For these cases, the agreement between the models was within 5% of the total concentration in both pore fluids and in the lake.

Figure 2 shows the results of this model applied to lakes of differing initial depths where the depth is allowed to vary with time. This figure illustrates the ion concentration of lake water with time for two initial lake depths of 10 and 100 m, which are allowed to fill with sediments at rates of 1.0, 0.1, and 0.01 cm yr⁻¹. In this figure, diffusion coefficients are assumed to be the same for both old and new sediment. In these illustrative examples we use a diffusion coefficient of 20 \times 10⁻⁶ cm² s⁻¹-the value for chloride at infinite dilution (Lerman 1979). It represents a case of extreme undercompaction which is accurate today for Lake Turkana. The general shapes of the shallowlake and deep-lake curves are similar, although the shallower lake becomes more saline at a much faster rate. The effect of using a lower diffusion coefficient for old sediment compared to new sediment is quite pronounced in calculated interstitial water profiles but is relatively unimportant in the evolution of the surface-water chemistry except for shallow lakes with low sedimentation rates. In the Lerman-Jones model where the lake depth is constant, lakes with sedimentation rates >1 mm yr⁻¹ reach a steady state composition after several thousand or tens of thousands of years; at all times lakes with higher sedimentation rates have salinities lower than lakes with lower sedimentation rates. In this model the reverse is true: a higher sedimentation rate results in a higher salinity because of the decrease in lake volume as time progresses.

Use of this model allows some insight into the recent history of Lakes Baringo, Naivasha, and Turkana in the African Rift. Several closed lakes in the African Rift have

Fig. 2. Concentration (units of C liter⁻¹) of species i in lake water as a function of time for a calculated input of 0.1 C cm⁻² yr⁻¹ where C represents some arbitrary mass unit (e.g. moles, milligrams, millimoles). Results are shown for two initial lake depths (10 m, dashed curves; 100 m, solid curves) for each of three different sedimentation rates (1.0, 0.1, and 0.01 cm yr^{-1}). Curves terminate when the lake becomes filled with sediment.

been postulated to have subsurface outflows because of their apparent freshness while having no visible outlet. Examples of such lakes are Baringo, Naivasha, and Turkana which have chlorinities of about 1,0.3, and 12 mmol liter-'. Although Lake Naivasha almost dried out in the early part of this century, it has been at a fairly high level since the 1930s (Gaudet and Melack 1981). Local legend has it that Baringo and Naivasha have subsurface outflows which issue in the hot springs at Kapedo and 01 Oserian, respectively. Lake Turkana has no evidence of outflow although it had been postulated to have a subsurface outflow (Beadle 1974); however, recent mass balance arguments (Beadle 198 1; Yuretich and Cerling 1983; Cerling 1986) suggest that no such outflow is necessary.

Figure 3 shows the application of our numerical salt accumulation model to the chemistries of Baring0 and Turkana. Lake Naivasha was not modeled because water balance and chemical balance studies (Gau-

Fig. 3. Model-calculated compositions for Lakes Turkana and Baringo. Input parameters, diffusion coefficients, and sedimentation rates are described in the text. The initial concentration is taken to be that of the river input. The blackened area on each set of curves represents the range in the composition of the modern lakes.

Core	Location	210P _b	Paleomagnetic data	Laminae counts
TL	N. north basin	0.81 ± 0.04		
TM	N. north basin	0.69 ± 0.02		
TA	E. north basin		$1.2*$	
TD	Central basin	1.38	$1.47*$	1.5†
TO.	Between central and south basins	0.93 ± 0.03		
TР	Between central and south basins	2.03 ± 0.03		

Table 1. Summary of sedimentation rate estimates (cm yr-I) for Lake Turkana cores (for the upper 0.5 m, uncompacted). Information from Barton and Torgersen (unpubl.).

* Averaged over 0-3 m. See text for explanation. t Adjusted to correspond to the upper 0.5 m of core

det and Melack 1981) and stable isotope studies (see discussion below) suggest that significant subsurface water loss occurs so that Lake Naivasha is not hydrologically closed. In these models, composition of the inflowing water and sedimentation rate must be specified. For Lakes Baringo and Turkana, we use the range from 0.1 to 0.05 $mmol$ liter⁻¹; this range includes the average values of the Molo and Perakera Rivers (Lake Baringo) and the Omo River (Lake Turkana) and of rivers draining the volcanic highlands of Kenya (T.E.C. unpubl. data). Unfortunately, neither the Molo nor the Omo (the two principal rivers flowing into Lakes Baringo and Turkana, respectively) are gauged. Therefore, volume estimates of inflows are estimated from the areas of the lakes and their net surface evaporation (evaporation minus precipitation) which are estimated to be about 100 and 210 cm yr^{-1} for Baring0 and Turkana; estimates use a pan correction of 0.6 and data from the East African Meteorological Department (1975). Initial depths of the lakes are taken to be 8 and 80 m for Baring0 and Turkana (present mean depths based on echo soundings are about 6 and 35 m). Values used for sedimentation rates are discussed below.

Organic carbon contents in the sediments from Lake Turkana are generally too low for dating with conventional radiocarbon techniques. Estimates based on other techniques are summarized in Table 1. Paleomagnetic data from cores 6 m long from Lake Turkana show unusually smooth, longwavelength variations in direction of magnetization which suggest high sedimentation rates in those cores. These fundamental characteristics are reproducible between sites and must therefore reflect the secular change in direction of the ambient geomagnetic field at, or shortly after, the time of deposition. Furthermore, the forms of the curves of declination and inclination as functions of depth correspond to the known and estimated historical variation of the field in the region (Skinner et al. 1975) and form the basis of the paleomagnetic sedimentation rates given in Table 1. The paleomagnetically determined rates are compatible with laminae counts in core TD, and 210Pb profiles from five cores (Barton and Torgersen unpubl.).

Cores listed in Table 1 are in sequence from north to south in Lake Turkana. The 210Pb profiles were obtained from the upper 55 cm of each core. Paleomagnetic estimates for cores TA and TD are averages over the upper 3 m. Corrections for compaction and the suspected finite locking-in depth of the paleomagnetic signal tend to cancel and are ignored in the present context. Laminae within core TD (255-286 cm) have an average spacing of 1.2 cm. Assuming that they are annual and allowing for compaction indicates a sedimentation rate of about 1.5 cm yr^{-1} in the upper 0.5 m of the core.

Paleomagnetic data from Lake Baring0 were not of sufficient quality to permit estimation of sedimentation rates. One 210Pb profile from core BC, which is representative of the flat central region of the lake surrounding 01 Kokwe Island, indicates rates of either 0.83 ± 0.16 or 2.5 ± 0.4 cm yr^{-1} , depending on the assumption made about secular equilibrium of 226Ra through the sediment column (F. El-Daoushy pers. comm.).

From the standpoint of modeling the geochemical behavior of Lakes Turkana and Baringo, it is reasonable to use a value of

Fig. 4. Water content for Lake Baringo core BD. Abrupt change in the water content at about 130 cm probably corresponds to a desiccation event.

about 1 cm yr^{-1} for the upper part of each of the two sequences. The water content of sediments in 12-m cores from Lake Turkana indicates that some compaction takes place so that the net compacted sedimentation rate is actually lower, perhaps on the order of 0.5 cm yr^{-1} . However, for a first approximation, we will use a net sedimentation rate of 1 cm yr^{-1} for both Baringo and Turkana.

Results of these computations (Fig. 3) show that Lakes Baringo and Turkana have computed closure times on the order of 100– 200 and 3,000-5,000 yr, respectively. Such a time seems reasonable for Lake Baring0 whose sediments show a large change in water content at about 130-cm depth in a core collected from the lake (Fig. 4). However, Baringo has shown only a slight increase in chloride content between 193 1 and 198 1; it is compatible with a scenario where the lake has been closed for 100 yr or more but not less than 100 yr. A closure time between 3,000 and 5,000 yr also appears reasonable for Lake Turkana based on mass balance arguments put forward by Yuretich and Cerling (1983) and Cerling (1986). High resolution seismic profiles taken on the lake indicate a low stand about 50-60 m below

Fig. 5. Isotopic composition of waters from the Baringo and Naivasha regions. Rivers in the Baringo region are the Molo and Perakera. Rivers in the Naivasha region are the Gilgil and Malewa. Samples were collected over the period 1977-l 98 1. Meteoric water line of Craig (1961) shown for reference.

the present lake surface; they indicate that at least 20 m of sediment have been deposited on that old surface in some parts of the lake (Johnson et al. 1987). Such a drop in lake level would result in desiccation of most of the area presently covered by the lake. A simulation using an initial depth of 60 m and a sedimentation rate of 0.5 cm yr-* for Lake Turkana give similar curves to those shown for the lake in Fig. 3. This approach suggests that the chemical composition of the lake is compatible with a scenario where closure took place 3,000- 5,000 yr ago, with subsequent sedimentation rates on the order of $0.5-1.0$ cm yr^{-1} . Although this method does not prove absence of subsurface outflow for these two lakes, it does show that the model is compatible with present lake compositions and reasonable sedimentation rates and input concentrations. Complete or near-complete desiccation of Lakes Baring0 and Turkana could be due to changing climatic conditions or to major changes in drainage patterns of the inflowing rivers.

Isotopic evidence also suggests that Lake Baring0 is not a major contributor to the hot springs at Kapedo. Water samples for isotopic analyses were collected during the period 1977-l 982. They were analyzed according to standard methods (Bigeleisen et al. 195 1; Epstein and Mayeda 1953). Figure 5 shows that the isotopic composition of Lake Baringo has been strongly evaporated compared to its inflowing waters, the Molo and Perakera Rivers: four samples from the lake, collected in 1977, 1979, 1980, and 198 1 all show considerable isotopic enrichment compared to its inflowing waters, which fall on the meteoric water line. Samples from the Kapedo hot spring are slightly evaporated compared to local meteoric water. This disparity could be from a small amount of mixing of meteoric water with an evaporated water such as that from Lake Baringo. However, if the observed trend of the Kapedo and Lake Baringo waters are interpreted as a mixing line, the meteoric water endmember required would have a δD value less than -60% relative to SMOW-much lower than values measured locally. We feel that it is more likely that evaporation occurred between the time the spring issued from the ground and its collection, since the spring flowed for about 0.5 km before the sampling point.

Isotopic measurements from the Lake Naivasha region show that the lake is highly evaporated relative to its major inflows, the Malewa and Gilgil Rivers. The isotopic data suggest that the host springs to the south of the lake at the 01 Oserian geothermal field originated from the heating of lake water since the isotopic composition of the hot springs is virtually identical to that of the lake water. The hot springs to the north of the lake near Eburru settlement have a meteoric origin and cannot be derived from Lake Naivasha water. These conclusions agree with the previous suggestion that Lake Naivasha loses a significant amount of water to subsurface outflow (Gaudet and Melack 1981).

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Geochemical and mineralogical indications of pH in lakes and soils in central New Hampshire in the early Holocene'

Abstract-In central New Hampshire, sediments of some early Holocene lakes were alkaline and contained carbonate minerals despite granitic bedrock and currently acid soils and surface water in their watersheds. Nearby calcareous bedrock contributed to the till of these watersheds while other lakes, more remote from calcareous bedrock, had early Holocene sediments of neutral pH and devoid of carbonate minerals. Calcite rock fragments in alkaline sediments were eroded from alkaline soils in the watershed. Chemical weathering later acidified these soils and surface waters before modem acid precipitation.

Modem acidification of waters in terrestrial and aquatic ecosystems by air pollutants has received intensive study in eastern North America and northern Europe (Hutchinson and Havas 1980; Drabos and Tollan 1980). In strongly affected ecosystems, soil solutions and waters of headwater lakes and streams have been observed to be acidic with resulting elevated aluminum concentrations (Cronan and Schofield 1979; Johnson et al. 1981; Hooper and Shoemaker 1985). Anion chemistry of these waters is dominated today by sulfate and nitrate, whereas before acid precipitation bicarbonate and organic ligands probably dominated (Cronan et al. 1978). However, relatively little is known about biogeochemistry in these regions before modern times. Even without anthropogenic pollution, water chemistry in these ecosystems may have

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been altered by natural processes such as rainfall, organic acid production by growth and decomposition of vegetation, and changes in the physical or chemical form of soil parent material. We here report evidence that the pH of lakes and soils in central New Hampshire declined during the early Holocene.

Andersen (1966) studied fossil pollen of lake sediments over three separate interglacial periods in northern Europe and found that the abundance of acidophilous species of land plants increased from early to late in each interglacial. He concluded that soils were not acidic immediately after deglaciation but acidified during each interglacial as a result of natural soil weathering processes. Whitehead et al. (1986) used sedimentary fossil diatoms to reconstruct the pH history of several lakes in the Adirondack Mountains of New York. They found that some were alkaline shortly after deglaciation but acidified markedly in the early Holocene. They also attributed preindustrial acidification to natural soil weathering in the lakes' watersheds and noted the role of vegetation in this process.

Understanding how waters become acidified over the long term would be useful as a baseline for studies of pollution-caused acidification. It would also be useful in evaluating the effects on terrestrial and aquatic ecosystems of the natural processes that control water chemistry, such as soil formation. Because soil formation is a longterm phenomenon, we examined sediments from early Holocene lakes in central New Hampshire for evidence of the pH in surface