Mechanisms controlling the chemical composition of lakes and rivers: Data from Africa

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Abstract

Data for natural lakes, rivers, and springs in intertropical Africa indicate that the chemical compositions of these waters are controlled primarily by rock dominance (weathering reactions) and the evaporation-crystallization process (evaporative concentration and calcite precipitation). There are minor deviations from the primary pattern observed in Africa and elsewhere. They usually occur as a result of contamination by cyclic salts or salts ultimately derived from ancient lakes or oceans.

Three natural mechanisms are said to control the chemistry of lakes and rivers: atmospheric precipitation, rock dominance, and the evaporation-crystallization process (Gibbs 1970; Clarke 1924). One can evaluate the relative importance of each mechanism by plotting the weight ratio $Na^+/(Na^+ + Ca^{2+})$ vs. salinity for selected waters. A boomerang-shaped envelope of data is produced if all three mechanisms are of more or less equal importance and the contribution of ancient salts is not taken into account (Feth 1971; Gibbs 1971). I show here that the envelope of data for African waters is shaped like an alchemist's retort rather than a boomerang (Wetzel 1983). The chemical composition of African waters is largely controlled by rock weathering, evaporative concentration, and the precipitation of calcium carbonate. Concentrated waters (>1,000 ppm of total dissolved salts, TDS) that plot outside the primary envelope are dominated by salt from either the ocean or ancient sedimentary deposits. Natural waters studied in other parts of the world appear to fit the African pattern (Banens

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1987; Stallard and Edmond 1983; Wetzel 1983).

Feth (1971, p. 870) summarized Gibbs's original argument.

> Some streams, especially those draining well-leached, tropical basins, have water compositions dominated by Na^+ and Cl^-, an indication that the composition is controlled by airborne salt with strong oceanic affinities (figure 2 in Gibbs [1970]). Another end-member is dominated by Ca^{2+} and HCO_3^- with generous contributions from K^+ and SiO_2, an indication that the composition is controlled by mineral components leached from the rocks of the drainage basin. The third type of water, also dominated by Na^+ and Cl^-, but with high concentration of dissolved solids reflects, "evaporation, which increases salinity, and . . . precipitation of $CaCO_3$ from solution, which increases the relative proportion of Na to Ca. . . ." [Gibbs 1970, p. 1090.]

Gibbs's ideas have proven to be very stimulating, but they require some modification. The data set used here contains water analyses for 424 lakes, rivers, and springs throughout intertropical Africa (Kilham 1971; Viner 1975). These data have not been corrected for present day cyclic salts, but this correction produced few changes in similar data from Australia (Banens 1987) and South America (Stallard and Edmond 1983).

African waters do not plot consistently within either arm of the well-known boomerang. The explanation for this discrepancy for the upper arm (high salinities) is simple. The major mechanism controlling the evolution of African waters during evaporative concentration is precipitation of $CaCO_3$ (Kilham 1971; Eugster and Jones

1979). Carbonate minerals begin to precip-
itate once saturation with respect to calcite
is reached. As a rule, this represents an al-
kalinity of ~2.5 meq liter^{-1} (Cerling 1979)
or about 250 ppm of TDS. Above 1,000
ppm of TDS most of the Ca^{2+} ions have
been removed from solution. The only ex-
ceptions to this rule are the low-alkalinity
springs and the relatively dilute sodium
chloride lakes (stars, Fig. 1). The low-al-
kalinity springs commonly emanate from
Precambrian metamorphic rocks. The larg-
est springs are in the Mwashya Series of
calcareous schists in Shaba, Zaire (Cahen
1954; Symoens 1968). The dilute sodium
chloride lakes in central Tanzania are of
problematic origin. One hypothesis is that
they result from evaporation of NaCl-dom-
inated rainwater in a semiarid region un-
derlain by relatively insoluble Precambrian
rocks (Hecky and Kilham 1973; Kilham and
Hecky 1973). This region lies on a storm
track that passes over the Indian Ocean.

Examination of the behavior of Cl$^-$ and
CO$_3^{2-}$ + HCO$_3^-$ during evaporative con-
centration further supports recent interpre-
tations of the geochemical evolution of Af-
rican waters (Kilham 1971; Jones et al. 1977;
Talling and Talling 1965). Figure 2 shows
that there is little correspondence between
Gibbs's plot for these anions (dashed en-
velope) and the African data. Again, only
the low-alkalinity springs and the sodium
chloride lakes (stars and diamonds with dots)
fall within the upper diagonal arm of his
envelope. Swamp waters (solid diamonds)
contain little HCO$_3^-$ owing to their low pH
(<6).

The evaporation-crystallization process
is illustrated in Fig. 3 for African waters.
This figure indicates that a substantial loss
of carbon occurs during every step of evap-
orative concentration. CaCO$_3$ precipitation
is primarily responsible for the loss of car-
bonate from dilute waters. Calcite predom-
inates in lake sediments because Mg/Ca
molar ratios in African waters are generally
low (<2: Müller et al. 1972). Carbon is also
lost from alkaline lakes and springs by CO$_2$
degassing. In brines, carbon is precipitated
as trona and other carbonate minerals
(Eugster and Jones 1979; Kilham and Me-
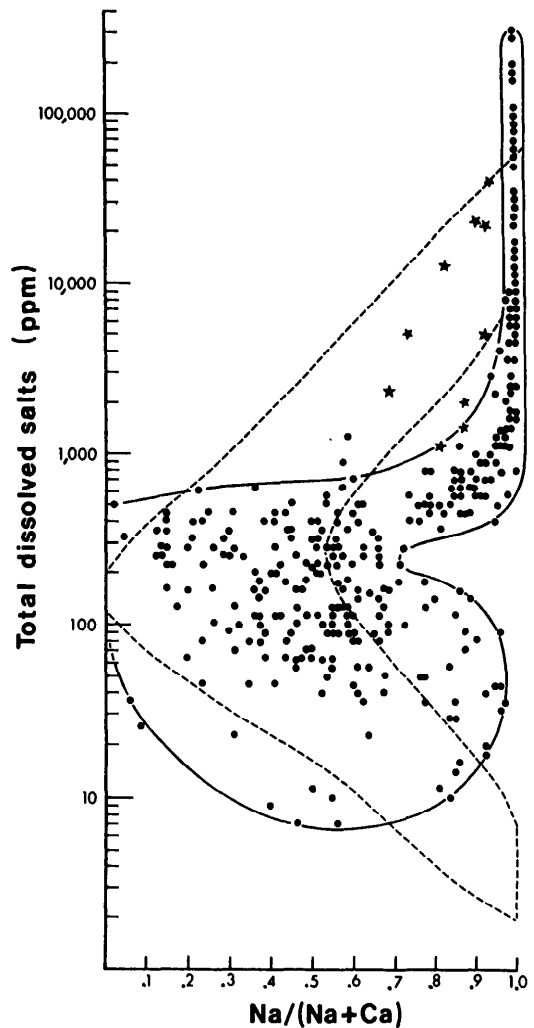lack 1972). The alkalinity (and thus the car-

Fig. 1. Variation of the weight ratio Na$^+$/(Na$^+$ + Ca^{2+}) as a function of the total dissolved salts of world surface waters. The boomerang-shaped envelope (– – –) was observed by Gibbs (1971) for 135 surface waters from various regions of the world. The retort-shaped envelope (——) surrounds data for normal African waters (●). Stars represent springs with Cl$^-$ or SO$_4^{2-}$ as the dominant anion and moderate-salinity sodium chloride lakes (<10,000 ppm of TDS).

bon content) of these waters is also affected
by two additional processes. Reverse weath-
ering (clay formation) decreases alkalinity
(Von Damm and Edmond 1984), while the
loss of sulfur (as sulfide) to either the sedi-
ments or atmosphere increases alkalinity
(Kilham 1984; Kilham and Cloke 1990).

There is little doubt that atmospheric pre-
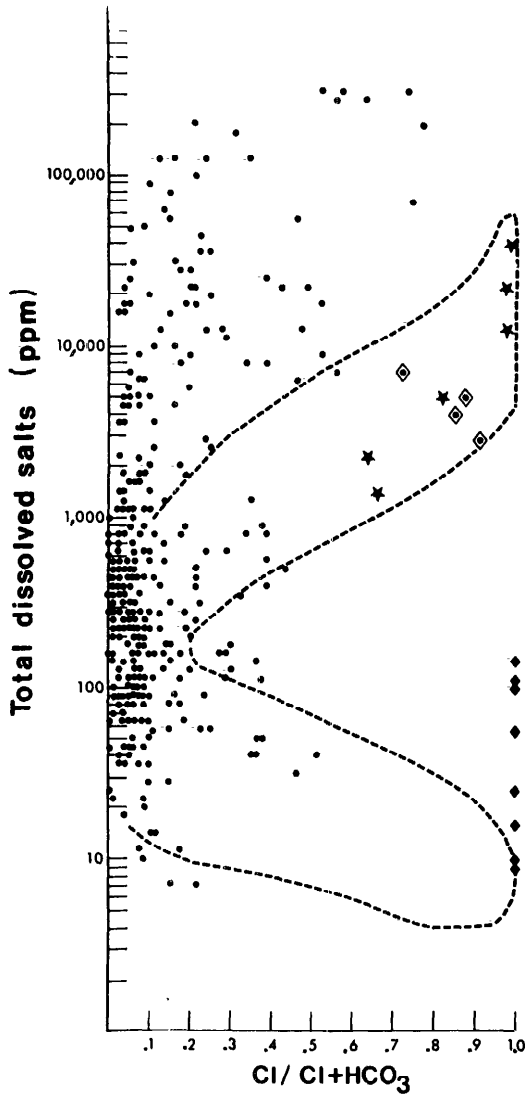cipitation and rock dominance are poten-

Fig. 2. Variation of Cl⁻/(Cl⁻ + HCO₃⁻) as a function of the total dissolved salts of world surface waters. Envelope surrounds data presented by Gibbs (1971). Normal African waters—●; springs with Cl⁻ as the dominant anion—★; moderate-salinity sodium chloride lakes—◈; swamps—◆.
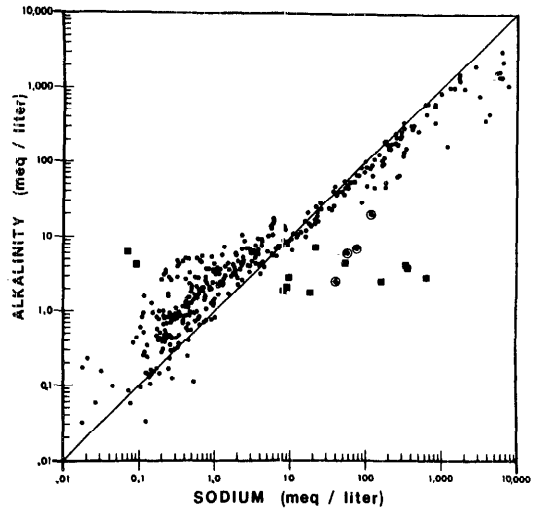

Fig. 3. Total alkalinity (mainly CO_3^{2-} + HCO_3^-) vs. sodium for waters of intertropical Africa. Normal African waters—●; springs with either Cl⁻ or SO_4^{2-} as the dominant anions—■; moderate-salinity sodium chloride lakes—◉.

tially important mechanisms controlling world water chemistry, but atmospheric precipitation plays a lesser role in Africa and elsewhere (Banens 1987; Stallard and Edmond 1983). Very few African waters plot within the lower arm (i.e. atmospheric precipitation arm) of the original data envelope for the weight ratio Cl⁻/(Cl⁻ + HCO_3^-) (Fig. 2). There are two possible reasons for this

discrepancy. First, rock weathering is so intense in humid regions that the ionic composition of the rain may be quickly masked by the rapid solution of the rocks (Hecky and Kilham 1973). This is supported by observations that indicate that African waters strongly reflect the chemical composition of the rocks they have leached (Kilham and Hecky 1973; Gaudet and Melack 1981). Second, the few analyses of African rainwater that exist indicate that terrigenous dust and the ash from fires often determine the composition of the rain (Viner 1975; Rodhe et al. 1981). Also, much of the rain falling in the interior of the continent originates from inland waters. Cyclic salts are only likely to be important near the coasts and along a few major storm tracks over weather-resistant rock, as in central Tanzania. In short, African rainwaters are rarely dominated by NaCl or any particular salt.

Rock dominance is the major mechanism controlling the dilute African waters (<600 ppm of TDS). In Figs. 1 and 2 this is shown by the clustering of most of the waters in the central region of each figure. In Fig. 1 many of the rock-dominated waters plot to the right of the boomerang-shaped envelope. This is possibly explained by the chemical composition of many of the so-

dium-rich feldspathoidic volcanic rocks that are common in East Africa (*also* Banens 1987). They generally contain little calcium. But, the indentation at ~250 ppm of TDS on the right of the African data envelope (solid line, Fig. 1) may reflect the fact that some calcium is present in all African rocks.

The principal differences between Gibbs's (1970, 1971) analysis of the mechanisms controlling world water chemistry and the mechanisms proposed here for African waters are that atmospheric precipitation is relatively unimportant and that the evaporation-crystallization process produces sodium carbonate-bicarbonate lakes containing little calcium.

The major mechanisms controlling the chemical composition of inland waters operate almost everywhere according to the pattern observed in Africa. Deviations from the basic pattern are caused primarily by contamination with salts from ancient lacustrine deposits or salts ultimately of marine origin which are transported by ocean-derived atmospheric precipitation (cyclic salts), leached from rocks (connate waters), or dissolved from evaporite deposits.

References

BANENS, R. J. 1987. The geochemical character of upland waters of northeast New South Wales. Limnol. Oceanogr. **32:** 1291–1306.

CAHEN, L. 1954. Géologie du Congo Belge. Vaillant-Carmanne.

CERLING, T. E. 1979. Paleochemistry of Plio-Pleistocene Lake Turkana, Kenya. Paleogeogr. Paleoclimatol. Paleoecol. **27:** 247–285.

CLARKE, F. W. 1924. The data of geochemistry, 5th ed. U.S. Geol. Serv. Bull. 770.

EUGSTER, H. P., AND B. F. JONES. 1979. Behavior of major solutes during closed-brine evolution. Am. J. Sci. **279:** 609–631.

FETH, J. H. 1971. Mechanisms controlling world water chemistry: Evaporation-crystallization process. Science **172:** 870–871.

GAUDET, J. J., AND J. M. MELACK. 1981. Major ion chemistry in a tropical African lake basin. Freshwater Biol. **11:** 309–333.

GIBBS, R. J. 1970. Mechanisms controlling world water chemistry. Science **170:** 1088–1090.

———. 1971. Mechanisms controlling world water chemistry: Evaporation-crystallization process [reply to J.H. Feth]. Science **172:** 871–872.

HECKY, R. E., AND P. KILHAM. 1973. Diatoms in alkaline, saline lakes: Ecology and geochemical implications. Limnol. Oceanogr. **18:** 53–71.

JONES, B. F., H. P. EUGSTER, AND L. RETTIG. 1977. Hydrogeochemistry of the Lake Magadi basin, Kenya. Geochim. Cosmochim. Acta **41:** 53–72.

KILHAM, P. 1971. Biogeochemistry of African lakes and rivers. Ph.D. thesis, Duke Univ. 199 p.

———. 1984. Sulfate in African inland waters: Sulfate to chloride ratios. Int. Ver. Theor. Angew. Limnol. Verh. **22:** 296–302.

———, AND P. L. CLOKE. 1990. The evolution of saline lake waters: Gradual and rapid biogeochemical pathways in the waters of the Basotu Lake District, Tanzania, in press. *In* Proc. 4th Int. Symp. Athalassic (inland) saline lakes. Develop. Hydrobiol. Junk.

———, AND R. E. HECKY. 1973. Fluoride: Geochemical and ecological significance in East Africa waters and sediments. Limnol. Oceanogr. **18:** 932–945.

———, AND J. M. MELACK. 1972. Primary northupite deposition in Lake Mahega, Uganda? Nature **238:** 123.

MÜLLER, G., G. IRION, AND U. FÖRSTNER. 1972. Formation and diagenesis of inorganic Ca-Mg carbonates in the lacaustrine environment. Naturwissenschaften **59:** 158–164.

RODHE, H., E. MUKOLWE, AND R. SÖDERLUND. 1981. Chemical composition of precipitation in East Africa. Kenya J. Sci. Technol. (A) **2:** 3–11.

STALLARD, R. F., AND J. M. EDMOND. 1983. Geochemistry of the Amazon. 2. The influence of geology and weathering environment on the dissolved load. J. Geophys. Res. **88:** 9671–9688.

SYMOENS, J.-J. 1968. The mineral content of natural waters. Cercle Hydrobiol. Brux. **2:** 1–199.

TALLING, J. F., AND I. B. TALLING. 1965. The chemical composition of African lake waters. Int. Rev. Gesamten Hydrobiol. **50:** 421–463.

VINER, A. B. 1975. The supply of minerals to tropical rivers and lakes (Uganda), p. 227–261. *In* A. D. Hasler [ed.], Coupling of land and water systems. Springer.

VON DAMM, K. L., AND J. M. EDMOND. 1984. Reverse weathering in the closed-basin lakes of the Ethiopian Rift and in Lake Turkana (Kenya). Am. J. Sci. **284:** 835–862.

WETZEL, R. G. 1983. Limnology, 2nd ed. Saunders.