

# FLUORIDE: GEOCHEMICAL AND ECOLOGICAL SIGNIFICANCE IN EAST AFRICAN WATERS AND SEDIMENTS<sup>1</sup>

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## ABSTRACT

The geochemistry of fluoride in East African lakes and rivers was examined to elucidate processes of fluoride acquisition, concentration, removal, and diagenesis in inland waters in a region relatively little influenced by man. The range of fluoride concentrations (0.02–1,627 mg liter<sup>-1</sup>) is the greatest found anywhere. A strong correlation was found between the concentration of fluoride in the predominant crystalline rocks of each particular drainage basin and the F:Cl ratio in surface waters. Because fluoride-rich volcanic rocks are common in East Africa very high fluoride concentrations, the products of chemical weathering, are often observed. Fluoride removal from surface waters is not significant; concentration by evaporation proceeds until saturation with respect to villiamite is reached. Fluoride : chloride ratios for the interstitial waters of a 7-m core from Small Momela Lake, Tanzania, indicate that in sedimentary environments fluoride may be removed from pore waters as fluorite and possibly fluorapatite.

Geographical evidence suggests that the high fluoride concentrations may influence the distribution of man, livestock, zooplankton, phytoplankton, and higher aquatic plants.

The geochemistry of fluoride in oceanic and estuarine environments has received increasing attention (Shiskina 1966; Carpenter 1969; Brewer et al. 1970; Warner 1969; Windom 1971). Fewer investigators have examined inland waters (Livingstone 1963; Mun et al. 1966; Reeder et al. 1972). Some favor rainwater of ultimate marine derivation as the primary source of fluoride in continental waters, while others view volcanic emanations with eventual washout by atmospheric precipitation as an important source. Rock weathering is generally considered less important. Attempts to resolve this controversy will be hampered in northern latitudes by industrial inputs (Mason 1966) which may overwhelm natural processes. Studies in equatorial and southern latitudes far re-

moved from industrialized regions present the best opportunity for elucidating the preindustrial fluoride cycle and thereby estimating man's impact.

Fluoride in surface waters concerns public health officials as well as geochemists. Fluoride is extremely reactive in biological systems, and its affect on enzymes and whole organisms is well documented (O'Brien 1967; Smith 1966; Moorc 1971; Hemens and Warwick 1972). Thus fluoride above trace levels could be a selection factor in determining the distribution of organisms. This aspect of fluoride biogeochemistry has received little attention because in most natural waters concentrations are below those recommended for human consumption (Livingstone 1963). However, fluoride may also be of interest to human ecologists in those areas where unusual concentrations are found.

The surface waters of East Africa have high fluoride concentrations and unusual anionic ratios (Baker 1958; Kilham 1971; Hecky 1971). East Africa is not industrialized and is far removed from significant causes of pollution. The region consists primarily of igneous and metamorphic

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rocks with only isolated, small patches of Pleistocene sediments. This geological simplicity facilitates understanding of the water chemistry (Kilham 1971) because there are no large, ancient, sediment deposits to contribute recycled salts. For these reasons, East Africa should be an ideal area to examine the geochemistry of fluoride in inland waters and to estimate its ecological importance. We have determined fluoride concentrations in over 200 water samples from 177 localities (Kilham 1971) and examined its fate during evaporative concentration and diagenesis of sediments in basins of internal drainage (Hecky 1971).

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#### METHODS

Surface water samples were collected in East and Central Africa between May 1969 and January 1970 and shipped to Duke University for chloride and fluoride analyses. Fluoride was determined with a lanthanum fluoride electrode (Orion model 94-09) and reference electrode (model 90-01). Samples and standards were prepared to contain 50% TISAB (Orion total ionic strength adjustment buffer) to adjust the pH and uncomplex the fluoride; this avoids anionic interferences (Orion Research 1967; Harwood 1969). Cationic interferences would not occur in these waters (*see* Warner 1971; Kilham 1971). All readings were made to 0.1 mV on a specific ion meter (Orion 404). Fluoride activity was measured directly in untreated water samples. The agreement

between measured and calculated coefficients (Davies 1962) was within ca. 5%, indicating that complexing is not significant. Declstra (1971) reported fluoride concentrations within ca. 5% of ours in samples collected a year later from waters investigated in common. A Cotlove chloridometer (Lab. Glass and Instr. Co.) was used for concentrations of chloride  $>2$  meq liter<sup>-1</sup> and a mercuric nitrate titration (Amer. Public Health Ass. 1965) was used for lower concentrations.

Interstitial waters from cores were extracted with a gas-operated sediment squeezer similar to one described by Reeburgh (1967). The samples were passed through 0.45- $\mu$ m membrane filters. Fluoride activities were measured as described above. Chloride concentrations were determined with the chloridometer.

When possible pH, alkalinity, calcium, chloride, magnesium, phosphate, and silica were measured in the field with a portable water laboratory (Hach model DR-EL). Unfiltered water was analyzed for conductivity, sodium, potassium, calcium, magnesium, sulfate, chloride, alkalinity, pH, silicon, and fluoride at Duke University within 3 to 6 months of collection on samples shipped from Africa in polyethylene bottles. Agreement between laboratory and field data were very good for the major ions; only laboratory values are given here unless otherwise noted.

Chemical techniques were selected for precision and availability. Sodium, potassium, calcium, magnesium, and silicon were determined by atomic absorption spectrophotometry (Perkin-Elmer 303: methods described in Perkin-Elmer 1964). Sodium, potassium, calcium, and magnesium were analyzed in an air-acetylene flame; silicon and sometimes calcium were done in a nitrous oxide-acetylene flame to preclude the formation of refractory compounds (Slavin 1968). When necessary, calcium and magnesium were determined by EDTA titration (Amer. Public Health Ass. 1965). Total alkalinity was determined by titration to the Bromocresol Green-Methyl Red end point (Amer. Public Health Ass. 1965).

Table 1. Chemical analyses of the East African surface waters specifically discussed. Waters considered representative of each generic class are indicated. Conductivity (C) in  $\mu\text{mhos cm}^{-1}$  at 20°C; all other analyses in  $\text{mg liter}^{-1}$  except alkalinity ( $\text{A}$ ,  $\text{HCO}_3^- + \text{CO}_3^{2-}$ ) in  $\text{meq liter}^{-1}$ . Int denotes interference; - not detectable or not determined. Phosphate analyses  $< 10 \text{ mg liter}^{-1}$  were done in the field. S+ and S- are the sum of the cations and anions in  $\text{meq liter}^{-1}$

Common	C	Na	K	Ca	Mg	SO <sub>4</sub>	Cl	A	F	SiO <sub>2</sub>	PO <sub>4</sub>	S+	S-	Date	Location
Sodium bicarbonate (low chloride)															
Nanyuki*	1,758	460	84	7.6	2.1	130	91	15.6	28.5	31	2.4	22.7	22.4	16 Jun 69	3°15'S, 36°47'E
Small Momeia†	4,720	1,230	188	0.9	1.8	285	117	47.7	110	4.3	int	58.5	61.7	26 May 69	3°14'S, 36°54'E
Reshitani†	13,500	4,200	588	3.8	3.4	300	427	164	361	7.5	int	198.2	201.2	25 May 69	3°14'S, 36°54'E
Tulustai†	14,390	4,600	726	3.2	6.1	422	646	189	437	5.0	int	219.3	238.8	1 Jun 69	3°12'S, 36°54'E
Bisina	260	22.5	6.7	23	12	4.7	2.3	3.1	6.65	54.6	0.01	3.3	3.3	9 Oct 69	1°38'N, 33°56'E
Nativasha	208	24.2	12.3	16.2	5.3	5.2	6.9	6.9	0.95	24.6	-	2.6	2.5	11 Jul 69	0°46'S, 36°21'E
Oloidiien	628	142	15.5	9.4	5.8	23.8	23	6.7	5.41	42.8	int	7.5	7.9	11 Jul 69	0°48'S, 36°17'E
Karlandusi	251	44.8	10.7	10.3	1.6	29.4	3.1	2.2	7.13	74.9	-	2.8	2.8	13 Sep 69	0°27'S, 36°16'E
Elmenteta	11,700	3,800	284	0.0	0.0	133	1,970	107	323	177	9.2	172.6	182.3	23 Jul 69	0°27'S, 36°15'E
Megadi	69,960	32,200	525	0.0	0.0	403	16,200	963	437	143	14	1,414	1,451	Nov 69	1°50'S, 36°16'E
Sodium bicarbonate (high chloride)															
Gidaburk*	11,120	3,700	174	8.7	80	1,500	1,970	87.4	9.31	11.8	19	172	175	22 Jul 69	4°23'S, 35°05'E
Sodium-potassium-magnesium bicarbonate (high fluoride)															
Saka*	535	30	16	54	33.4	11.8	1.9	7.04	1.52	30	0.1	7.2	7.3	3 Nov 69	0°42'N, 30°14'E
Sodium-potassium-magnesium bicarbonate (low fluoride)															
Kivuv*	1,110	120	68	5.9	87	32	28.5	13.15	1.9	12.8	-	14.4	14.6	25 Sep 69	2°12'S, 29°16'E
Tanganyika	649	63	32	10.4	40	13.9	27.0	6.67	1.06	-	-	7.4	7.7	11 Aug 69	8°46'S, 31°10'E
Sodium chloride															
Singida*	5,740	1,240	10	56.4	68.8	740	1,890	5.66	3.61	21.4	1.9	62.7	62.1	17 May 69	4°47'S, 34°45'E
Calcium-magnesium bicarbonate															
Mahoma*	17	0.5	0.3	0.7	0.1	4.2	1.0	-	0.04	2.1	-	-	-	18 Jul 60	0°21'N, 30°00'E
Unusual springs															
Shantanda	1,980	394	15	59	0.6	613	209	1.71	-	50	-	20.5	20.4	21 Apr 65	- - -

\* Analyses considered representative of the class.

† Momeia lakes.

Talling and Talling (1965) consider the contribution of hydroxide, silicate, phosphate, and borate to total alkalinity to be negligible and refer to total alkalinity as  $\text{HCO}_3^- + \text{CO}_3^{2-}$ . We have followed this convention. Sulfate was determined turbidimetrically in the field using Hach reagents (Sulfaver III, Hach Chemical Co.) and in the laboratory using an ion exchange method (Mackereth 1963). The different methods for calcium, magnesium, and sulfate agreed within 5% for those samples treated by two methods. Conductivity was measured on a Philips PR9501 meter.

#### GEOCHEMISTRY OF AFRICAN WATERS

The distribution and abundance of fluoride in the waters of East and Central Africa are best understood by examining their general geochemistry. The main features of water chemistry in intertropical Africa can be explained by the chemical weathering of crystalline rocks and, in closed basin lakes, by subsequent evaporative concentration (Kilham 1971). A genetic classification based on this observation has been proposed and six geochemically distinct water types discriminated: common, sodium bicarbonate, sodium-potassium-magnesium bicarbonate, calcium-magnesium bicarbonate, sodium chloride, and unusual springs (Table 1). Waters of the sodium bicarbonate, sodium-potassium-magnesium bicarbonate, and calcium-magnesium bicarbonate types are geochemically determined by the solution of identifiable crystalline rocks. The sodium bicarbonate type can be further divided into low and high chloride subtypes (Hecky and Kilham 1973): the first is generated under humid climates where acquisition of solutes by weathering processes masks the chemical composition of the rain, the second is found in drier areas where chemical weathering is less intense. The high chloride subtype grades into the sodium chloride waters that develop in arid regions where chemical weathering is not pronounced. These waters probably reflect the chemical composition of the rain (Kilham 1971). Waters of the common type

develop through interaction of rainwater and clay minerals on the deeply weathered planation surfaces of Africa and are similar in origin and composition to the many tributaries of the Amazon River (Gibbs 1970). Waters classified as unusual springs are those whose solutes have presumably been acquired from evaporites, particularly soluble metamorphic rocks, or both. Table 1 also gives the chemical compositions of all the lakes and rivers specifically referred to here.

The relative volumetric importance of specific water types is not known. Waters of the common type are most prevalent in the drainage basin of the Victoria Nile. The great lakes of the western Rift Valley—Albert, Edward, Kivu, and Tanganyika—belong to the sodium-potassium-magnesium bicarbonate type.<sup>4</sup> Waters of the sodium bicarbonate and sodium chloride types are primarily found in basins of internal drainage and presumably are not influenced by waters of other types. The unusual springs type and the calcium-magnesium bicarbonate type are rare.

#### RESULTS

We present our data as F:Cl ratios because these ratios can separate rock-derived fluoride from atmosphere-derived fluoride. This is possible if we assume chloride to be completely conservative and assume further that F:Cl ratios of  $>0.10$  (by meq) are indicative of rock weathering. The ratio 0.10 has been chosen because it is close to the maximum ratios reported for atmospheric precipitation in industrial countries (*see* Carpenter 1969); there are no reported fluoride analyses for African rainwater. Table 2 shows mean F:Cl ratios for particular water types from 177 localities.

The mean F:Cl ratios given in Table 2 for each water type would presumably be much higher if the volcanic rocks in East Africa were impoverished in chloride.

<sup>4</sup>Lakes Albert and Edward have recently been renamed Lakes Mobutu Sese Seko and Idi Amin Dada, respectively.

Table 2. Mean F:Cl ratios (*M*) for genetic classes (*G*) of East African waters. Subtypes (*S*), ranges (*R*), standard deviations ( $\sigma$ ), and number of surface waters from different localities averaged (*N*). The F:Cl ratio of the surface water considered representative of the class (*W*) is given. C—common; U—unusual springs

G	S	M F:Cl (meq liter <sup>-1</sup> )	R	$\sigma$	N	W	F:Cl (meq liter <sup>-1</sup> )
C (Clays and rainwater)		0.11	0.01-0.38	0.075	56	Kagera	0.16
Na-HCO <sub>3</sub> -CO <sub>3</sub> (Na-rich alkalic rocks)	Total	0.54	0.00-5.39	0.86	85		
	Low Cl (High F)	0.63	0.01-5.39	0.90	72	Nanyuki	0.58
	High Cl (Low F)	0.022	0.00-0.06	0.018	13	Gidaburk	0.01
Na-K-Mg HCO <sub>3</sub> (K-rich alkalic rocks)	Total	0.42	0.00-3.12	0.65	34		
	High F	1.26	0.61-3.12	0.79	9	Saka	1.49
	Low F	0.11	0.00-0.53	0.13	25	Kivu	0.12
NaCl (Precipitation only)		0.005	0.00-0.02	0.01	4	Singida	0.00
Ca-Mg HCO <sub>3</sub> (Metamorphic rocks)		0.09	0.07-0.11	0.028	2	Mahoma	0.07
U (Sedimentary and metamorphic rocks)		No data	-	-		Shantanda	-

Chloride analyses are available for 21 of the rocks for which fluoride analyses are summarized in Table 3. The data show that these rocks contain between 0.01 and 0.41% chloride (mean =  $0.13 \pm 0.12\%$ ,  $n = 21$ ). In spite of their high chloride contents the F:Cl ratios of the rocks are high (mean  $5.60 \pm 7.5$ ,  $n = 21$ ). The high chloride contents of these rocks strengthen our assumption that F:Cl ratios  $> 0.10$  in surface waters are indicative of rock weathering.

#### Common

Waters of common type are found throughout the nonvolcanic regions of Africa. These waters have F:Cl ratios from 0.01 to 0.38. Fluoride in these waters may come from atmospheric precipitation if the ratio for rainwater is as high as 0.10; if it is actually lower most of the fluoride may be derived from the weathering of various clay minerals rather than of rock. The lowest fluoride concentration observed was

for Katoro Stream in West Lake District, Tanzania. Katoro Stream drains a region of Precambrian metamorphic rocks overlain by a thick mantle of well-leached lateritic clay.

#### Sodium bicarbonate

Sodium bicarbonate waters can be divided into high and low chloride subtypes as discussed above. Waters of the high chloride subtypes are impoverished in fluoride, and waters of the low chloride subtype are rich in fluoride. These subtypes may directly reflect the relative importance of rainwater-derived chloride in the high chloride subtype or the chemical composition of the predominant volcanic rocks in the drainage basin in waters of the low chloride subtype (*see* Table 2).

In the eastern Rift Valley extreme F:Cl ratios (0.4-1.76) characterize the sodium bicarbonate waters draining the caldera of Mount Meru (Kilima Ujamaa), Tanzania, which contains a cinder cone of fluoride-

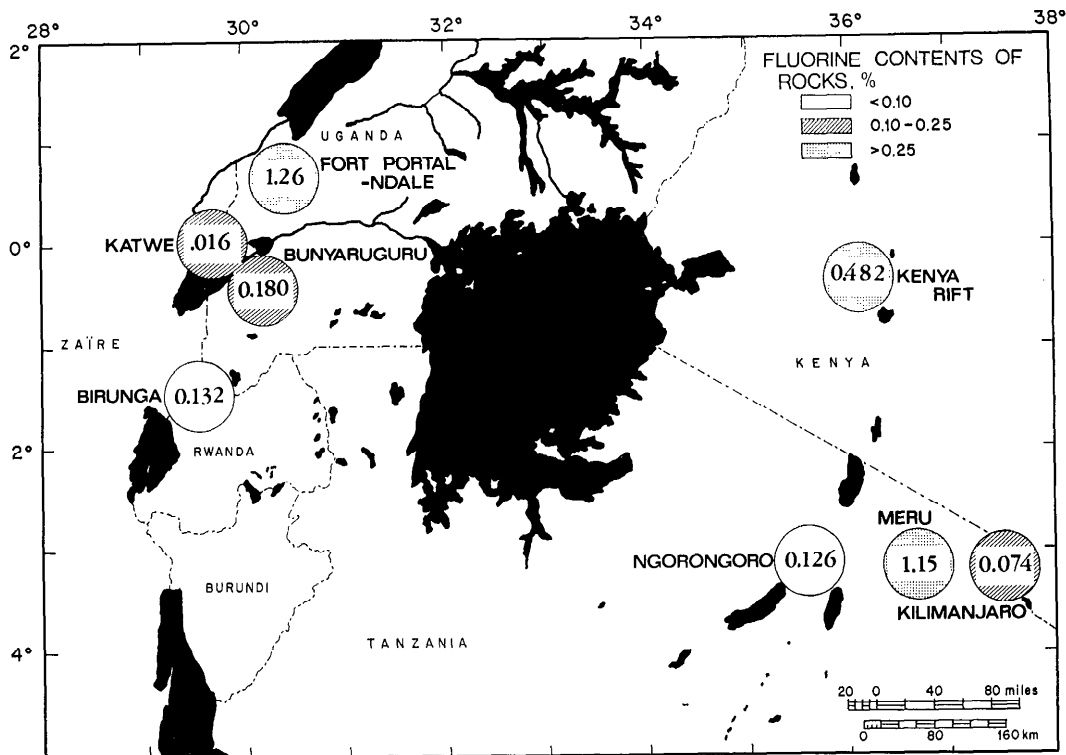


Fig. 1. The mean F:Cl ratios (meq liter<sup>-1</sup>) for surface waters in particular volcanic fields are given by the large numerals within circles. The shaded portion of each circle indicates the fluorine concentration of the rocks.

rich nephelinitic rocks (0.37% fluoride, Table 3). High F:Cl ratios are also observed for the sodium bicarbonate waters which leach fluoride-rich volcanic rocks in central Kenya. The highest fluoride value ever reported for a surface water is for Lake Elmenteita (1,627 mg liter<sup>-1</sup>; Baker 1958) at a time when the lake was far more concentrated than when we visited it (Table 1). Lake Elmenteita is fed in part by the Kariandusi River (fluoride = 7.13 mg liter<sup>-1</sup>) which drains fluoride-rich rocks in central Kenya.

Lake Bisina (formerly Lake Salisbury) has perhaps the most anomalous fluoride concentration of all the lakes we studied because it has a high F:Cl ratio in a region where the other lakes have low ratios. The high fluoride concentration in Lake Bisina presumably reflects the fluoride-rich volcanic rocks in its drainage basin. Although

Lake Bisina is connected through papyrus swamps with Lake Kioga, it receives most of its water from the slopes of Mount Elgon, a large nephelinitic Miocene volcano on the Kenya-Uganda border. Unfortunately few data exist for the fluoride content of the predominant volcanic rocks of Mount Elgon. If our hypothesis is correct, these rocks will be relatively fluoride rich.

The surface waters of both Mount Kilimanjaro and Ngorongoro Crater (Tanzania) have generally lower F:Cl ratios. These waters drain volcanic rocks with considerably less fluoride than those found on Mount Meru or in the Rift Valley of central Kenya (Table 3), supporting the hypothesis that the chemistry of these waters is controlled essentially by the chemical weathering of crystalline rocks in humid drainage basins.

Table 3. Compilation of fluoride analyses of rocks from volcanic regions of East Africa. All analyses in % F. Country and volcanic region (C), number of samples (N), range (R), mean (M), analysis location (A) in referenced papers, and main rock types (T) are given. References (R No.): 1—Gerasimovskiy and Savinova (1969); 2—Bowen (1937); 3—MacDonald et al. (1970); 4—von Knorring and DuBois (1961); 5—Holmes and Harwood (1932); 6—Higazy (1954); 7—Bell and Powell (1969)

C	N	R	M	R no.	A	T
Tanzania						
Meru, foot	1	-	0.15	1	Table 1, p. 1125	Nephelinites
Meru, peak	3	0.23-0.37	0.32	1	Table 1, p. 1125	Nephelinites
Meru	2	0.21-0.22	0.215	1	Table 1, p. 1125	Phonolites
Meru mean	6	0.21-0.37	0.268			
Kilimanjaro	1	-	0.13	1	Table 1, p. 1125	Nephelinites
Kilimanjaro	1	-	0.13	1	Table 1, p. 1125	Picrites
Kilimanjaro	3	0.048-0.14	0.082	1	Table 1, p. 1125	Picrite basalts
Kilimanjaro	4	0.078-0.12	0.10	1	Table 1, p. 1126	Olivine basalts
Kilimanjaro	2	0.15-0.18	0.165	1	Table 1, p. 1126	Rhomben-porphry
Ngorongoro	1	-	0.076	1	Table 1, p. 1125	Picrites
Ngorongoro	2	0.078-0.091	0.085	1	Table 1, p. 1126	Olivine basalts
Ngorongoro	1	-	0.14	1	Table 1, p. 1126	Trachyandesite
Ngorongoro mean	4	0.076-0.14	0.096			
Kenya						
Naivasha area	4	0.17-0.68	0.387	2	Table 1, p. 14 samples 6-9	Rhyolite & Commen- dite obsidian
Menengai	4	0.17-0.36	0.307	3	Table 1, p. 511 samples 43/1/S 5,6,6a,11	Glass peralkaline trachytes
Uganda						
Fort Portal Field	4	0.14-0.30	0.25	4	Table 1, p. 1065	Vesicular carbona- titic lava
				5	Table 1, p. 381 sample 1	
				5	Table 11, p. 420 sample 1	Melilite-leucite
Katwe Field mean	7	0.02-0.27	0.11	6	Table 1, p. 53 samples D,E,	Biotite pyroxenite
				6	Table 2, p. 57 samples A,B,J	Biotite, Katungite, Olivine ouachitite
				6	Table 3, p. 59 sample A	Leucite ankaratrite
				7	Table 3, p. 549 sample 19	Leucite ankaratrite
Bunyaruguru mean	7	0.08-0.18	0.12	6	Table 1, p. 53 sample A	Biotite peridotite
				6	Table 2, p. 57 samples C,D,E,I	Katungite, Olivine- rich ugandite
				7	Table 3, p. 550 samples 29,30	Mafurite, Leucite mafurite
Birunga mean	13	0.00-0.15	0.06	6	Table 1, p. 53 samples B,F	Biotite peridotite, Biotite pyroxenite
				6	Table 4, p. 60 samples A-G	Kivite, Melilite, Limburgite, Leu- cite trachybasalt
				7	Table 3, p. 549, 551. samples 12,45,48,50	Nephelinite, Absaro- kite, Banakite, Kentallenite

### Sodium-potassium-magnesium bicarbonate

The western Rift Valley of East Africa contains both low and high fluoride sodium-potassium-magnesium bicarbonate

waters. The high fluoride waters (F:Cl = 1.26) leach high fluoride potassic alkalic rocks in the Fort Portal and Ndale volcanic fields (Uganda). The low fluoride waters

(F:Cl=0.11) leach low fluoride potassic alkalic rocks in the Katwe (Uganda), Bunyaruguru (Uganda), and Birunga volcanic fields (Uganda, Rwanda, Zaïre).

#### *Sodium chloride*

Sodium chloride waters have particularly low F:Cl ratios ( $< 0.01$ ) because rainwater is probably low in fluoride and relatively high in calcium. Calcium availability in these waters (*see* Table 1) increases the likelihood of codeposition of fluoride as fluorapatite or fluorite along with calcium carbonate.

#### *Calcium-magnesium bicarbonate and unusual springs*

Few data are available on fluoride concentrations in waters of the calcium-magnesium bicarbonate and unusual springs types since these waters are rare in East Africa; F:Cl ratios ranged from 0.07 to 0.11.

Figure 1 summarizes the relationship between the fluoride content of the volcanic rocks (Table 3) and the F:Cl ratios of the surface waters (Table 2). Surface waters in the Katwe volcanic field and those sampled on the slopes of Mount Kilimanjaro both have lower ratios than one would expect from the rock analyses alone. The lakes in the Katwe volcanic field are very concentrated; possibly some fluoride has coprecipitated with other minerals, or as villiaumite (NaF), while chloride was not affected. The waters draining Mount Kilimanjaro probably have lower F:Cl ratios than expected because we have tested only three samples.

#### *Correlation coefficients*

The correlation coefficients for fluoride with other solutes (Table 4) also suggest that fluoride comes primarily from chemical weathering because the highest correlation is between fluoride and alkalinity ( $\text{HCO}_3^- + \text{CO}_3^{2-}$ ). Alkalinity is a major product of the incongruent solution of silicate rocks (*see* Stumm and Morgan 1970). The comparatively low correlation between fluoride and chloride suggests that the fluoride contribution from atmospheric precipita-

Table 4. Pearson correlation coefficients for the major ions and conductivity on fluoride. *r*—Correlation coefficients; *n*—number

	<i>r</i>	<i>n</i>	sig.
Cond.	0.67	207	0.001
Na	0.53	210	0.001
K	0.35	209	0.001
Ca	-0.17	193	0.009
Mg	-0.10	190	0.077
SO <sub>4</sub>	0.34	208	0.001
Cl	0.40	210	0.001
HCO <sub>3</sub> +CO <sub>3</sub>	0.67	206	0.001
PO <sub>4</sub>	0.54	113	0.001
Si	0.40	193	0.001

tion is of only secondary importance. Calcium and magnesium have significant ( $< 0.08$ ) negative correlations with fluoride. Without other information these could be interpreted as indicating that various minerals containing calcium, magnesium, and fluoride have precipitated. However, the alkaline earths are most likely removed as carbonate precipitates or by ion exchange on clays before fluoride precipitates are formed. Solubility calculations for these waters often indicate that fluorite should precipitate before calcite, but we have observed only calcite precipitation when the solubility data would favor the formation of both fluorite and calcite. This suggests a kinetic problem involving the formation of fluoride-rich minerals.

#### *Fluoride in saline lakes*

Fluoride in surface water may either be transported to the ocean or removed by precipitation in continental basins. The latter alternative is of special significance in East Africa because the eastern Rift Valley creates a large area of internal drainage extending from Ethiopia through Tanzania. We found the highest fluoride concentrations in the saline lakes of the Rift Valley, e.g. Hannington, Elmenteita, and Magadi.

Some of the highest F:Cl ratios are found in the Momela Lakes, a series of closed basin lakes on the slopes of Mount Meru. Hecky (1971) has detailed their origin, geochemical history, and paleoecology. They are set in depressions on the surface



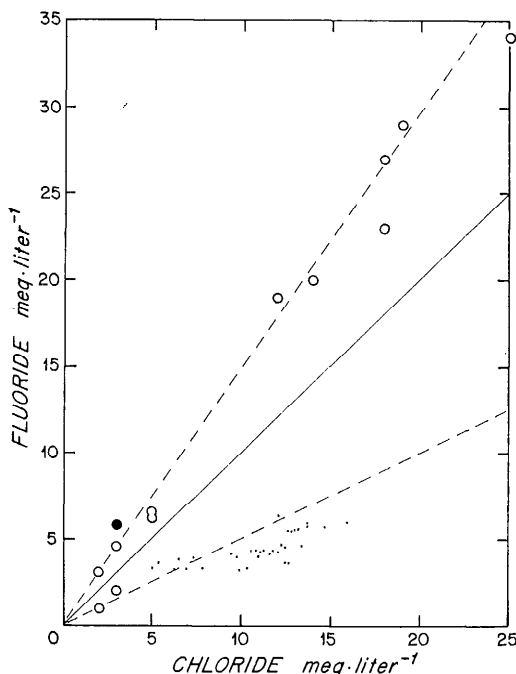


Fig. 2. Circles represent fluoride and chloride in the surface waters at Momela. The black circle is Small Momela Lake. The dots symbolize fluoride and chloride in the interstitial waters of a 7-m core from Small Momela Lake. The dashed lines represent slopes of 1.5 and 0.5; the solid line indicates a slope of 1.0.

of an extensive mudflow resulting from the collapse of the northern caldera wall of Mount Meru and share a homogeneous geological and climatic setting. The ionic composition of the lakes is nearly constant, but they do exhibit a 10-fold range of concentrations ( $k_{20} = 1,758\text{--}22,500 \mu\text{mhos cm}^{-1}$ ). These characteristics, combined with their high F:Cl ratios, make these lakes a convenient natural system for observing the geochemical behavior of fluoride during evaporative concentration in surface waters and early diagenesis in sediments of saline lakes.

The F:Cl ratios of the surface waters of the Momela Lakes and the Nanyuki River which drains the Meru caldera and part of the mudflow surface are represented in Fig. 2. The ratio is essentially constant at 1.5 for all surface waters except the river (F:Cl = 0.5) and Silver Sea, an artificial

lake maintained by water pumped from the river. This lower ratio represents surface runoff while the higher values for the other lakes reflect the significant input of groundwaters which maintain these closed lakes at their nearly constant level. The groundwater leaches more fluoride than the river waters because of its longer residence time in association with the fluoride-rich rocks of the mudflow (Table 3) and, thus, yields the higher ratio.

The constancy of the F:Cl ratio over the concentration gradient suggests that neither fluoride nor chloride is precipitated during evaporative concentration. Eugster (1970) also noted that fluoride accumulated without loss during the evaporative concentration of springs and brines of Lake Magadi and concluded that the high alkalinity of the Magadi waters removed calcium by precipitation of calcium carbonate, thus effectively preventing formation of fluorite ( $\text{CaF}_2$ ). The Momela Lakes, Lake Magadi, and other saline lakes of the eastern Rift Valley are sodium bicarbonate-carbonate lakes. The high fluoride values reflect the nearly complete removal of calcium by carbonate precipitation; therefore in these lakes fluoride can increase until saturation with respect to villiumite ( $\text{NaF}$ ) is reached.

The F:Cl ratios in the interstitial waters of a 7-m core from Small Momela Lake, based on calculated fluoride concentrations, are presented in Fig. 2. Fluoride activity was measured by electrometric methods and an activity coefficient was computed with the Davies (1962) equation. The assumption implicit in such a computation that there is no complexing is supported by our comparison in surface waters of calculated and measured activity values. A salinity gradient exists in the sediment because a wetter climate over the past 600 years has caused the lake to become diluted. The concentrations of the various ions in the sediment reflect this historical dilution as well as readjustments dictated by the diffusional gradients imposed (Hecky 1971). The F:Cl ratio drops from 1.7 in the lake water to 0.7 in interstitial

water of the surficial sediments. The fluoride concentration in the lake is 5.8 meq liter<sup>-1</sup> while that of the pore water of the surficial sediment is 3.3, showing that the ratio reduction is due to an absolute removal of fluoride. Lake Reshitani, another of the Momela Lakes, shows the same phenomenon. The F:Cl ratio drops from 1.5 to 1.0 with a reduction in fluoride from 27 meq liter<sup>-1</sup> in the lake to 21 in the interstitial waters of the surficial sediments.

Clearly the sedimentary environment in these lakes favors relatively rapid reactions reducing the fluoride concentrations of pore waters. Previous studies of lake, estuarine, and ocean sediments have shown the opposite trend, i.e. enrichment of fluoride relative to chloride (Windom 1971; Shiskina 1966; Mun et al. 1966). Those studies invoke the release of fluoride from the degradation of organic matter and possibly submarine weathering of detrital minerals to explain the fluoride enrichment. Such processes can undoubtedly be important in low fluoride waters where a change of 1 mg liter<sup>-1</sup> is significant. However, in high fluoride lacustrine sediments we observe changes of opposite direction and orders of magnitude larger; the removal and subsequent release of fluoride by biological action is not detectable.

The magnitude and specificity of the reduction in fluoride favor a hypothesis of precipitation. Carpenter (1969) has shown that the major process removing fluoride from the oceans is codeposition as fluorite or fluorapatite with calcium carbonate minerals. Fluorite, CaF<sub>2</sub>, and fluorapatite, (CaF)Ca<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub>, are also the most likely authigenic minerals in these lakes. Both of these are very insoluble. Smyshlyaev and Edeleva (1962) gave  $k_{sp} = 10^{-10.57}$  for fluorite at 25°C. However, calcium is low (0.04–0.30 meq liter<sup>-1</sup>) in these highly alkaline surface and interstitial waters (see Table 1). Much of the calcium is removed as calcite in travertine deposits at springs and along streams on the mountain. Therefore, although these waters are in equilibrium with CaCO<sub>3</sub>, there is only a small amount of precipitation within the lakes.

Only in the sediment where CaCO<sub>3</sub> ranges from 1–5% by dry weight does the water come into intimate contact with a relatively abundant source of calcium. In addition, the long residence time in the sediments can overcome any kinetic problems involved in the formation of fluoride-rich minerals. Further evidence for the existence of a calcium fluoride solid phase is found in analyses of acid extracts (0.1 N HCl for 12 hr) from Reshitani sediments (Hecky 1971), where calcium and fluoride were positively correlated ( $r = 0.626$ , significant at  $< 0.05$  for  $n = 12$ ). These data corroborate Eugster's (1970) suggestion that fluoride-rich strata in cores from Lake Magadi might have formed by interaction of high fluoride brines with calcite-bearing muds. Calcium concentrations in the pore waters of cores from Reshitani and Small Momela were not lower than in the lake water; this should indicate that only pre-existing calcium carbonate crystals are involved in the removal of fluoride from solution.

#### DISCUSSION

##### *Fluoride in East Africa*

Previous workers have generally agreed that volcanic activity is in some way responsible for the high fluoride concentrations of East African waters, but the exact source of fluoride has remained obscure (Deelstra 1971). Until recently the acquisition of fluoride from juvenile water has been perhaps the prevalent explanation (Baker 1958; James 1967). The hypothesis that the high fluoride concentrations are the expected products of the chemical weathering of fluoride-rich volcanic rocks has been seriously suggested by Baker (1958) and Kilham (1971).

Our study indicates that the fluoride cycle in East Africa may be relatively simple. Rainwater acquires fluoride in small amounts from marine aerosols and continental dust in the atmosphere. After precipitation, rainwater, in conjunction with biologically produced carbon dioxide, leaches fluoride from soils and crystalline rocks. The fluoride derived from weather-

ing reactions is particularly conspicuous in these tropical environments because high temperature and humidity promote high rates of weathering. The volcanic rocks of East Africa are much richer in fluoride than analogous rocks in other parts of the world (Cerasimovskiy and Savinova 1969), so high fluoride concentrations (the products of weathering reactions) are to be expected in the surface waters. In the internal drainage basins of the eastern Rift Valley fluoride generally accumulates in lakes until the ion activity product of villiumite ( $\text{NaF}$ ) is exceeded; the precipitation of fluoride as fluorite or fluorapatite is not observed because calcium is not readily available. Waters leaving the open drainage basins of East Africa contain considerably more fluoride than the  $0.1 \text{ mg liter}^{-1}$  value suggested by Turekian (1969) as the approximate world river average. The Victoria Nile and Lake Tanganyika, tributary to the Zaire (formerly Congo) River system, contain  $0.38$  and  $1.08 \text{ mg liter}^{-1}$  fluoride (Table 1).

Fluoride analyses have heretofore been infrequent and analytically difficult (*see* Talling and Talling 1965). Probably for these reasons fluoride as a possible selective agent in the ecology of various organisms in East Africa has been ignored. An important medical and economic exception is fluorosis in man and domestic animals. The presence of fluoride in potable waters is a mixed blessing. At low concentrations ( $1 \text{ mg liter}^{-1}$ ) it is recommended by the American Public Health Association (1965) for prophylaxis of dental caries. However,  $10 \text{ mg liter}^{-1}$  is considered excessive and detrimental to teeth and bones. Concentrations considerably greater than this are observed in many East African lakes (Kilham 1971; Hecky 1971). In regions surrounding Mount Meru, Tanzania (*see* p. 937), for example, fluorosis is a recognized problem in livestock and human populations (Walker and Milne 1955). It could also be a problem for wild game in the high fluoride volcanic regions of East Africa.

High fluoride concentrations may also

influence the distribution of zooplankton, phytoplankton, and higher aquatic plants. Although experimental data are unavailable, we would like to mention some situations where high fluoride concentrations may be involved. Beadle (1932) and LaBarbera and Kilham (in prep.) have noted that copepods are not observed in East African lakes with conductivities  $> 23,500 \mu\text{mhos cm}^{-1}$  at  $20^\circ\text{C}$  even though copepods are found in more concentrated lakes in Australia. Lake Hannington, for example, with a conductivity of  $57,400 \mu\text{mhos cm}^{-1}$  and fluoride concentration of  $1,064 \text{ mg liter}^{-1}$  does not contain copepods. Lake Tulusia has the highest fluoride concentrations in which copepods are found ( $437 \text{ mg liter}^{-1}$ ).

Lewin (1962) has shown that fluoride inhibits silicon uptake and respiration in diatoms. Differences in fluoride concentration may be partially responsible for the differences in diatom floras between dilute sodium chloride and sodium bicarbonate lakes (Hecky and Kilham 1973). Particularly striking in East Africa is the distribution of the sedge *Cyperus papyrus*. It is usually not seen in lakes with conductivities  $> 1,000 \mu\text{mhos cm}^{-1}$ , but it is notably absent in relatively high fluoride lakes with lower conductivities such as Ololdien Bay and Lake Bisina. Ololdien Bay is connected to Lake Naivasha which has a much lower fluoride concentration and contains vast floating islands of *C. papyrus*. Lake Bisina stands out because it is the only papyrus-free lake in the massive papyrus swamp surrounding Lake Kioga (LaBarbera, personal communication).

#### *Other regions*

The role of chemical weathering and atmospheric precipitation in the major sedimentary cycle of fluoride outside of East Africa is a matter of considerable debate. Correns (1956) in his review of halogen geochemistry concluded that rock weathering played a role in the geochemical cycle of fluoride. In light of current concepts concerning the role of chemical weathering in freshwater solute acquisition (*see* Stumm

and Morgan 1970), the data reviewed by Fleischer and Robinson (1963) also suggest that chemical weathering is a significant source of fluoride. They report that many groundwaters have high fluoride and sodium bicarbonate contents in both volcanic and nonvolcanic regions. This is exactly the correlation one would expect if fluoride is a product of chemical weathering.

A study by Reeder et al. (1972) of the hydrogeochemistry of the surface waters of the Mackenzie River (Canada) is inconclusive as to the ultimate sources of fluoride in the drainage basin. Their investigation, using factor analysis, revealed that the fluoride in the river was associated mainly with other ionic species which were acquired from the solution of carbonate rocks. However, on the basis of Carpenter's (1969) data from the literature concerning the fluoride content of precipitation in industrial regions they tentatively suggest that much of the fluoride in the drainage basin may come from the rain. Because of the association they found between fluoride and the products of rock weathering they point out that Carpenter's hypothesis that most of the fluoride in river water is cyclic needs to be tested.

Carpenter (1969) argues that weathering is not a primary source of fluoride and suggests that atmospheric precipitation alone contains enough to account for that observed in most river waters. He estimates that fluoride deposition in the ocean amounts to only 10–20% of that delivered to the ocean by rivers and therefore concludes that 80–90% of the fluoride in freshwaters is recycled, assuming a steady-state ocean. Carpenter cites several determinations of F:Cl ratios in rainwater ranging from 0.03–0.12 by weight which agree well with the amounts required by the recycling hypothesis. However, the F:Cl ratio of the ocean is only  $6.8 \times 10^{-5}$  (Brewer et al. 1970). A recycling hypothesis must infer a mechanism operating on marine aerosols for the enrichment of fluoride relative to chloride. Recent data of Wilkness and Bressan (1971) show that fluoride is not preferentially en-

riched in laboratory aerosols produced from seawater. Marine aerosols collected above the sea surface are only slightly enriched in fluoride because of contamination processes that are not yet fully understood (Wilkness, personal communication).

Because marine aerosols are not greatly enriched in fluoride with respect to seawater, some other sources of rainwater contamination must be considered as a cause of the ratios Carpenter cites. Possible sources of fluoride include volcanic activity (which is little understood), atmospheric dust from continental sources, and industrial pollution (including freons and other volatile organo-fluorine compounds, as well as fluoride derived from the burning of fossil fuels) (Wilkness, personal communication). There are few reliable quantitative estimates for the acquisition of fluoride by rainwater from any of these sources. In addition, few data concerning the actual fluoride content of rainwater are available. Two of the potential sources of fluoride in rainwater, atmospheric dust and industrial pollution, are influenced by the activities of man. Atmospheric dust has increased as a result of deforestation and other disturbances of natural ecosystems.

We would like to propose, on the basis of the African data, that the apparent imbalance in the fluoride cycle may be the result of the activities of man. This hypothesis could be tested by examining lake sediment cores or ice cores (from polar regions) for changes in fluoride concentration. This historical fluoridation of the atmosphere, if it has occurred, may render chemical analyses of rainwater meaningless in reconstructing the natural fluoride cycle.

#### CONCLUSION

High weathering rates, geological simplicity, limited industrialism, and fluoride-rich rocks combine in East Africa to demonstrate that rock weathering is the primary source of fluoride in surface waters. We believe that a lack of these characteristics obscures the acquisition of fluoride from rocks in other regions. Therefore, we propose that weathering processes

have been the primary determinant of surface water fluoride concentration and the primary contributor of fluoride to the ocean through most of geological time. Other sources such as volcanic emanations and inputs resulting from man's activities may in the short term entirely mask weathering processes, but are minor in the long term. The imbalance in the current oceanic fluoride budget which Carpenter (1969) recognizes is probably real and may be a result of the activities of man. Otherwise the assumption of a steady-state ocean with respect to fluoride necessitates a recycling hypothesis that is not substantiated by the experimental and observational data. The effects of any imbalance on the world's oceans are difficult to predict. Because mechanisms exist for removal of fluoride from the ocean, fluoride concentrations perhaps would not increase significantly from their present level. The possible biological consequences of any increase should stimulate further investigation of the fluoride cycle.

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