FLUORIDE CONTAMINATION AND MINERALOGICAL COMPOSITION OF EAST AFRICAN MAGADI (TRONA)

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SUMMARY: Magadi from Lake Magadi, Kenya, Lake Natron, Tanzania, Lake Katwe, Uganda and lake El Atrun, Sudan, are analysed along with efflorescent crust magadi from the surface soil from Northern Tanzania. The fluoride and carbonates concentrations are measured chemically and the mineralogical composition is determined through X-ray diffraction analysis. Magadi from Lake Natron and Lake Magadi are found to be very similar consisting mainly of trona (CO_3^{2-}+HCO_3^->10.4 meq/g magadi), mixed with halite and either kogarkoite or villiaumite respectively. This is resulting in fluoride concentrations up to 8.7 mg F^-/g magadi. The scooped magadi is less pure with respect to trona, but its fluoride content is of the same order of magnitude (0.23-5.1 mg F^-/g magadi). The scooped magadi consists of trona (CO_3^{2-} + HCO_3^-= 3.5 - 9.5 meq/g magadi) with different mixtures of halite, quartz, villiaumite, kogarkoite, and thermonatrite. No fluoride containing minerals are identified in magadi from Uganda and Sudan, probably due to the very low fluoride concentrations, = 0.02 and < 0.24 mg/g magadi respectively. The Sudanese magadi consists of different mixtures of trona, halite, and quartz resulting in a variation its alkaline strength (CO_3^{2-} + HCO_3^- = 4.6-11.9 meq/g magadi). The magadi from Lake Katwe consists of trona (CO_3^{2-} + HCO_3^- = 7.0 meq/g magadi) mixed with burkeite and halite.

Key words: Trona; Magadi; Soda; African lakes; Fluoride contamination; Villiaumite; Kogarkoite; Alkaline lakes.

INTRODUCTION

Trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, is a commonly used salt in several countries in East, West, and Central Africa and it is the second most commonly used salt in Nigerian homes.[1] In East Africa trona is locally called *magadi* and the name probably originated from the Masai word magad meaning bitter. The main use of magadi is cooking tough food materials such as beans and maize utilising its ability to fasten the softening and the digestive property of the food during cooking. In addition magadi is used as a prophylactic agent and a feed supplement to cattle and goats. Furthermore, in some places, it is ground with tobacco in the preparation of snuff.[2-13]

In the Eastern Rift Valley magadi is formed, as the so-called crystalline magadi, in the alkaline lakes due to chemical weathering of rock minerals and high evaporation of the lake waters. Magadi is also formed, as the so-called scooped magadi, on the surface soil formed due to capillary evaporation of soil water.

Analyses of both crystalline and scooped magadi from Nigeria and Ghana have shown that crystalline magadi consists essentially of trona mixed with minor contents of halite (NaCl). The scooped magadi is rich in trona but it also contains admixtures of quartz, clays, chlorides, and sulphates.[1,2,12]

Investigations have shown that magadi from the alkaline lakes and from the surface soil in the Eastern Rift Valley is often heavily contaminated with fluoride.[3,6-9,14,15] The high fluoride concentration in the Eastern Rift Valley is strongly related to weathering of the volcanic rocks rich with fluoride and alkalis as found in the Rift

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Valley areas.[14,16,17] The ingestion of fluoride through magadi may in certain cases be significant in comparison to the total intake of fluoride[7], having in mind that the acceptable maximum daily fluoride intake given by WHO is 4.0 mg F^-/person/day.

It is the aim of this study to elucidate the differences in fluoride concentration in magadi from the Eastern and the Western Rift and the deposition of different fluoride containing minerals from the alkaline lake brines. The differences in the mineralogical composition caused by the differences in the composition of the lake brines will also be discussed.

Materials & Methods

Magadi samples from Lake Natron, Tanzania (n=9), Lake Magadi, Kenya (n=15), Lake Katwe, Uganda (n=1), El Atrun, Sudan (n=5) and efflorescent crust from Northern Tanzania (n=9) have been collected at the lakes or bought at market places in Magadi town, Kenya, in Khartoum, Sudan and in cities in Uganda and Tanzania. The origin of the magadi bought at the markets was determined according to the information given by the dealers (for location of the alkaline lakes see Figure 1). The magadi samples were crushed and homogenised in a mortar. An amount of 2.00 g magadi powder was dissolved in 100.0 ml distilled water. Hereafter the fluoride and carbonate concentrations were measured in the solutions. Fluoride concentrations were measured in samples from Uganda and Sudan. Fluoride concentrations of Tanzanian and Kenyan magadi are taken from Nielsen and Dahi.[15]

Fluoride measurements: The fluoride concentrations were measured using a Radiometer F1052 fluoride electrode and a Metrohm Ag/AgCl reference electrode with a sleeve type diaphragm connected to a Metrohm potentiometer (692 pH/Ion Meter). An aliquot of 10.0 ml of the sample solutions was mixed with 10.0 ml CDTA-tisab and the fluoride concentration was measured using the calibration method as described in the Standard Methods.[18]

Carbonate measurements: The carbonate (CO_3^{2-}+HCO_3^-) concentrations were measured using the end point titration method according to the Standard Methods[18], where the end point pH = 4.5 was used. An aliquot of 5.00 ml of the magadi solutions (2.00 g/100.0 ml) was diluted to 50.0 ml and titrated automatically with 0.1 N H_2SO_4 using a Metrohm pH-electrode connected to a Metrohm 719S Titrino. The values of pH and the added amount of acid were recorded at 5 seconds intervals on a PC. The calibration of the pH-electrode was done using Metrohm buffer solutions pH = 4.0 and pH = 9.0.

X-ray diffraction: Selected magadi samples were crushed to powder and analysed by X-ray diffraction using a Philips PW1050 automated diffractometer equipped with a graphite monochromator, an automatic divergence slit, and a 0.10º receiving slit. The radiation was CuKα and the XRD spectra were recorded as step scans in the interval $5° < 2\theta < 65°$ using a step size of 0.10º and a count time of 2.0 sec/step. The reflections with $I > 3\sigma(I)$ were recorded as observed.

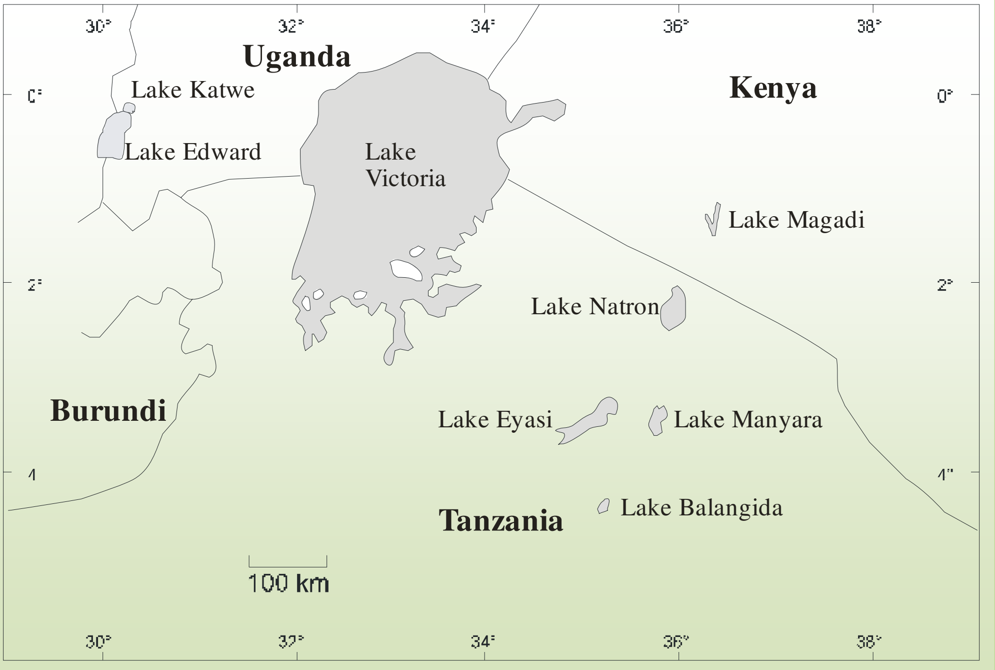

FIGURE 1. Location of some of the lakes in the Rift Valley area of East Africa.

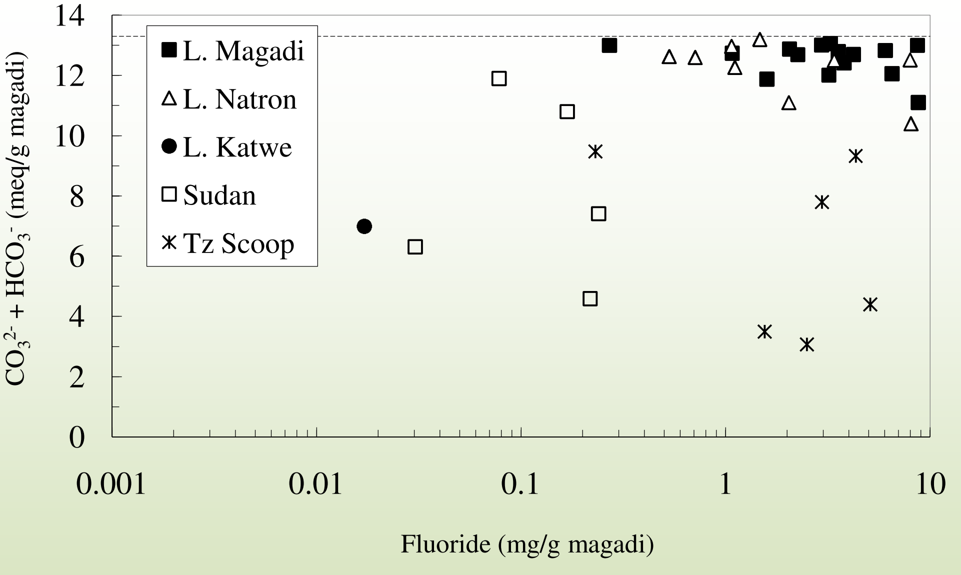

FIGURE 2. The carbonate (CO_3^{2-}+HCO_3^-) concentration versus the fluoride concentration in magadi from Africa (for location of lakes see Figure 1).
The dashed line indicates pure trona.

TABLE 1. Minerals identified by XRD in selected magadi from Africa (for location of lakes see Figure 1).

Origin of Sample	n	Minerals detected
Lake Magadi	3	Trona, halite, villiaumite
Lake Natron	5	Trona, halite, kogarkoite, thermonatrite
Lake Katwe	1	Trona, halite, burkeite
Sudan	4	Trona, halite, quartz
Northern Tanzania, scooped	6	Trona, halite, quartz, villiaumite, kogarkoite, thermonatrite

RESULTS

The results of the measurements of the fluoride and the carbonate concentrations in magadi can be seen in Figure 2, where the carbonate concentration is plotted versus the logarithmic fluoride concentration. The results from the XRD analyses can be found in Table 1, where the identified minerals in selected magadi samples are stated.

DISCUSSION

It is seen from the results in Figure 2 that there is a wide variation in the carbonate concentration of the magadi. The carbonate concentration in the magadi is mainly due to the content of trona but also due to the contents of thermonatrite, $Na_2CO_3{\cdot}H_2O$, and burkeite, $Na_2CO_3{\cdot}2Na_2SO_4$, cf. Table 1. The highest carbonate concentrations, 10.4-13.1 meq/g magadi are found in magadi from Lake Magadi and Lake Natron. These magadi samples are almost equal to pure trona indicated by the dashed line in Figure 2. The scooped magadi is less pure with respect to trona as the crystalline magadi from Lake Magadi and Lake Natron. The carbonate concentration in the scooped magadi is also subject to considerable variation, 3.5-9.5 meq/g magadi. The scooped magadi is mainly contaminated with halite (NaCl) and quartz (SiO_2). Makanjuola and Beetlestone[1] found out that scooped magadi from Nigeria consists of trona mixed with sand and clay. The magadi from Lake Katwe was bought at the local market and it is probably from the trona harvest. The magadi is not pure trona, the carbonate concentration being as low as 7.0 meq/g magadi. This is caused by contamination of halite and burkeite cf. Table 1. The carbonate concentration of the Sudanese magadi, 4.6-12.0 meq/g magadi, is subject to considerable variation like scooped magadi. The Sudanese magadi also contains impurities such as halite and quartz. However, magadi from Sudan is very different from the other magadi samples, it is not an evaporite from an existing lake or the surface soil but a salt deposit found in the mountains.

The fluoride concentration in the magadi is subject to considerable variation ranging from 0.02 to 8.7 mg F^-/g magadi, cf. Figure 2. The concentration of Tanzanian and Kenyan magadi is comparable to what has been reported by other researchers who have analysed magadi from Kenya and Tanzania.[3,7,9,14] The highest fluoride concentrations are found in magadi from Lake Natron and Lake Magadi, up to 8.1 and 8.7 mg F^-/g magadi, respectively. The high fluoride concentration in the Kenyan and Tanzanian magadi is caused by the high fluoride content of the volcanic rocks found in the Eastern Rift Valley.[16] The fluoride containing mineral, villiaumite (NaF), has been identified by X-ray diffraction in one of the magadi samples from Lake Magadi, cf. Table 1. Observations of villiaumite have also been reported by Baker.[3] The double salt, kogarkoite ($Na_2SO_4 \cdot NaF$) is identified in three of the magadi samples from Lake Natron. Darragi[19] also identified kogarkoite in the salt crust of Lake Natron by X-ray diffraction and scanning electron microscope observations. The presence of this rare mineral is not known in evaporites of the alkaline lakes in the African Rift Valley, but it has been observed in thermal deposits (84°C) at Mt. Princeton Hot Springs, Colorado[20] and in the Lovozero Massif, Kola Peninsula in nepheline syenite pegmatite.[21] The deposition of kogarkoite in Lake Natron, in contrary to villiaumite in Lake Magadi, is caused by a relatively higher sulphate concentration in the lake brine, of Lake Natron compared to Lake Magadi.[22] The fluoride concentration of the scooped magadi is in the same order of magnitude, 0.2 - 5.1 mg F^-/g magadi as the crystalline magadi from Lake Magadi and Lake Natron even though the carbonate concentration is significantly lower. Fluoride containing minerals have been identified both as villiaumite and kogarkoite in the scooped magadi. The lowest fluoride concentrations are found in the Sudanese rock samples, 0.03-0.24 mg F^-/g magadi and in the evaporite from Lake Katwe, 0.02 mg F^-/g magadi. The fluoride concentration of the magadi from Lake Katwe is very low compared to the concentration of magadi from Tanzania and Kenya. This is caused by the differences in fluoride concentration of the lake brines. Deelstra[23] found out that the saline lake waters of the Western Rift contain much smaller amounts of fluoride than the lake waters of the Eastern Rift. No reflections from fluoride containing minerals have been observed on the XRD data for the Sudanese and Ugandan magadi. This is probably due to the very low fluoride concentrations. Fluoride containing minerals have not been identified in all the magadi samples from Lake Natron and Lake Magadi but it is assumed that the measured fluoride is present as villiaumite or kogarkoite and not as fluorite (CaF_2) in these calcium poor environments.

Halite (NaCl) is identified in all the magadi samples. The evaporite from Lake Katwe contains much more halite than magadi from Lake Natron and Lake Magadi. This is related to a higher chloride concentration of the brines. Brines from Lake Katwe have an equivalent Cl/TAL ratio of 2-3[24] whereas the equivalent Cl/TAL ratio of Lake Magadi and Lake Natron brines is 0.23-1.0.[3,25,26]

In the extensive phase relations reported by Teeple[27] burkeite is found to be a phase in the system $Na\text{-}Cl\text{-}SO_4\text{-}CO_3\text{-}H_2O$ but burkeite is only identified in the magadi from Lake Katwe not in magadi from Lake Magadi or Lake Natron.

The quartz (SiO_2) identified in the scooped magadi is probably due to mixing with soil when collecting the efflorescent crust, and the quartz in the Sudanese magadi is assumed to origin from rock minerals.

Thermonatrite is observed in magadi from Lake Natron and in the scooped magadi. Eugster[28] has observed thermonatrite in shallow surface pools during the late stages of evaporation of Lake Magadi brines. Thermonatrite is normally deposited after the precipitation of trona if the brine keeps on being under-saturated with respect to atmospheric CO_2.[29]

The analyses of magadi from Tanzania and Kenya show that these samples contain high amounts of fluoride. Thus, the use of magadi heavily contaminated with fluoride as a tenderiser may in certain cases result in very high fluoride intake, even higher than the maximum daily fluoride intake of 4 mg/person/day recommended by WHO. Therefore, it may be necessary to purify the fluoride contaminated magadi before using it as a food additive. Alternatively this study indicates that other magadi sources with low fluoride contamination are likely to be found, e. g. in Sudan and Uganda.

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