

**Chemical  
composition of  
modern and fossil  
Hippopotamid teeth**

G. Brüggmann et al.

**Chemical composition of modern and fossil Hippopotamid teeth and implications for paleoenvironmental reconstructions and enamel formation – Part 2: Alkaline earth elements as tracers of watershed hydrochemistry and provenance**

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## Abstract

For reconstructing environmental change in terrestrial realms the geochemistry of fossil biapatite in bones and teeth is among the most promising applications. This study demonstrates that alkaline earth elements in enamel of Hippopotamids, in particular Ba and Sr are tracers for water provenance and hydrochemistry. The studied specimens are molar teeth from Hippopotamids found in modern and fossil lacustrine settings of the Western Branch of the East African Rift system (Lake Kikorongo, Lake Albert, and Lake Malawi) and from modern fluvial environments of the Nile River.

Concentrations in enamel vary by ca. two orders of magnitude for Ba ( $120\text{--}9336\ \mu\text{g g}^{-1}$ ) as well as for Sr ( $9\text{--}2150\ \mu\text{g g}^{-1}$ ). Concentration variations in enamel are partly induced during post-mortem alteration and during amelogenesis, but the major contribution originates from the variable water chemistry in the habitats of the Hippopotamids which is dominated by the lithologies and weathering processes in the watershed areas. Amelogenesis causes a distinct distribution of Ba and Sr in modern and fossil enamel, in that element concentrations increase along profiles from the outer rim towards the enamel-dentin junction by a factor of 1.3–1.5. These elements are well correlated with MgO and Na<sub>2</sub>O in single specimens, thus suggesting that their distribution is determined by a common, single process. Presuming that the shape of the tooth is established at the end of the secretion process and apatite composition is in equilibrium with the enamel fluid, the maturation process can be modeled by closed system Rayleigh crystallization.

Enamel from many Hippopotamid specimens has Sr/Ca and Ba/Ca which are typical for herbivores, but the compositions extend well into the levels of plants and carnivores. Within enamel from single specimens these element ratios covary and provide a specific fingerprint of the Hippopotamid habitat. All specimens together, however, define subparallel trends with different Ba/Sr ranging from 0.1 to 3. This ratio varies on spatial and temporal scales and traces provenance signals as well as the fractionation of the elements in the hydrological cycle. Thus, Sr concentrations and Ba/Sr in

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enamel differentiate between habitats having basaltic or Archean crustal rocks as the ultimate sources of Sr and Ba. The provenance signal is modulated by climate change. In Miocene to Pleistocene enamel from the Lake Albert region, Ba/Sr decreases systematically with time from about 2 to 0.5. This trend can be correlated with changes in climate from humid to arid in vegetation from C<sub>3</sub> to C<sub>4</sub> biomass as well as with increasing evaporation of the lake water. The most plausible explanation is that with time, Ba mobility decreased relative to that of Sr. This can arise if preferential adsorption of Ba to clay and Fe-oxide-hydroxide is related to increasing aridification. Additionally, weathering solutions and lake water can become increasingly alkaline and barite becomes stable. In this case, Ba will be preferentially deposited on the watershed of Lake Albert and rivers with low Ba/Sr will feed the habitats of the Hippopotamids.

## 1 Introduction

Alkaline earth elements are valuable proxies in studies on marine and terrestrial environments because they trace the water chemistry and can be used to reconstruct provenance characteristics of seawater and terrestrial water reservoirs or life histories of organisms. In lacustrine and fluvial environments Ba and Sr concentrations and their isotopic compositions are used to monitor element cycling in watersheds taking into account the effects of climate and tectonic processes on the weathering of different lithologies and on soil formation (Cameron et al., 1995; Dupre et al., 1996; Gaillardet et al., 1997; Shiller, 1997; White et al., 1999; Land et al., 2000; Dalai et al., 2002, 2003; Riebe et al., 2004; Garzanti et al., 2010, 2011; Padoan et al., 2011). The mobilization of elements during weathering mainly depends on the disintegration of primary minerals and the authigenic formation of clay minerals, the leaching of dissolvable cations, and the degree of fixation by adsorption on secondary minerals. As a general rule, Ca, Na and Sr are more easily mobilized and removed from the watershed by groundwater and rivers than Mg and Ba. The reason is that the latter metals are either incorporated in, or preferentially exchanged and adsorbed on secondary clay minerals such as illite,

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chlorite, smectite, and, therefore, are retained in the weathering cycle (Nesbitt et al., 1980; Kronberg et al., 1987). In many large watersheds the limited Ba mobility is reflected in the dissolved fraction of ground water and rivers having lower Ba/Sr than the parent lithologies, whereas the suspended load and sediments show the complementary ratio (Dupre et al., 1996; Dalai et al., 2002, 2003). Intensive weathering, however, may replace the clay minerals by phases having low exchange capacities, for example kaolinite and hydroxides, causing more effective Ba mobilization by ground or with river waters (Kronberg et al., 1987). Yet, the presence of sulfate ions and saline waters may favor the stability of hardly soluble barite which minimizes Ba loss from the catchment area (Hanor, 2000).

The alkaline earth metals Mg, Sr and Ba can substitute Ca in calcified biogenic and inorganic hard tissues, such as calcite, aragonite or apatite. Calcified materials mostly grow incrementally adding on daily, seasonal and annual scales new mineralized layers. The alkaline earth elements store information on both, ambient environmental chemistry and physiological conditions during the calcification process. These archives can be used to reconstruct chronologies of metal concentrations, dietary habits, migration paths, paleoclimate and -environmental changes in marine and terrestrial settings by performing high-resolution chemical and isotope analyses. For example ancient ocean salinity and sea surface temperature have been estimated using Sr/Ca, Ba/Ca and Mg/Ca with  $\delta^{18}\text{O}$  determinations in corals, foraminifera, otholites and fish scales (McCulloch et al., 1994; Lear et al., 2000; Balter and Lécuyer, 2010). These proxies appear to be reliable proxies of tracing water reservoirs allowing the reconstruction of fish movements between freshwater, estuarine, marine and saline habitats (Wells et al., 2003; McCulloch et al., 2005; Elsdon and Gillanders, 2006; Milton et al., 2008; Balter and Lécuyer, 2010; Phillis et al., 2011).

An important observation is the stepwise evolution of Ba/Ca and Sr/Ca in terrestrial ecosystems which has been used to reconstruct trophic levels and the feeding habits of mammals in ancient ecosystems (Elias et al., 1982; Sillen, 1988; Sillen and Lee-Thorp, 1994; Burton et al., 1999; Blum et al., 2000; Balter et al., 2002; Balter, 2004). Thus,

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Sr/Ca and Ba/Ca in bones and teeth can be used to distinguish herbivory, carnivory and insectivory as well as browsing and grazing herbivores. This differentiation relies on the process of biopurification, which discriminates against Sr and Ba relative to Ca along the food chain. According to this model, Sr/Ca and Ba/Ca in bones and teeth of mammals are lower than those of the animal's diet. The slopes of the trends in the Ba/Ca versus Sr/Ca diagrams do not depend on environmental characteristics, but are a function of physiological processes and can be defined by an allometric scaling law (Balter, 2004; West and Brown, 2005).

Discrimination between Ba and Sr, though, appears to be inefficient, because Sr/Ca and Ba/Sr in different ecosystems evolve along almost parallel trends each having a distinct Ba/Sr (Balter, 2004). Thus, Ba/Sr in bones and teeth tissues probably represents a regional diet average. Herbivores display a large variation in Sr/Ca, Ba/Ca and Ba/Sr which reflects the large compositional variations in plants. In addition, studies on enamel from African herbivores indicate that Sr/Ca and Ba/Ca browsers are lower than those of grazers indicating different extent of biopurification in the plant food, for instance different Sr/Ca in roots, stems, leaves, and fruits (Sillen, 1992; Sponheimer et al., 2005; Sponheimer and Lee-Thorp, 2006). Alternatively, the difference must reflect physiological adaptations to herbivore nutrition, for example among hindgut and foregut fermenters. However, it must be emphasized, that differences in trophic level or dietary compositions can only be recognized within single, geographically well defined habitats. On a global scale, the large variations between habitats (climate, geology, and hydrology) and within a trophic level might obliterate any categorization. In addition, the covariation of Ba and Sr along the food chain appears to be broken up if seafood is a major part of the diet (Burton et al., 1999).

Post-mortem, during fossilization and diagenesis, chemical components from the sediment and its interstitial water may migrate into the pore spaces of bones and teeth and become adsorbed at the surface of the apatite crystals and eventually incorporated into the mineral lattice (Millard and Hedges, 1996; Trueman et al., 2004; Kohn, 2008; Tütken et al., 2008). The structure of bone and dentin is rather porous because

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it contains only about 70 wt % of the mineral component. In contrast, enamel contains about 96 wt % of apatite leaving only a small volume for intruding diagenetic fluids (Pas-  
teris et al., 2008). This explains why many studies observe that the chemical composi-  
tion of enamel remains better preserved than that of bone and dentin during diagenesis  
(Hoppe et al., 2003; Sponheimer and Lee-Thorp, 2006; Tütken et al., 2008; Domingo  
et al., 2009; Brügmann et al., 2012). Certain element concentrations of fossil enamel,  
however, are often severely modified during diagenesis. The secondary precipitation  
of Fe- and Mn-oxides and oxyhydroxides is a common process as well as the addition  
of F and the recrystallization to fluorapatite. The effect of diagenesis on the Sr and Ba  
distribution in bone and teeth is often severe and even the application of sequential  
leaching techniques in order to recover the primary biogenic component does not pro-  
vide reliable results (Koch et al., 1992; Hoppe et al., 2003; Lee-Thorp and Sponheimer,  
2003).

Here we complement the study of Brügmann et al. (2012) describing the major el-  
ement variation in Neogene Hippopotamid teeth from the East African Rift System  
(EARS) by discussing the distribution of alkaline earth elements, in particular those of  
Sr and Ba, in enamel. The results show that although alteration and vital effects during  
amelogenesis have significant impact on the element distribution, the largest influence  
on concentration variations are induced by external environmental conditions, such as  
water provenance and hydrochemistry, and climate.

## 2 Samples and methods

### 2.1 Samples

Given the large compositional variation in plants, bioapatite from migrating herbivores,  
such as elephants, rhinoceros, or bovids, would be an unsuitable target in order to  
identify the signature of discrete ecosystems or habitats. More promising is bioap-  
atite from non-migratory animals, such as Hippopotamids, which are water-dependent

and have small territories (Chansa et al., 2011a, b). These animals are regarded to be opportunistic grazers adapted to a variety of different habitats ranging from lakes to rivers, and from freshwater to saline and brackish environments (Boisserie et al., 2005; Cerling et al., 2008; Harris et al., 2008). Hippopotamid teeth are very robust environmental archives and represent the most common mammalian fossils in African terrestrial sediments. It is expected that the chemical composition of the diet (food and drinking water) is reflected in the chemical composition of bioapatite forming the tooth. The chemical and isotopic compositions of teeth also depend on tooth type and stage of development. During infancy maternal food sources and underdeveloped physiology may compromise the environmental signal. In order to avoid these effects, we only analyzed molar teeth. They have been sampled from various habitats in Eastern Africa, representing modern and fossil ( $\leq 6.5$  Ma) lacustrine settings (Lake Albert and Lake Kikorongo in Uganda; Lake Malawi in Malawi), and modern fluvial environments (Blue, White, and Upper Nile in the Sudan). The modern teeth belong to the species *Hippopotamus amphibious*. Some of the fossil teeth collected in Uganda, however, are conspicuous for their small size and are for the time being classified as “Small Hippopotamids” (Boisserie et al., 2005). Sampling locations and the geological ages of the studied specimens have been described in detail by Brachert et al. (2010) and Brüggmann et al. (2012). The freshwater lakes Lake Albert and Lake Malawi occur belong to the western branch of the EARS. The tectonic history as well as litho- and biostratigraphy of the lakes have been comprehensively described (Van Damme and Pickford, 2003; Senut and Pickford, 1994; Pickford et al., 1993; Beuning et al., 1997; Betzler and Ring, 1995; Ring and Betzler, 1995; Bobe et al., 2007).

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## 2.2 Analytical methods

### Trace element analysis by laser ablation – inductively coupled plasma mass spectrometry (LA-ICPMS)

A New Wave UP193 Nd-YAG laser system with a wavelength of 193 nm was used for the ablation in order to determine Ba and Sr concentrations in the bioapatite of the tooth specimens. Ablation craters with a diameter of 80  $\mu\text{m}$  were produced applying a laser frequency of 10 Hz and energies between 2 and 8  $\text{J cm}^{-2}$ . Helium carried the ablated material into a ThermoFinnigan Element2 sector field ICPMS which was run in the low resolution mode. Counting time amounted to 20 s on the background and 80 to 100 s on the sample. NIST612 and KL2-G glasses were reference materials and  $^{43}\text{Ca}$  the internal standard. The trace element measurements were done on the same spots where major elements have been determined by Brüggmann et al. (2012), although with larger diameters. The measured CaO content has been used as an internal reference for Ba and Sr analyses. The analytical procedure is described in detail by (Jochum et al., 2006, 2007). The detection limit for Ba and Sr is better than 500  $\text{ng g}^{-1}$ , and this is at least two orders of magnitude lower than the measured concentrations in the samples. The measured standard data agree with published compilation values within 95 % confidence limits (Jochum et al., 2007). Brüggmann et al. (2012) also measured Sr concentrations by electron microprobe. A regression line for both data sets indicates an average difference of about 10 %, which is within the analytical error of the electron probe analyses. The data of the alkaline earth elements Mg and Ca, as well as the  $\text{Na}_2\text{O}$  data discussed in the following paragraphs are from Brüggmann et al. (2012) and have been determined using the electron microprobe.

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### 3 Results

The complete set of laser ablation data of Ba and Sr is provided in Table S1 of the Supplement. Table 1 summarizes average concentrations of the alkaline earth metals Ca, Mg, Ba, and Sr in enamel, cement and dentin. Overall, Sr and Ba display vast concentration variations in all tooth tissues. For example, overall Ba concentrations in enamel vary from 9 to 2150  $\mu\text{g g}^{-1}$  and those of Sr vary from 120 to 9336  $\mu\text{g g}^{-1}$ . For comparison, MgO contents vary just from 0.09 to 1.18 wt% and CaO only from 50 to 57 wt% (Brügmann et al., 2012). As a result, the coefficient of variation (COV) of Ba and Sr in enamel and dentin is between 0.8 and 1.0 and is significantly higher than that of CaO or MgO (COV < 0.45). The concentration variation in cement is smaller than that in enamel (COV of cement:  $\sim 0.55$  for Ba and Sr) but it is still higher than that of CaO, and MgO in cement (COV < 0.4; Brügmann et al. (2012). However, the relatively low number of analyses (31; Table 1) might be not representative for this material.

Barium and Sr concentrations differ between modern and fossil specimen and among dentin and enamel. Modern enamel has on average lower Ba and Sr contents (111  $\mu\text{g g}^{-1}$  and 437  $\mu\text{g g}^{-1}$ , respectively) than fossil enamel (586  $\mu\text{g g}^{-1}$  and 1023  $\mu\text{g g}^{-1}$ , respectively; Table 1; Fig. 1). This is also true for dentin, as fossil material has Ba and Sr concentrations of more than 900  $\mu\text{g g}^{-1}$ , whereas those of modern dentin are less than 450  $\mu\text{g g}^{-1}$  (Table 1; Fig. 1). A systematic concentration difference between modern and fossil cement cannot be documented because fossil cement has been observed in just one specimen. In teeth of recent animals average Sr concentrations in dentin tend to be lower than in enamel (Table 1; Fig. 1a). This becomes evident at the enamel-dentin junction (EDJ), where Sr concentrations in modern teeth abruptly decrease (Fig. 2a), but increase sharply by a factor of about two in fossil specimens (Fig. 2b).

The overall variation of Ba and Sr concentrations reflects the sum of variations which occur at two different scales. There are enormous differences among teeth from different geographical locations and there are systematic variations within single tooth

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specimen (Fig. 2). The enamel from teeth found along the river Nile has on average the lowest Ba and Sr concentrations ( $58 \mu\text{g g}^{-1}$  and  $271 \mu\text{g g}^{-1}$ , respectively), but specimens from Lake Albert ( $633 \mu\text{g g}^{-1}$  Ba) and Lake Kikorongo ( $2860 \mu\text{g g}^{-1}$  Sr) contain 10 times as much Ba and Sr (Fig. 2; Table 1). However, the enrichment of Ba and Sr does not necessarily run in parallel. For example, the tooth from Lake Kikorongo has the highest Sr concentration but Ba is the lowest among the fossil samples (Fig. 2b, d). Overall the correlation of Sr and Ba concentrations in the teeth is very poor ( $R^2 = 0.055$  in enamel). Even among specimens from single settings, such as Lake Albert, Lake Malawi or the Nile River, the variation amounts to 50 % to 90 % for Ba, and 30 % to 45 % for Sr (Table 1).

In a single specimen the standard deviation follows a similar pattern in that Ba in enamel varies by 60 % to 11 % whereas Sr only varies from 35 to 5 % (Table 1). Thus, this variation is significantly smaller than that observed on a regional scale and therefore diagenetic overprint should not be the major cause for the large differences observed between sample locations. The variation in single specimens reflects the systematic increase of Ba and Sr concentrations from the outside enamel rim towards the EDJ (Fig. 2). Similar element distributions in enamel have been observed for  $\text{Na}_2\text{O}$  and  $\text{MgO}$ , whereas Cl displays the opposite trend and CaO is constant along such a profile (Brügmann et al., 2012). In modern specimens the enrichment towards the EDJ is highest for Ba ( $1.93 \pm 0.41$ ; enrichment is defined as the concentration ratio of the average of the outer 30 % to the inner 30 % of the enamel width), whereas that of Sr is about  $1.39 \pm 0.13$  and similar to that of  $\text{MgO}$  and  $\text{Na}_2\text{O}$ . The similar distribution for Sr,  $\text{Na}_2\text{O}$  and  $\text{MgO}$  is confirmed by Sr/MgO and Sr/ $\text{Na}_2\text{O}$  ratios close to unity ( $\pm 10\%$ ), whereas ratios involving Ba are higher ( $1.3$  and  $1.4 \pm 20\%$ , respectively). In fossil specimens the enrichment factors tend to be smaller (Ba:  $1.42 \pm 0.61$ , Sr:  $1.22 \pm 0.24$ ) but display a larger variation. These lower ratios are due to Sr and Ba enrichment of many outer enamel rims and may indicate secondary addition of Sr and Ba during diagenesis.

In modern specimens the concentration of Sr drops at the EDJ, whereas fossil samples display the opposite trend (Fig. 2a, b). Barium distribution in modern specimens

is continuous across the EDJ in that the enrichment trend observed in the enamel extends into the dentin (Fig. 2c). This pattern is not preserved in fossil samples; indeed, enrichment and depletion of Ba occurs across the EDJ (Fig. 2d). No systematic distribution patterns are observed in cement and across the enamel-cementum junction. There are no systematic variations in dentin and cement that could be related to the formation of these tissues or to environmental influences. Therefore, we will focus the discussion on the element distribution in enamel, in single specimen and among specimens.

## 4 Discussion

In order to evaluate the sensitivity of trace elements with regard to environmental change, it is necessary to decode the changes induced by apatite deposition during tooth development from those imposed externally by changing diet composition at different geographical and geochronological scales. This has been done in the current study which includes specimens collected over a large area in eastern Africa and from different time slices going back to about 6.5 Ma.

Although overall Sr and Ba have similar COV values of about 1, in individual specimens COV is on average only 0.25 and 0.4, respectively, and Ba concentrations are more variable than those of Sr. Overall, the concentrations of both elements are highly variable if compared with those of MgO and Na<sub>2</sub>O (COV(MgO) = 0.42; COV(Na<sub>2</sub>O) = 0.25). Comparison at the individual scale again reveals that the concentration variations are lower and rather similar among these elements (average COV = 0.2; Brüggmann et al., 2012). The higher MgO variation is explained by its high sensitivity to environmental changes, whereas Na<sub>2</sub>O, like CaO, is very well controlled by the physiology of the Hippopotamid that does not accommodate diet provoked variations. Accordingly, the overall high variability of Sr and Ba concentrations may indicate an even higher sensitivity towards environmental change than MgO. The variations

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observed in individual specimens are controlled by the mechanisms of tooth formation and diagenetic remobilization.

#### 4.1 Concentration variations in single specimens: recognizing alteration and implications for amelogenesis

##### 4.1.1 Recognizing secondary redistribution of Ba and Sr

Diagenetic overprint has been detected in many of the studied specimens (Brüggmann et al., 2012). Fluorine is always added during diagenesis obscuring the primary distribution. The most obvious indication for alteration is the intense red-brownish staining, in particular of dentin, which identifies infiltration of the tooth with Fe-Mn-bearing solution and the precipitation of Fe- and Mn-oxides and hydroxides in the pore spaces of the bioapatite matrix (Brüggmann et al., 2012; Kohn et al., 1999). However, major components, such as Ca, P, Mg or Na, indicate minimal remobilization in most specimens. The addition of F or Fe did not produce recognizable amounts of new Ca- or P-bearing minerals, but could cause a dilution of the main components in bioapatite. Even in this case, relative abundances such as Mg/Ca or Mg/Na represent excellent monitors of the primary distribution of these elements in enamel.

Along all profiles through modern enamel Ba and Sr concentrations increase towards the EDJ (Fig. 2a, c) which is similar to the trends observed for MgO and Na<sub>2</sub>O. In fossil enamel the profiles show similar distribution trends, however, in most specimen concentration of both elements increase near the outside rim of the tooth (0–300 µm). Some specimens show distinct Ba and Sr enrichments within 200 µm of the EDJ (Fig. 2b, d). Trace element enrichments, for example of REE and U, near the outside rim are common in fossil bioapatite from bones and teeth and are due to the secondary addition during taphonomic degradation (Brüggmann et al., 2008; Kohn, 2008; Tütken et al., 2008; Trueman et al., 2004). Barium and Sr are also known to become enriched in bone and tooth tissues when being exposed to post-mortem alteration (Koch et al., 1992; Hoppe et al., 2003; Lee-Thorp and Sponheimer, 2003). In order to evaluate

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the influence of alteration on Ba and Sr in the Hippopotamid teeth, we performed linear regression analysis for data along the enamel profiles perpendicular to the EDJ. Enamel from different tooth specimens or from different parts within single specimens has variable thicknesses (2–4 mm) and therefore enamel thickness ( $x$ ) is normalized to 1. Regression lines are calculated with data between  $x = 0.2$  and  $x = 0.9$  (up to 600  $\mu\text{m}$  away from the enamel rim and up to 200  $\mu\text{m}$  away from the EDJ) in order to avoid a potentially altered enamel fraction. Using the linear equations, we calculated the expected Ba and Sr concentrations near the enamel rim (at point 0.1) and compared these values with the averages of the measured concentrations within the range 0–0.2. Figure 3 shows this comparison for modern and fossil specimens found in different habitats. In modern enamel calculated and measured Sr concentrations agree very well plotting along the 1:1 line. Many fossil enamel specimens follow this trend in particular those where enamel is enclosed by cement or the profiles were measured within deep folds of the tooth crown, surrounded by dentin. In cases where enamel is at the surface of the tooth, directly exposed to the sedimentary environment, significant Sr enrichment ranging up to a factor of 2 has been detected (Fig. 3a). A few examples also suggest Sr depletion relative to the expected primary concentration.

The Ba distribution is rather complex even in modern enamel. Comparing measured and expected Ba concentrations near the rim, fossil and modern enamel can be enriched in Ba up to a factor of 3 (Figs. 2c, d, 3b). Several modern specimens show a concentration increase near the outside enamel rim and in addition in a few cases the trend of Ba enrichment towards the EDJ appears to be exponential rather than linear (Fig. 2). Therefore, the linear regression models tend to underestimate the true Ba concentration near the enamel rim (for example specimen Alb10-1/2AB from Lake Albert, Fig. 2b). This explains that even data from modern enamel plot above the 1:1 line in Fig. 3. In most specimens Ba and Sr distribution patterns are similar either showing no concentration increase (specimens Nile-1, -2, -3, Mal8.1-1CD) or a concurrent increase at the outer rim (specimens Nile-4, S276, Mal 8.1-1AB; Fig. 2a, c). Along apical and cervical profiles Ba and Sr variations are almost identical (specimen Nile 1, Nile-2,

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Alb10-1AB, Alb10-2AB), however, near the enamel rim different trends could occur (compare profiles Mal8.1-1AB and 1CD; Fig. 2a, c; Table S1). Because the modern specimen had not been in contact with sediments, diagenetic overprint cannot explain the Ba and to a smaller degree Sr enrichment near the rim. It is a primary feature developed during the live time of the Hippopotamid. Possibly, during or after eruption the molar enamel equilibrates with saliva and these elements diffuse through the pore spaces and become adsorbed at the surface of the bioapatite crystallites. Alternatively, this feature is the result of a diet change during the late stages of amelogenesis. Barium enrichment at the outer rim is also seen in fossil enamel, but because of the uncertainty about the origin of Ba enrichment in modern enamel, it is not possible to identify unambiguously secondary Ba additions.

Fossil dentin has always higher Sr and Ba concentrations than modern dentin (Table 2; Fig. 1a, b) which would imply secondary enrichment of dentin during diagenesis. The element distribution across the EDJ supports this conclusion. Whereas modern dentin has lower Sr concentrations than enamel, fossil material shows the opposite pattern. Similarly, Ba displays a continuous concentration trend across the EDJ in modern specimens (Fig. 2c). However, there is a well defined discontinuity in fossil teeth indicating either Ba loss or Ba addition in dentin relative to enamel during the fossilization process. If dentin is significantly enriched in Ba and Sr, then sometimes even the nearby enamel has unexpectedly high Ba or Sr concentrations (Fig. 2b, d). This would indicate a post-mortem chemical exchange across the EDJ.

#### 4.1.2 Implications for amelogenesis

Several reviews summarized the basic principles of the structure and the biochemistry of teeth and in particular of enamel in mammals (Robinson et al., 1995; Smith and Nanci, 1995; Boskey, 2007; Pasteris et al., 2008; Simmer et al., 2010). The tooth forms extracellularly, but in a confined space which is separated from the environment by epithelial cells. This epithelium controls the in- and outflow of the building stones and regulates the structure and composition of the mineral-protein composite (Smith

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and Nanci, 1995; Hubbard, 2000; Simmer et al., 2010). According to these studies, enamel development can be divided into two stages: the secretion and the maturation phase. During the first period the final shape and the size of the tooth is established. Ameloblasts deposit a matrix of proteins which confines the deposition of apatite crystallites (Smith, 1998; Margolis et al., 2006; Simmer et al., 2010). At the end of this phase enamel tissue consists mainly of organic and fluid components; the mineral proportion is small, possibly in the range of 14 wt% (Smith, 1998). Maturation starts after appositional growth is completed and it involves in essence the enlargement of the existing crystallites by replacing protein and fluid with bioapatite (Robinson et al., 1995). Enamel formation is finished at the time of tooth eruption, thus this tissue is metabolically inactive afterwards. Secretion and maturation phases involve different fluid compositions, which control the compositional evolution of enamel apatite (Aoba and Moreno, 1992; Smith, 1998; Hubbard, 2000). However, the mechanisms of how alkaline earth ions, particularly,  $Ba^{2+}$ , and  $Sr^{2+}$ , permeate the epithelium and leak into the crystallization cavity, actively transcellular or passively paracellular, are not well understood. Similarly, the concentrations of the alkaline earth elements in the enamel forming fluids are not known.

Brügmann et al. (2012) quantitatively described the evolution of the chemical composition of enamel during its formation. The model considered the two step evolution of enamel and applied a fractional crystallization model in order to explain the observed trends of  $MgO$ ,  $Na_2O$  and  $Cl$  in enamel. These authors suggested that at the end of appositional growth crystallites of the entire enamel tissue should be in equilibrium with the enamel fluid because there should be a fully interconnected fluid network due to the low mineral density in enamel at this time. Maturation starts at the EDJ (Simmer et al., 2010) and this is where the highest  $MgO$  and  $Na_2O$  were observed. Thus, the concentrations of these components near the EDJ can be used to determine the composition of the enamel fluid at the begin of maturation. The chemical evolution of the fluid during the maturation process has been described by applying the Rayleigh fractionation law. This model explains the systematic decrease of  $Na_2O$  and  $MgO$  in apatite

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from the EDJ towards the outside enamel rim by the continual depletion of the enamel fluid during apatite crystallization due to the compatible behavior of MgO and Na<sub>2</sub>O.

Ignoring the outer rims of the enamel profiles ( $x < 0.1$  and  $x > 0.9$ ), Ba and Sr display a systematic concentration increase towards the EDJ in all specimens (Fig. 2).

This is analogous to the distribution of MgO in enamel and indeed Ba, Sr, and MgO concentration of single specimens are well correlated (Fig. 4). These trends represent mixing lines between two end member compositions of enamel fluids present at the end of the secretion and at the end of the maturation stage during amelogenesis. This suggests that the element distribution is controlled by a single process in which with advancing maturation the enamel fluid becomes depleted in Ba and Sr as well as MgO. The hypothesis that apatite precipitation occurs in an isolated or semi-isolated chamber and crystallization follows a Rayleigh fractionation law can explain this distribution. The epithelial cells control the transport of Ba, Sr, and MgO into the crystallization compartment, but at the same time crystallizing apatite incorporates these elements into its lattice. Using the model applied by Brüggmann et al. (2012) the observed and calculated distribution of Ba and Sr in enamel is described in Fig. 4 and Table 2 and compared with the variation of MgO previously published by these authors. There is a very good agreement between model and observation if apatite-fluid partition coefficients ( $D_{Ap-Fi}$ ) of 1.25, 1.2 and 1.15 for Ba, MgO and Sr, respectively, are assumed (Table 2). For example, in cases where the enamel profile is completely preserved, the calculations imply that 99 to 95 % of crystallization is necessary in order to explain the element distribution (Table 2; Fig. 4). This agrees very well with the amount of mineral present in enamel after maturation.

Partition coefficients of  $>1$  imply that Na<sub>2</sub>O, MgO, Ba and Sr behave compatibly during apatite crystallization. Qualitatively, the relative partitioning behavior can be estimated using correlation diagrams of these elements. The regression line of an element pair with similar  $D_{Ap-Fi}$  will pass through the origin of the diagram and a constant element ratio is determined by the slope of the trend. In cases where element pairs have different partition coefficients element ratios are not constant and the regression

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trend crosses the axes of the element with lower  $D_{Ap-Fi}$ . This analysis suggests that partition coefficients increase in the order of  $Sr < MgO < Ba$ , which is consistent with the calculated sequence. There are only a few studies investigating the partition behavior between apatite and fluid at low temperatures. For example, the experiments of Balter and Lecuyer (2004) studied the inorganic precipitation of hydroxyapatite. They suggested average Nernst partition coefficients of 1.42 and 1.92 for Ba and Sr, respectively. These values overlap with results from in vivo experiments with fishes where the partitioning behavior of Ba and Sr between bone, enamel or scales and sea water has been investigated (Wells et al., 2000; Balter and Lécuyer, 2010). Thus, our estimated partition coefficients for bioapatite and enamel fluid are reasonable considering the principal uncertainties associated with low temperature experimental results and their application to natural, in particular biological processes and our simplified modeling approach. Enamel formation occurs in an open system, where in- and out-fluxes of the elements are controlled by the surrounding epithelium. These fluxes are not known, though, which rules out a detailed quantitative description. These fluxes may increase the absolute value of the partition coefficients if the elements are continuously added to the crystallization compartment during maturation. The relative sequence of partition coefficients, nonetheless, should be preserved.

## 4.2 Concentration variations on the regional and temporal scale: environmental implications

On the scale of an individual Hippopotamid tooth there is a very good correlation between MgO, Sr and Ba concentrations in enamel. This covariation among the alkaline earth elements is even reasonably well preserved when looking at the scale of a habitat. Thus, element ratios such as Sr/Ca and Ba/Ca have been used to categorize hierarchical structures in a specific food web and information about the trophic, climatic and geological background of a given environment can be obtained. However, on a regional scale this covariation is obliterated, because the availability of these elements strongly depends on the local climate and geology. Both characteristics can be observed in our

specimens: in terms of the alkaline earth element contents Hippopotamids represent a well defined group within the food chain, but there are differences among sedimentary environments, and even systematic changes with geologic time can be observed.

#### 4.2.1 Trophic level of Hippopotamus in different ecosystems

5 Feeding habits of mammals can be distinguished on the basis of Sr/Ca and Ba/Ca of bone and tooth tissues (Elias et al., 1982; Burton et al., 1999; Blum et al., 2000; Balter et al., 2002; Balter, 2004). There is an overall positive correlation between these ratios, but this becomes more distinct if only variations in single habitats are considered (Fig. 5a). Hippopotamids are grazers, however, the variation of Ba/Ca and Sr/Ca  
10 in enamel completely covers the herbivore array, including that of browsers, and even extends well into the fields defined by plants and carnivores (Fig. 5b). Even so, the variation of the element ratios in Hippopotamid enamel follows the trends observed in habitats in general (Fig. 5a). At higher trophic levels from discrete habitats the relationship between Ba/Ca and Sr/Ca can be quantitatively described so that given one ratio the other one can be predicted (Elias et al., 1982; Burton et al., 1999; Balter et al., 2002; Balter and Lécuyer, 2004). The slopes of the Ba/Ca and Sr/Ca variation in  
15 different ecosystems are fairly similar. This was recognized by Balter (2004), who summarized the data from several ecosystems and suggested that the slope represents an allometric constant of the biopurification process in mammalian food chains. Ba/Ca and Sr/Ca in enamel from single hippopotamus specimens follow this trend very well (Fig. 5a). As discussed in the previous paragraph this trend is controlled by the partitioning behavior of Ba and Sr between apatite and enamel fluid. It appears that overall the slopes defined in different ecosystems are dominated by the Ba/Sr ratio in the apatite tissue. If this suggestion is valid, it is apparent why Ba/Ca and Sr/Ca in bone and  
20 tooth tissues provide the same information regarding the affiliation of mammals to specific trophic levels. Both materials consist of bioapatite, which is deposited from fluids with similar major element compositions. Therefore, partition coefficients for trace elements such as Ba and Sr should be alike during the formation of these tissues. Even  
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so, Ba and Sr are special in that both elements are not essential nutrients of mammals and it may be that extracellular Ba and Sr are not under strict homeostatic control. In addition, Ba and Sr are concentrated to 93 % and 99 %, respectively, in the skeletal parts of animals (Schroeder et al., 1972; Nielsen, 2004). Thus, the crystallization of bioapatite is the key process controlling the distribution of these elements in the body and this makes Ba/Ca and Sr/Ca in teeth and bones of mammals to precious monitors of the ingested diet.

However, one should expect that elements having different apatite-fluid partition coefficients define different slopes. Indeed, the variation of Pb/Ca and Ba/Ca follows a different path with a lower slope (Balter, 2004). This is plausible, because of its larger ionic radius, Pb should have a lower apatite-fluid partition coefficient than Sr. For toxic elements, such as Pb, or essential elements (Cu, Zn) the discrimination relative to Ca may be subjected to additional metabolic controls and to significant incorporation in different organs, which also influence the element's pathway from ingestion to incorporation into bioapatite. Therefore, different taxa may induce vital effects which significantly overprint the diet signal, and this would explain why Pb/Ca is a less diagnostic tool for recognizing diet variations (Hirao and Patterson, 1974; Balter, 2004).

Although the slope in the Sr/Ca versus Ba/Ca in bone and teeth are very similar, the parallel trends in different habitats indicate different Ba/Sr in the bioapatite (Fig. 5). This observation requires a variable composition of the enamel fluid regarding Ba and Sr concentrations as well as their relative abundances.

#### 4.2.2 Spatial variation of alkaline earth elements: tracers of ecosystems

In the Hippopotamus specimens collected in different geographic regions Sr and Ba concentrations vary by up to 2 orders of magnitude (Figs. 4, 6). Among the Nile specimens enamel from the Blue Nile has the highest Sr concentrations ( $\sim 447 \mu\text{g g}^{-1}$ ) whereas the MgO-richer enamel from the White Nile has among the lowest Sr concentration of all specimens ( $\sim 172 \mu\text{g g}^{-1}$ ; Fig. 6b; Table 1). Thus, Sr and MgO do not correlate very well in the Nile river habitats. Enamel from Lake Kikorongo has extraordinary

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of the specimens from the Upper Nile supports this suggestion. Their enamel has intermediate Sr isotopic compositions ( $^{87}\text{Sr}/^{86}\text{Sr}$ :  $0.7120 \pm 0.0001$ ) and Ba and Sr concentrations, which is to be expected taking into account that the upper Nile specimens were found downstream of the confluence of Blue and White Nile (Fig. 6b, d). This bimodal distribution of the Sr isotope composition can be even observed in the sediment record all along the River Nile into its delta and the Mediterranean margin (Revel et al., 2010; Padoan et al., 2011).

The distribution of MgO, Ba and Sr in enamel from the different sections of the Nile River is very similar and Ba and Sr correlate very well (Fig. 6d, f, h). For example, concentrations of these elements are highest in the enamel from the Blue Nile and lowest in that from the White Nile. The correlation of Ba with Sr in the enamel from the Nile River evokes that Ba concentrations also trace the water provenance. The low Ba concentration in enamel from the White Nile, however, is unexpected, because Archean upper crustal rocks have typically higher Ba contents than mafic volcanic rocks (Rudnick et al., 2003; Kieffer et al., 2004). Typically, the upper crust has Ba/Sr of about 2 whereas basaltic rocks have ratios  $< 1$ . Enamel from the Nile River has low Ba/Sr of less than 0.3 (Table 1). This suggests that Ba in the sedimentary environments along the River Nile is either dominantly of volcanic origin or its availability is controlled by processes overwhelming the input of the source rock. Indeed, there is no systematic relationship between Sr and Ba in the lake specimens and even Ba/Sr ratios are highly variable ranging from about 0.2 in modern enamel from Lake Malawi to 2 in fossil samples from Lake Albert (Table 1; Figs. 6g, 7). The most plausible explanation is that Ba is less mobile than Sr during erosion and weathering of upper continental crust and uptake by plants. Due to their similar chemical features Ba and Sr are often used to monitor the source availability of the essential macronutrient Ca in soils. In forest soils Sr and Ca behave similarly during nutritional uptake by higher plants, but Ba appears to be preferentially adsorbed on the exchange complex suggesting a lower availability relative to Sr and Ca (Bullen and Bailey, 2005; Drouet and Herbauts, 2008). A low Ba/Sr ( $< 1$ ) is a typical feature in watersheds of several modern rivers including such draining

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granitic source rocks (Dalai et al., 2002), and even East-African lakes (Tanganyaika, Malawi) have low Ba/Sr (Sako et al., 2007; Branchu et al., 2010). The reduced mobility of Ba relative to Sr in granite-gneiss watersheds is probably caused by preferred adsorption of Ba on clay minerals and oxy-hydroxides or barite precipitation after Ba and Sr became released during the weathering of plagioclase, K-feldspar and mica (Hanor, 2000). In particular in alkaline and saline environments Ba mobility is reduced compared to low pH surface and groundwater reservoirs (Hanor, 2000; Witherow and Lyons, 2011).

The relationship between MgO contents and provenance appears to be complex. Although enamel from Lake Kikorongo has relatively high MgO contents, which would be consistent with a basaltic source rock, this is not the case for enamel from the Blue Nile, which has even lower MgO contents than the enamel from the White Nile (Fig. 6a, b). Thus, it appears that the MgO content in enamel is not exclusively controlled by the input from the source rock, but is also modified by the local hydrological conditions. For example, MgO/Na<sub>2</sub>O in enamel from modern Lake Albert is higher than that of modern Lake Malawi (Fig. 6e). This could mirror a difference in the salinity of the lakes because the salinity of Lake Albert is five times higher than of Lake Malawi (Talling and Talling, 1965). The higher MgO/Na<sub>2</sub>O in enamel of modern Lake Albert compared to that in fossil Lake Albert probably also reflects the evolution of the lake water chemistry. This is supported by the evaporation trend in Lake Albert since at least about 6.5 Ma ago as indicated by increasing  $\delta^{18}\text{O}$  of Hippopotamid enamel during that time (Brachert et al., 2010). The MgO content in enamel from the White Nile, which undergoes substantial evaporation in the north-central Sudan (Salama and Selley, 1997), is higher than in enamel from the Upper and Blue Nile. Thus, Brüggmann et al. (2012) suggested that in the saline habitat MgO availability to plants is higher than in fresh water habitats, which results in high MgO concentrations in enamel from such environments.

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### 4.2.3 Temporal variation of alkaline earth elements: tracers of environmental change

Another conspicuous feature is the highly variable Ba concentration in enamel from Lake Albert. Whereas Sr concentrations in these specimens vary on average by about a factor of less than 3, Ba concentration vary by one order of magnitude causing a large variation of the Ba/Sr (Table 1; Figs. 6a, c, g, 7a). There is a systematic decrease of Ba concentration as well as Ba/Ca (not shown) or Ba/Sr with geological age: Miocene enamel has higher Ba/Sr or Ba/Ca than Pliocene, Pleistocene as well as Holocene and modern enamel, respectively (Fig. 7a). In contrast, Sr concentrations or Sr/Ca are rather constant during this time span (Fig. 7b).

This decrease of Ba/Sr with time could be caused by post-mortem alteration processes or by changing diet compositions reflecting vital effects or hydrological conditions. It may seem likely that the Ba increase with geological time is due to secondary addition during diagenetic alteration. This is a time dependant, diffusive process, where ions are moving along a concentration gradient in fluid saturated pores of the tooth and become adsorbed on the surface of apatite crystals (Millard and Hedges, 1996; Kohn, 2008). No other major or trace element, however, shows a relationship with geological age. It is also not seen for those elements which are most severely affected by post-mortem alteration, such as FeO or F (Brügmann et al., 2012). In addition, as discussed in Sects. 4.1.1 and 4.1.2, modern and fossil specimens show the same Ba distribution, which even correlates well with Mg, Na or Sr within individual enamel samples. This likely represents a primary feature, which can be quantitatively described by crystallization of bioapatite during amelogenesis. Secondary overprint, therefore, is an unlikely process explaining the temporal Ba variation.

An alternative explanation is that the composition of the Hippopotamid diet has changed, either because of a change of dietary preferences or a change of its chemical composition. Indeed, our set of specimens includes different taxa; the modern teeth belong to the large-size species *Hippopotamus amphibious*, but the fossil teeth include

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both large and small size animals, which may belong to different taxa. Hippopotamids, however, are regarded as opportunistic feeders. Even if these taxa had different dietary preferences, however, an influence of vital effects on the Ba/Ca or Ba/Sr with time is unlikely, because we do not have a systematic chronological distribution of the taxa populations.

Hence, the variation of these ratios with geological age indicates systematic change of diet, including drinking water, composition. This can be attributed to a decrease of the availability of Ba relative to Sr for plants and ultimately to Hippopotamids, i.e. it is controlled by environmental change. The western branch of the East African Rift System experienced a regional or mesoscale climate change during the Miocene-Pleistocene, which is supported by sedimentary and paleobotanical observations and stable isotope compositions of Hippopotamid enamel. From 7.5 to 2.5 Ma, a large paleolake (Palaeolake Obweruka) covered the present regions of Lake Albert, Lake Edward, and Lake George (Pickford et al., 1993; Van Damme and Pickford, 2003). The average  $\delta^{18}\text{O}$  values of the surface water of the paleolake in the Albertine Rift, as calculated from the  $\delta^{18}\text{O}$  values of Hippopotamid enamel, systemically increase from  $-8\text{‰}$  to  $+2\text{‰}$  at 6.5 to 2 Ma (Brachert et al., 2010). This variation implies increasing evaporation of the water reservoir in the Albertine Rift and probably aridification with time. Ferruginized plant remains in sediments of the palaeolake indicate the dominance of  $\text{C}_3$  vegetation typical for tropical forests between 7 and 4 Ma (Dechamps and Ergo, 1994; Pailler et al., 2000).  $\delta^{13}\text{C}$  values of our Hippopotamid enamel vary between  $-12$  and  $-9\text{‰}$  during this period also indicating a  $\text{C}_3$  diet (Brachert et al., 2010). During such tropical-humid climate conditions, intensive erosion and weathering of the upper crustal Lake Albert watershed may have effectively transported Sr and Ba towards Paleolake Obweruka minimizing the fractionation of these elements. At around 3 to 2 Ma, Paleolake Obweruka disintegrated into a lake configuration similar to that of today (Pickford et al., 1993). At the same time, arid steppe and open savannah type vegetation became dominant (Dechamps and Ergo, 1994; Pailler et al., 2000). This is also supported by  $\delta^{13}\text{C}$  data in Hippopotamid enamel indicating a propagation of  $\text{C}_4$  grasses during that

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time (Brachert et al., 2010). Under arid conditions chemical weathering is less intense, which could cause a decreasing Ba and Sr flux towards Lake Albert. Rather constant Sr/Ca, however, do not show this effect (Fig. 7b). Thus, the low Ba/Sr suggests lower mobility of Ba relative to Sr under these climate conditions. This may be caused by the preferred adsorption of Ba on clay minerals and oxy-hydroxides. In addition, the formation of alkaline, even saline lake and soil waters is a typical feature of arid regions. There is no indication for a saline Lake Albert during the Pliocene-Pleistocene, however, aridification could increase the alkalinity of weathering solutions, which would inhibit the mobility of Ba due to precipitation of barite.

Stable isotope data of mammalian fossils and palaeosol carbonates from various areas of the East African Rift System have been interpreted to indicate an enduring regional aridification during the Neogene (Trauth et al., 2007). However, as Brachert et al. (2010) noticed the studied archives are preferentially in depositional environments of the graben floor and thus may dominantly monitor the mesoclimate of the rift valleys. Thus, the alternative interpretation, which is in agreement with systematics in element concentrations and ratios (e.g. Ba/Sr) as well as with stable and radiogenic isotope proxies, is that the temporal variation rather reflects the response to a tectonic reorganization of the Albertine Rift system (graben subsidence/shoulder uplift) during the Neogene (Brachert et al., 2010).

## 5 Synthesis and perspective

The alkaline earth elements Ca, Mg, Sr and Ba are prominent inorganic components of bone and teeth. They transport chemical information from the external environment into these tissues, which contain, therefore, records of historical and ancient environmental change. In higher organisms Ca and Mg are essential elements and their concentrations are fixed in intra- and extracellular fluids of higher animals (~1 mM). Barium and Sr are not known to be essential, although they can interfere with biochemical processes, for example bone formation (Schroeder et al., 1972; Nielsen, 2004). Bioapatite is in

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mammals a large buffer for alkaline earth elements, because for example in humans 99% of Ca and Sr, 93% of Ba, and 50% of Mg are stored in this mineral (Schroeder et al., 1972; Wester, 1987; Kunsch and Kunsch, 2006).

The archive investigated here is molar Hippopotamid tissue from lacustrine and fluvial environments (<6.5 Ma to recent) of Eastern Africa. The variation of the concentrations of Ca ( $1\sigma \sim 1\%$ ), Mg ( $1\sigma \sim 38\%$ ), as well as Ba and Sr ( $1\sigma \sim 85\%$  and  $91\%$ , respectively) in enamel is controlled in vivo, by the function of these elements in the animal, and in vitro, by the distribution of these elements in the habitats which in turn is determined by biochemical and inorganic processes. The very low variation of Ca in enamel is expected because of its fixed concentration in extracellular fluids as well the tight stoichiometric control during apatite deposition. Such an overwhelming physiological control, however, precludes the use of Ca concentration as an environmental proxy. Although Mg is also an important essential element animals living in fresh water ecosystems have to pump this element into their cells – in contrast to cells of marine organisms, which have to reject Mg – in order to maintain homeostatic conditions. This in turn means that the Mg budget in terrestrial organisms in addition could underlie an extrinsic control, which is most probably reflected in the higher concentration variation compared to that of Ca. This weaker physiological control allows the identification of environmental signals in the archive and, for example, saline and freshwater habitats or provenance signals can be distinguished using ratios such  $MgO/Na_2O$ .

In contrast, the large variation of Ba and Sr concentrations in tooth tissues reflects their non-essential nature in mammals. The variations are caused by secondary post-mortem effects, crystallization processes during amelogenesis, and compositional differences of the ingested nutrition. Secondary alteration severely modified Ba and Sr distributions in dentin and cement and no information regarding amelogenesis and environmental change has been documented. The outside rim of enamel (<600  $\mu\text{m}$ ) and the transition zone towards the EDJ (<100  $\mu\text{m}$  wide) can be enriched in Ba and Sr up to a factor of three. Although this secondary addition has no significant influence

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on the overall population statistics, it is relevant for the interpretation of the element distribution in single specimens.

On the scale of a hippopotamus tooth there are linear correlations between MgO, Sr and Ba concentrations in enamel. These trends suggest that one common process controls the behavior of the alkaline earth elements during amelogenesis. This process can be quantitatively described by a Rayleigh crystallization model which presumes that after appositional growth the element distributions are controlled by apatite crystallization during the maturation stage of amelogenesis. Model consistent apatite-fluid Nernst partition coefficients for Sr, Mg and Ba would be 1.15, 1.2, and 1.25, respectively, and they are consistent with experimental data. Enamel formation, however, occurs in a semi-permeable open system, where element transport is physiologically controlled. Although these fluxes are not known and the absolute value of the partition coefficients may vary, the relative sequence of partition coefficients should be preserved.

On a regional scale, however, the chemical changes in enamel caused by the variability of natural environments overwhelm Ba and Sr variations brought about by secondary effects and enamel formation by at least one order of magnitude. They can be related to variable diet compositions in different habitats which in turn reflect different water provenance and hydrochemical conditions. The large variation of Ba/Ca (2.4 log units, Sr/Ca (1.5 log units) and Ba/Sr (1.3 log units) implies that the plant signal entering the food chain is highly heterogeneous with regard to these elements. Enamel of each Hippopotamid, however, shows a specific, well defined signal which reflects the live style of the animal being water-dependent and restricted to small territories. Thus, it is possible to calculate the Ba/Sr of the food ingested by Hippopotamids by adjusting the observed ratio with that of the partition coefficients of Ba and Sr. This prediction is reliable for elements for which body concentrations are buffered by bones and teeth. In addition, elements should not have physiological functions, so that in vivo effects are very small and dominated by the behavior during apatite crystallization. For ratios involving elements, such as Zn or Cu, which are essential micronutrients and become

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incorporated into different organs, the slope has to be corrected for the vital effect, in order to determine the element ratios of the ingested food.

Overall, Ba/Sr varies by more than one order of magnitude. This fractionation of Ba and Sr in enamel most likely reflects differences in provenance and differences of the hydrochemical availability of these elements during weathering. The catchment areas of lakes and rivers impose a dominant signature onto the Hippopotamid habitats. For example, within fluvial and lacustrine environments, enamel from Hippopotamids which were dependent on water masses draining basaltic source rocks have higher Sr concentrations and lower Ba/Sr, than enamel from animals living in water reservoirs draining Archean crustal rocks. Thus, these proxies trace a provenance signal, because basaltic rocks have higher Sr and lower Ba/Sr ratios than upper crustal rocks. This provenance influence is supported by the Sr isotopic composition of enamel.

The temporal decrease of Ba/Sr in enamel from the Lake Albert Rift may indicate a hydrochemical adjustment in the watershed of the Albertine Rift due to a change from humid to arid climate during the Neogene. The Miocene record of the rift is characterized by a tropical climate. Intense weathering in the catchment area of the lake may have mobilized Ba and Sr to similar degrees. Thus, Ba/Sr values of 1.5 to 2, which are typical for Archean upper crust, are preserved in the sediment trap of Lake Albert. From ca. 6.5 to 2 Ma the region underwent pronounced aridification. During this time, Sr/Ca or Mg/Ca in enamel remained constant, indicating no significant fractionation of these elements at the watershed of the rift lake. Ba/Sr in enamel, though, decreased to values as low as 0.5 suggesting a restricted mobility of Ba. This decrease is interpreted to be the effect of aridification aggravating the preferential adsorption of Ba to clay and Fe-oxide-hydroxide minerals or causing the formation of more alkaline, possibly sulfate-bearing weathering and soil solutions. In this case, river and ground water fluxes from the watershed to Lake Albert would transport a low Ba/Sr signal to the Hippopotamid habitat.

Barium and Sr concentrations in enamel turned out to be proxies which fingerprint specific sedimentary environments and can trace changes of provenance, climate and

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hydrochemistry. These elements are also important constituents of biological and inorganic carbonates and provide proxies tracing environmental information, such as salinity or temperature changes. The partition behavior of Ba and Sr towards carbonates and apatite is very similar which should facilitate the cross calibration of these archives. This would integrate a highly persuasive amount of chemical information on a variety of diverse sedimentary environments. Eventually, a comprehensive fundament builds up which permits the prediction of the influence of climate change on regional environments – one of today's foremost scientific problems.

**Supplementary material related to this article is available online at:**

**<http://www.biogeosciences-discuss.net/9/3645/2012/bgd-9-3645-2012-supplement.pdf>**

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**Table 1.** Average concentrations of alkaline earth elements in modern and fossil hippopotamid enamel, dentin and cement.

Enamel Averages	Age (Ma)	<i>N</i>	Ba $\mu\text{g g}^{-1}$	1 $\sigma$	Sr $\mu\text{g g}^{-1}$	1 $\sigma$	CaO wt%	1 $\sigma$	MgO wt%	1 $\sigma$	Ba/Sr	1 $\sigma$	Sr/Ca *1000	1 $\sigma$	Ba/Ca*1000	1 $\sigma$
All specimens		1408	388	374	767	778	54.52	0.76	0.34	0.14	0.61	0.54	1.97	1.99	1.00	0.96
All fossil		811	586	382	1023	935	54.57	0.85	0.27	0.12	0.85	0.60	2.66	2.39	1.53	0.98
All modern		490	111	65	437	177	54.47	0.66	0.40	0.09	0.25	0.12	1.12	0.46	0.29	0.17
All Nile		102	58	51	271	119	54.36	0.34	0.35	0.09	0.18	0.09	0.70	0.30	0.15	0.13
Upper Nile-1		24	16	6	166	27	54.28	0.16	0.27	0.07	0.095	0.02	0.43	0.07	0.04	0.01
Upper Nile-2		25	70	14	318	25	54.17	0.22	0.32	0.05	0.220	0.03	0.82	0.07	0.18	0.04
White Nile-3		29	19	8	172	24	54.20	0.26	0.47	0.04	0.11	0.03	0.44	0.06	0.05	0.02
Blue Nile-4		24	132	39	447	36	54.83	0.22	0.32	0.03	0.29	0.06	1.14	0.09	0.34	0.10
Zoo spec. S276		168	111	28	393	46	54.94	0.46	0.38	0.08	0.28	0.06	1.00	0.12	0.28	0.07
Lake Malawi modern		149	103	58	592	213	54.40	0.56	0.44	0.08	0.16	0.05	1.52	0.56	0.26	0.15
Lake Malawi fossil		77	576	285	913	137	54.94	0.38	0.28	0.04	0.62	0.28	2.32	0.35	1.47	0.73
Lake Albert modern		71	206	54	457	46	53.71	0.77	0.44	0.08	0.45	0.08	1.19	0.12	0.54	0.14
All Lake Albert fossil		599	633	405	624	206	54.40	0.89	0.22	0.06	1.04	0.57	1.62	0.54	1.67	0.14
5106	1.30	22	389	275	672	64	55.29	0.42	0.16	0.05	0.56	0.36	1.70	0.16	0.99	0.70
GPS421	1.80	60	216	112	608	217	53.53	0.78	0.23	0.06	0.36	0.09	1.59	0.57	0.56	0.29
GPS165	1.80	46	502	242	687	78	55.35	0.38	0.26	0.04	0.72	0.31	1.74	0.20	1.27	0.61
5306	2.30	83	248	42	505	72	54.04	0.76	0.32	0.06	0.49	0.06	1.29	0.14	0.61	0.07
GPS405	3.45	48	601	122	791	133	53.97	0.85	0.23	0.04	0.76	0.06	2.05	0.34	1.56	0.31
GPS387	3.45	30	688	103	551	64	54.20	0.33	0.22	0.04	1.26	0.18	1.42	0.17	1.77	0.26
1706	4.00	28	1087	334	874	90	54.37	0.98	0.21	0.04	1.23	0.28	2.25	0.22	2.79	0.84
GPS396	4.00	55	643	171	836	180	53.65	0.70	0.16	0.03	0.76	0.06	2.18	0.48	1.68	0.45
2106	5.50	30	878	290	453	85	54.87	0.27	0.20	0.03	1.90	0.35	1.15	0.22	2.24	0.74
5006	5.50	32	1803	205	918	182	54.85	0.28	0.20	0.04	2.03	0.16	2.34	0.47	4.60	0.52
1906	6.30	42	559	116	328	51	55.43	0.46	0.19	0.04	1.71	0.29	0.83	0.13	1.41	0.29
2806	6.30	33	767	95	636	34	54.90	0.30	0.19	0.04	1.21	0.14	1.62	0.09	1.96	0.2
3206	6.50	26	793	217	474	101	54.44	0.43	0.23	0.04	1.66	0.16	1.22	0.26	2.04	0.56
2706	6.50	15	850	347	529	38	55.51	0.24	0.23	0.03	1.61	0.68	1.33	0.10	2.14	0.88
0706	6.50	49	668	173	530	177	53.88	0.49	0.22	0.04	1.29	0.28	1.38	0.46	1.73	0.45
Lake Kikorongo	0.01	135	384	231	2860	987	55.08	0.53	0.47	0.14	0.13	0.05	7.26	2.48	0.98	0.58
<b>Dentin Average</b>		197	1236	983	1671	1582	54.45	4.19	1.15	1.52	0.88	0.81	4.18	3.75	3.16	2.52
<b>Cement Average</b>		31	304	164	423	231	52.82	2.60	1.05	0.42	0.75	0.25	1.14	0.70	0.81	0.45

*N*: number of analyses; Data of CaO and MgO from Brüggmann et al. (2012).

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Table 2. Rayleigh crystallization model for enamel formation.

$F^*$	Na <sub>2</sub> O wt%	MgO wt%	Ba $\mu\text{g g}^{-1}$	Sr $\mu\text{g g}^{-1}$	Na <sub>2</sub> O wt%	MgO wt%	Ba $\mu\text{g g}^{-1}$	Sr $\mu\text{g g}^{-1}$	Na <sub>2</sub> O wt%	MgO wt%	Ba $\mu\text{g g}^{-1}$	Sr $\mu\text{g g}^{-1}$	Na <sub>2</sub> O wt%	MgO wt%	Ba $\mu\text{g g}^{-1}$	Sr $\mu\text{g g}^{-1}$	
	Lake Malawi (modern)				Lake Albert (Fossil)				Lake Kikorongo (fossil)				Upper Nile-1 (modern)				
Calculation of the composition of the secretion fluid																	
$D_{\text{Ap/Fl}}^{**}$	1.2	1.2	1.25	1.15	1.2	1.2	1.25	1.15	1.2	1.2	1.25	1.15	1.2	1.2	1.25	1.15	
$C_{\text{Apatite}}^{***}$	1.5	0.5	85	550	1.4	0.3	799	950	1.5	0.56	500	3800	1.6	0.4	25	215	
$C_{\text{Fluid}}^{***}$	0.86	1.29	0.43	71	489	1.20	0.26	664	845	1.29	0.48	415	3380	1.37	0.34	21	191
Calculation of apatite composition during maturation																	
$C_{\text{Apatite}}^{***}$	0.9	1.51	0.50	86	554	1.41	0.30	808	957	1.51	0.57	506	3826	1.51	0.50	86	554
0.8	1.50	0.50	85	550	1.40	0.30	799	950	1.50	0.56	500	3800	1.50	0.50	85	550	
0.7	1.44	0.48	81	533	1.34	0.29	759	921	1.44	0.54	475	3684	1.44	0.48	81	533	
0.6	1.40	0.47	78	521	1.30	0.28	730	900	1.40	0.52	457	3600	1.40	0.47	78	521	
0.5	1.35	0.45	74	507	1.26	0.27	698	876	1.35	0.50	437	3503	1.35	0.45	74	507	
0.4	1.29	0.43	70	490	1.20	0.26	660	847	1.29	0.48	413	3388	1.29	0.43	70	490	
0.3	1.22	0.41	65	470	1.13	0.24	614	811	1.22	0.45	384	3245	1.22	0.41	65	470	
0.2	1.12	0.37	59	442	1.05	0.22	555	763	1.12	0.42	347	3053	1.12	0.37	59	442	
0.1	0.98	0.33	50	398	0.91	0.20	467	688	0.98	0.36	292	2752	0.98	0.33	50	398	
0.05	0.85	0.28	42	359	0.79	0.17	392	620	0.85	0.32	246	2480	0.85	0.28	42	359	
0.01	0.62	0.21	28	282	0.57	0.12	262	487	0.62	0.23	164	1948	0.62	0.21	28	282	

\*  $F$ : fraction of fluid remaining; \*\*  $D$ : partition coefficient Apatite/Fluid; \*\*\*  $C$ : concentration (wt %) of fluid or apatite.

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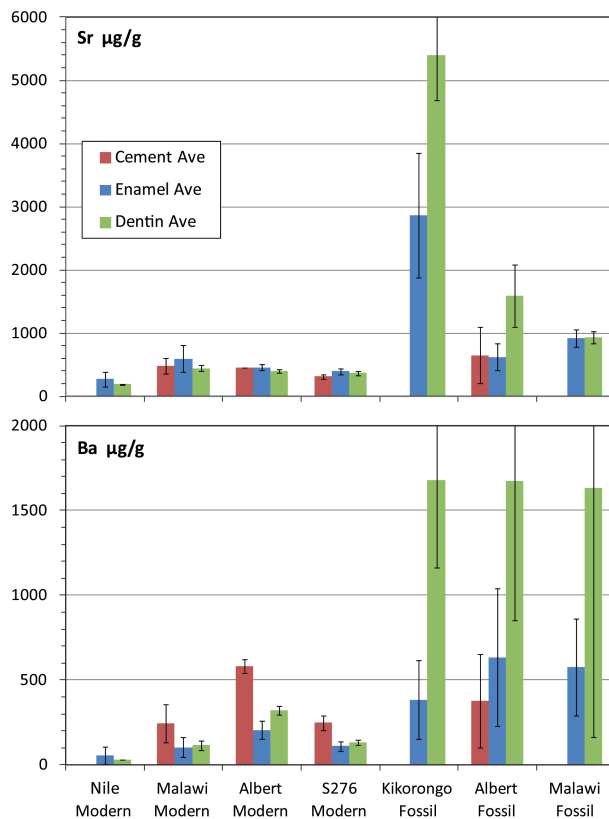
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**Fig. 1.** Average Ba and Sr concentrations in cement, enamel and dentin of modern and fossil Hippopotamid teeth. Bars represent the  $1\sigma$  error of the average.

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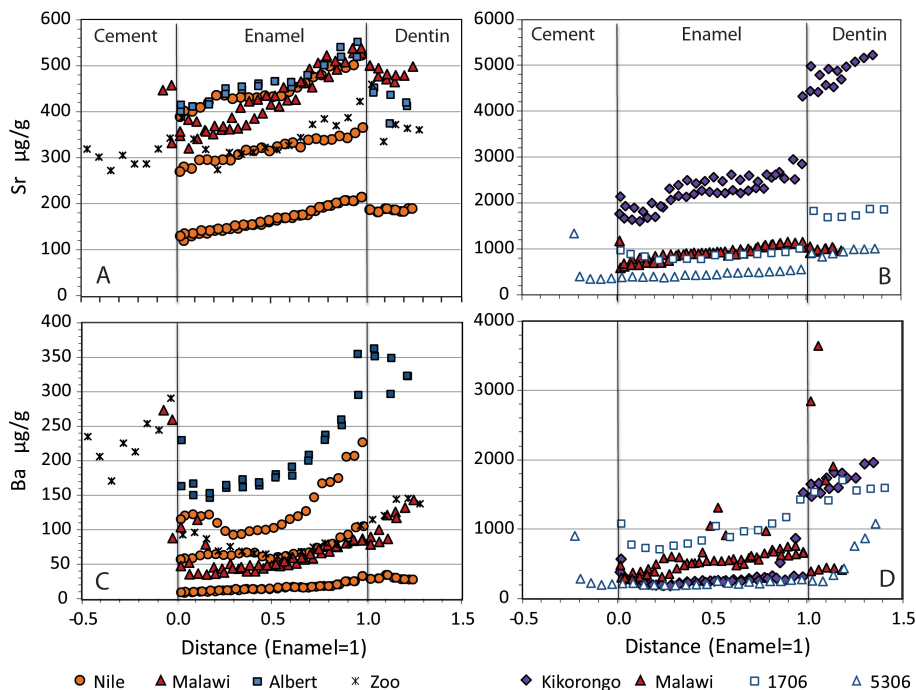
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**Fig. 2.** Ba and Sr variations along selected tooth profiles from the outside margin through cementum, enamel into dentin. The distance is normalized to the length of the enamel = 1. **(a–c)** Ba and Sr variation in modern enamel from molar teeth. **(b–d)** Ba and Sr variation in fossil enamel from molar teeth.

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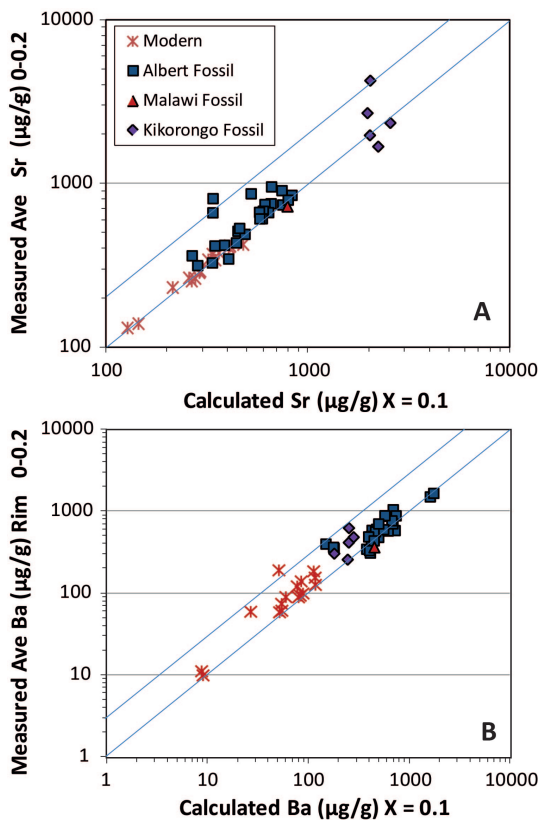
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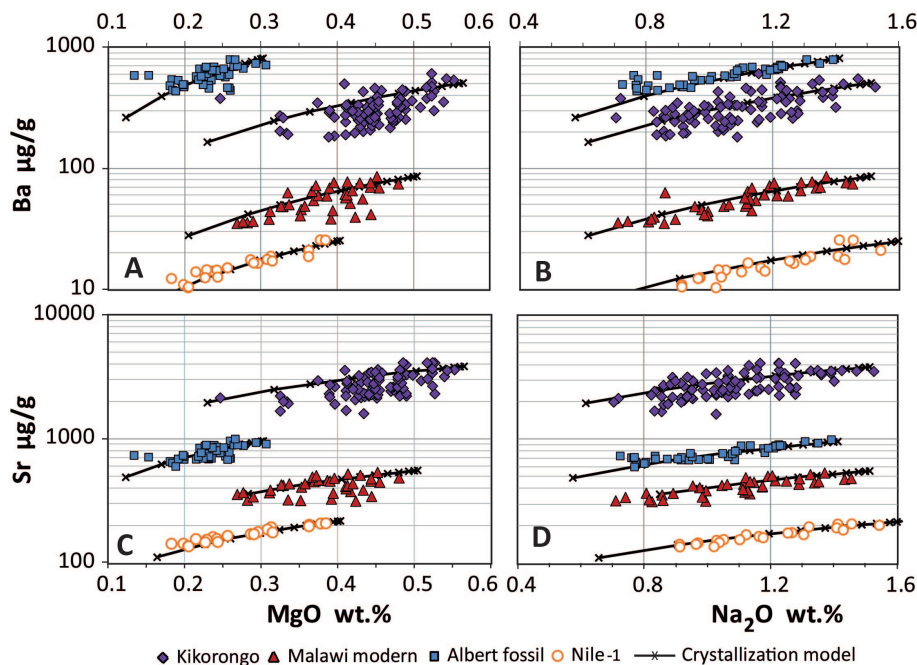




**Fig. 3.** Comparison of **(a)** Sr and **(b)** Ba concentration measured at the outside enamel rim of single modern and fossil tooth specimens with values expected there based on linear regression analyses. Regression line has been calculated from data along profiles from the outside rim towards the enamel-dentin junction. Values above or below the 1:1 line suggest secondary addition or removal, respectively, of Ba and Sr. For details see Sect. 4.1.1.

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**Fig. 4.** Variation of MgO, Na<sub>2</sub>O, Sr and Ba in modern and fossil enamel from Hippopotamid teeth. Note the large variation of Ba and Sr concentrations relative to MgO and Na<sub>2</sub>O. The coherent variation of all elements regardless of age and element concentrations implies that the concentrations are controlled by a common process. Black lines represent model calculation assuming fractional crystallization of apatite. For details see Sect. 4.1.2 and Table 2.

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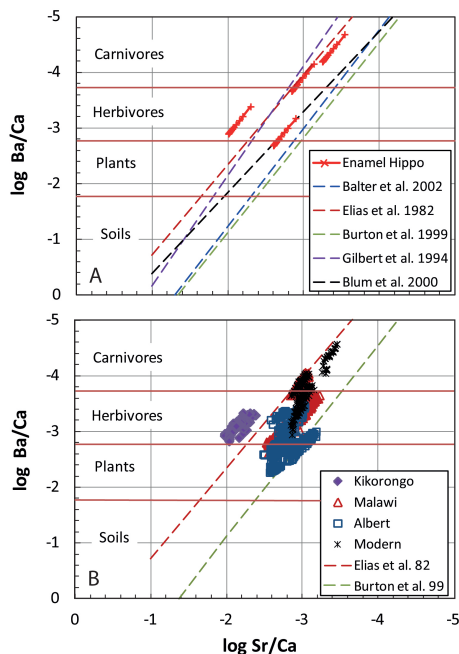
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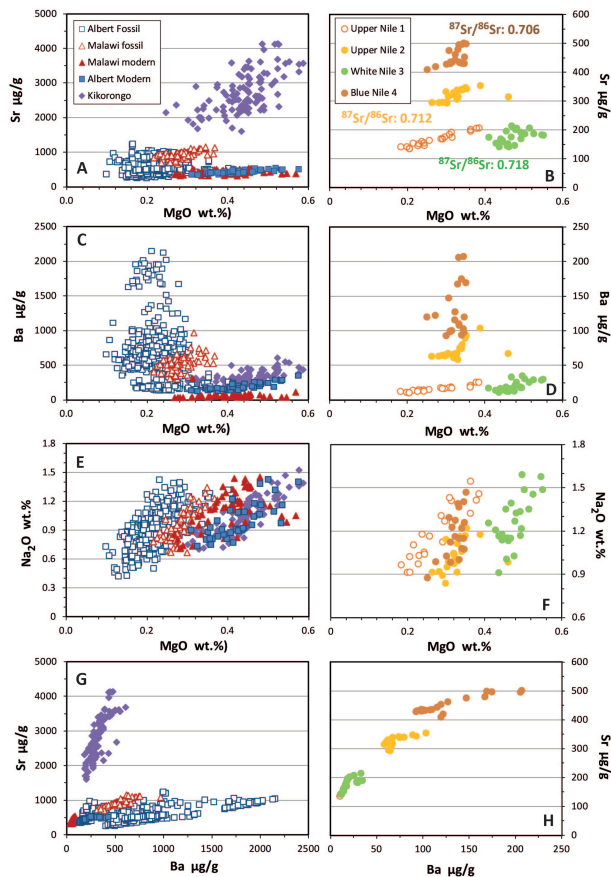
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**Fig. 5.** Trophic levels in different ecosystems as defined by the Sr/Ca and Ba/Ca variation in bones and teeth. The ranges of Ba/Ca defining the trophic levels are from (Balter et al., 2002). **(a)** Compilation of published Sr/Ca and Ba/Ca values representing different ecosystems. The dashed lines represent regression lines of data covering several trophic levels in single ecosystems or represent averages summarizing several ecosystems. Red lines with crosses show crystallization models of the variation of Sr/Ca and Ba/Ca in enamel from Hippopotamids of this study as shown in Fig. 4. Note that the slope of the variation of enamel is similar to that observed in ecosystems. Data sources are given in the legend. **(b)** Variation of Sr/Ca and Ba/Ca in enamel of Hippopotamids teeth analyzed in this study. Enamel displays a large range which extends from the field of herbivore well into the fields of carnivores and plants.

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**Fig. 6.** Variation of Ba, Sr, MgO and  $\text{Na}_2\text{O}$  in modern and fossil molar enamel from Hippopotamids. Data of MgO and  $\text{Na}_2\text{O}$  are from (Brügmann et al., 2012). (a, c, e, g) MgO-Sr, MgO-Ba MgO- $\text{Na}_2\text{O}$  and Ba-Sr variation in lacustrine enamel. (b, d, f, h) MgO-Sr, MgO-Ba MgO- $\text{Na}_2\text{O}$  and Ba-Sr variation in enamel from the Nile River.

