



# 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.** This study demonstrates that alkaline earth elements in enamel of hippopotamids, in particular Ba and Sr, are tracers for water provenance and hydrochemistry in terrestrial settings. The studied specimens are permanent premolar and molar teeth found in modern and fossil lacustrine sediments 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 two orders of magnitude for Ba (120–9336  $\mu\text{g g}^{-1}$ ) as well as for Sr (9–2150  $\mu\text{g g}^{-1}$ ). The variations are partially induced during post-mortem alteration and during amelogenesis, but the major contribution originates ultimately from the variable water chemistry in the habitats of the hippopotamids which is controlled by the lithologies and weathering processes in the watershed areas. Amelogenesis causes a distinct distribution of MgO, 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 1.3–1.9. These elements are well correlated in single specimens, thus suggesting that their distribution is determined by a common, single process, which can be described by closed system Rayleigh crystallization of bioapatite *in vivo*.

Enamel from most hippopotamid specimens has Sr/Ca and Ba/Ca which are typical for herbivores. However, Ba/Sr ranges from 0.1 to 3 and varies on spatial and temporal scales. Thus, Sr concentrations and Ba/Sr in enamel differentiate between habitats having basaltic mantle rocks or Archean crustal rocks as the ultimate sources of Sr and Ba. This provenance signal is modulated by climate change. In Miocene to Pleistocene enamel from the Lake Albert region, Ba/Sr decreases systematically with time from 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 Ba mobility decreased with increasing aridification due to preferential deposition with clay and Fe-oxide-hydroxide or barite on the watershed of Lake Albert.

## 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). 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, 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 analyzes. 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, ooliths and fish scales (McCulloch et al., 1994; Lear et al., 2000; Balter and Lécuyer, 2010). These proxies also trace 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, 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. Discrimination between Ba and Sr, though, appears to be inefficient in single habitats. In different ecosystems Sr/Ca and Ba/Ca 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.

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 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 (Pasteris et al., 2008). This explains why many studies observe that the chemical composition 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; Brüggmann 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 provide reliable results (Koch et al., 1992; Hoppe et al., 2003; Lee-Thorp and Sponheimer, 2003).

Here we complement the study of Brüggmann et al. (2012) describing the major element 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 bioapatite from non-migratory animals, such as hippopotamids. Extant species (*Hippopotamus amphibius*,

*Choeropsis liberensis*) have terrestrial foraging habits, are water-dependent and adapted to a variety of different habitats ranging from lakes to rivers, and from freshwater to saline and brackish environments (Eltringham and Barrett, 2010; Chansa et al., 2011a, b). Recent studies confirm that fossil species primarily fed on terrestrial plant assemblages, such as C<sub>4</sub> or C<sub>3</sub> grasses (e.g. Boisserie and Merceron, 2011). The high abundances of fossil hippopotamid remains in river and lacustrine basin deposits indicate that the ancestral forms were also adapted to a semi-aquatic life similar to their modern analogues (Boisserie et al., 2005; Cerling et al., 2008; Harris et al., 2008). Hippopotamid teeth are chemically robust environmental archives and are common mammalian fossils in African terrestrial sediments. It is expected that the chemical composition of bioapatite forming the tooth is reflected in the chemical composition of the diet (food and drinking water), but it also depends 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 permanent premolar and molar teeth from 24 different animals. 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 amphibius*. 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 belong to the western branch of the EARS. The tectonic history as well as litho- and biostratigraphy of the lakes have been comprehensively described (Pickford et al., 1993; Senut and Pickford, 1994; Betzler and Ring, 1995; Ring and Betzler, 1995; Beuning et al., 1997; Van Damme and Pickford, 2003; Bobe et al., 2007).

## 2.2 Analytical methods

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

New Wave Nd-YAG laser systems with wavelengths of 193 nm and 213 nm were 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 J cm<sup>-2</sup>. 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 materi-

als and <sup>43</sup>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 ng g<sup>-1</sup>, 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 analyzes. The MgO, CaO, and Na<sub>2</sub>O data discussed in the following paragraphs are from Brüggmann et al. (2012) and have been determined using the electron microprobe.

## 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 CaO, MgO, Ba, and Sr in enamel, cement and dentin. Overall, Sr and Ba display vast concentration variations in all tooth tissues. For example, Ba concentrations in enamel vary from 9 to 2150  $\mu\text{g g}^{-1}$  and those of Sr vary from 120 to 9336  $\mu\text{g g}^{-1}$ . 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 tissue 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; Brüggmann et al., 2012). However, the relatively low number of analyzes (31; Table 1) might be not representative for this material.

Barium and Sr concentrations differ between modern and fossil specimens 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 modern dentin has less than 450  $\mu\text{g g}^{-1}$  (Table 1; Fig. 1). 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 large range of Ba and Sr concentrations reflect the enormous differences among teeth from different geographical locations and the systematic variations within single tooth specimens (Fig. 2). The enamel from teeth found along the

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

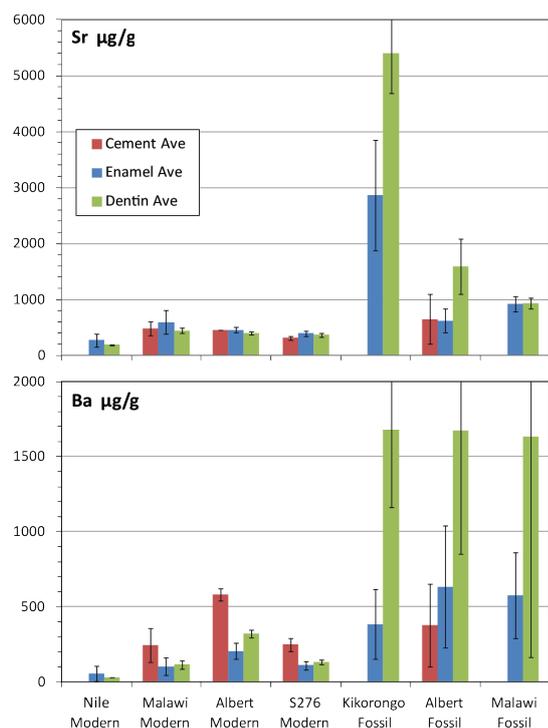
Enamel Averages	Age (Ma)	<i>N</i>	Ba $\mu\text{g g}^{-1}$	$1\sigma$	Sr $\mu\text{g g}^{-1}$	$1\sigma$	CaO wt %	$1\sigma$	MgO wt %	$1\sigma$	Ba/Sr	$1\sigma$	Sr/Ca *1000	$1\sigma$	Ba/Ca *1000	$1\sigma$
All specimens		1408	388	374	767	778	54.52	0.76	0.34	0.14	0.61	0.54	1.97	1.99	1.00	0.96
All fossil		811	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	1.04
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
Dentin Average		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
Cement Average		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).

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 its Ba concentration 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 the concentration variations of these elements among specimens from single settings, such as Lake Albert, Lake Malawi or the Nile River, vary: 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). This

is seen in apical and cervical profiles of enamel. Indeed the Ba and Sr concentrations as well as the concentration gradients along such profiles are very similar (Fig. 2; apical and cervical profiles are shown from specimens from modern Lake Malawi and Lake Albert and fossil Lake Kikorongo and Lake Malawi). This implies that these animals did not experience a significant diet change at least until the end of molar and premolar amelogenesis. Similar element distributions in enamel have been observed for  $\text{Na}_2\text{O}$  and MgO, whereas Cl displays the opposite trend and CaO is constant along such a profile (Brüggmann 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 MgO and  $\text{Na}_2\text{O}$ . The similar distribution for Sr,  $\text{Na}_2\text{O}$  and 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 they are more variable. These lower ratios are due to Sr and Ba enrichment of many outer enamel



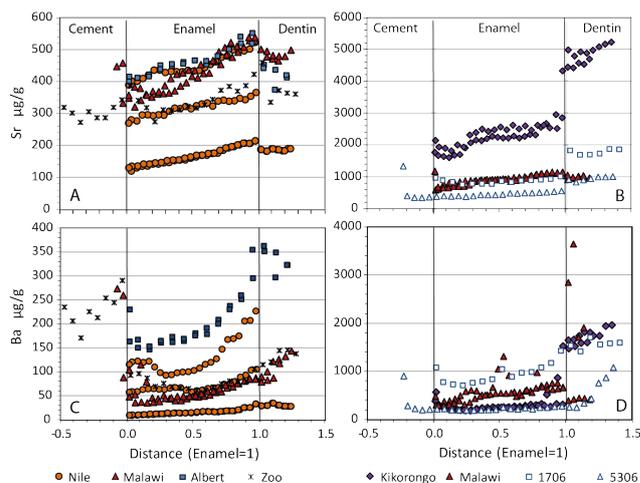
**Fig. 1.** Average Ba and Sr concentrations in cement, enamel and dentin of modern and fossil hippopotamid teeth. Error bars represent the  $1\sigma$  error of the average.

rims and may indicate secondary addition of Sr and Ba during diagenesis.

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, of single specimens 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 biapatite deposition during tooth development from those imposed externally by changing diet composition at different geographical and geochronological scales. Overall, Sr and Ba have similar COV values of about 1 and their concentrations 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). The low COV of Na<sub>2</sub>O, like that of CaO, suggests that the abundance of this element in enamel is very well controlled by the physiology of the hippopotamid that does not accommodate diet provoked variations. In contrast, the increasing COV of MgO, Sr and Ba, may indicate an increasing sensitivity to environmental changes.



**Fig. 2.** Ba and Sr variations along selected tooth profiles from the outside margin through cementum, enamel into dentin. Several specimens (modern and fossil Malawi; modern Lake Albert; Lake Kikorongo) are represented by data along apical and cervical profile locations. Significant differences of concentrations and gradients are not observed. The distance is normalized to the length of the enamel = 1. (a, c) Ba and Sr variation in modern enamel. (b, d) Ba and Sr variation in fossil enamel.

In individual specimens Ba concentrations are more variable than those of Sr (average COV(Ba) = 0.4; average COV(Sr) = 0.25). The concentration variations of MgO and Na<sub>2</sub>O are lower and rather similar (average COV = 0.2; Brüggmann et al., 2012). These variations 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

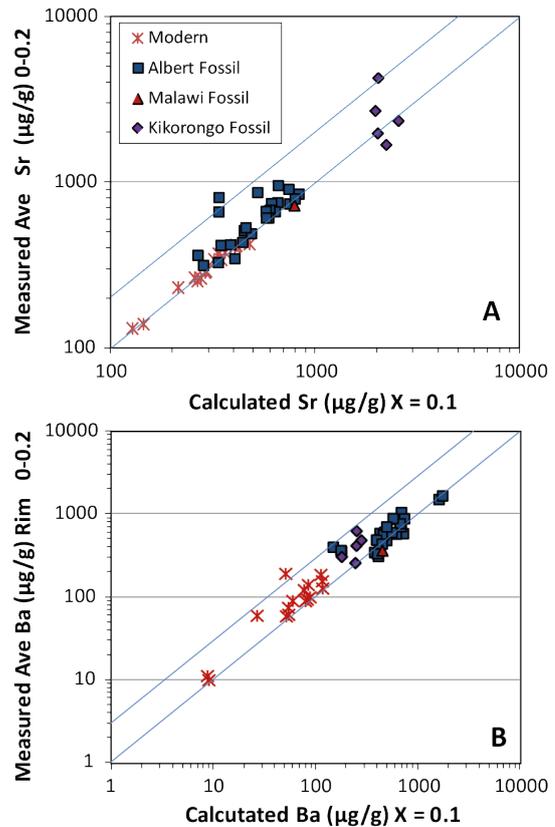
#### 4.1.1 Recognizing secondary redistribution of Ba and Sr

Diagenetic overprint has been detected in many of the studied specimens (Brüggmann et al., 2012). Fluorine, Fe and Mn are always added during diagenesis obscuring their primary distribution. However, major components, such as CaO, P<sub>2</sub>O<sub>5</sub>, MgO or Na<sub>2</sub>O, indicate minimal remobilization in most specimens. Along all profiles through modern enamel Ba and Sr concentrations systematically increase towards the EDJ (Fig. 2a, c). However, in most fossil specimens anomalous high concentrations of both elements occur near the outside rim of the tooth (0–300 µm) and within 200 µm of the EDJ (Fig. 2b, d). Barium and Sr are known to become enriched in bone and tooth tissues when being exposed to post-mortem alteration (Koch et al., 1992; Sandrock et al., 1999; Hoppe et al., 2003; Lee-Thorp and Sponheimer, 2003). In order to evaluate the influence of alteration on the distribution

of these elements, we performed linear regression analyzes 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 potentially altered enamel fractions. 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. In modern enamel calculated and measured Sr concentrations agree very well plotting along the 1 : 1 line (Fig. 3). Many fossil enamel specimens follow this trend, in particular those where enamel is enclosed by cement tissue 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 two 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 three (Figs. 2c, d, 3b). Several modern specimens show a concentration increase near the outside enamel rim and 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. 2c). This explains that even data from modern enamel plot above the 1 : 1 line in Fig. 3. In some modern specimens, however, Ba concentrations de facto increase at the outer rim (specimens Nile-4, S276, Mal 8.1-1AB; Fig. 2a, c). Because the modern specimen had not been in contact with sediments, this must be a primary feature developed during the live time of the hippopotamid. Possibly, during or after eruption the 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 implies 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 de-



**Fig. 3.** Comparison of (a) Sr and (b) Ba concentrations measured at the outside enamel rim of single modern and fossil tooth specimens with values expected there based on linear regression analyzes. 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.

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

Enamel development can be divided into two stages: the secretion and the maturation phase (Robinson et al., 1995; Smith and Nanci, 1995; Boskey, 2007; Pasteris et al., 2008; Simmer et al., 2010). During the first period, the final shape and the size of the tooth is established and ameloblasts deposit a matrix of proteins which confines the deposition of apatite (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 at the EDJ after appositional growth is completed (Simmer et al., 2010) and it involves in essence the

**Table 2.** Rayleigh crystallization model for enamel formation.

	*F	Na <sub>2</sub> O wt %	MgO wt %	Ba µg g <sup>-1</sup>	Sr µg g <sup>-1</sup>	Na <sub>2</sub> O wt %	MgO wt %	Ba µg g <sup>-1</sup>	Sr µg g <sup>-1</sup>	Na <sub>2</sub> O wt %	MgO wt %	Ba µg g <sup>-1</sup>	Sr µg g <sup>-1</sup>	Na <sub>2</sub> O wt %	MgO wt %	Ba µg g <sup>-1</sup>	Sr µg g <sup>-1</sup>
		Lake Malawi (modern)				Lake Albert (Fossil)				Lake Kikorongo (fossil)				Upper Nile-1 (modern)			
Calculation of the fluid composition at the end of secretion																	
**D <sub>Ap/Fl</sub>		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 <sub>Apatite</sub>		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 <sub>Fluid</sub>	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 <sub>Apatite</sub>	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.

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.

Beyond the rims of altered enamel, Ba, Sr, Na<sub>2</sub>O and MgO concentrations of single specimens systematically increase towards the EDJ (Fig. 2) and are well correlated (Fig. 4). This suggests that the element distribution is controlled by a single process in which with advancing apatite crystallization, from the EDJ towards the outside rim, the enamel fluid becomes depleted in Ba and Sr as well as Mg and Na. The epithelial cells control the transport of Ba, Sr, and Mg into the crystallization compartment, but there crystallizing apatite incorporates these elements into its lattice. Thus, apatite-fluid partition coefficients ( $D_{Ap-Fl}$ ) are greater than one. Qualitatively, the relative partitioning behavior can be estimated using the correlation diagrams of these elements (Fig. 4). The regression line of an element pair with similar  $D_{Ap-Fl}$  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 trend crosses the axes of the element with lower  $D_{Ap-Fl}$ . This analysis suggests that partition coefficients increase in the order of Sr < Mg < Ba.

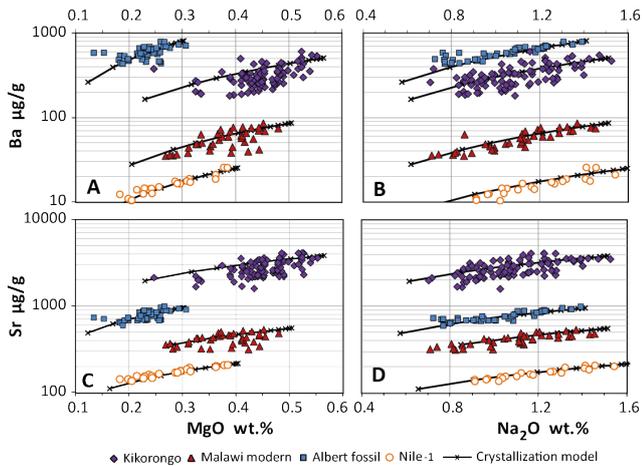
Brüggmann et al. (2012) suggested that apatite precipitation occurs in an isolated or semi-isolated chamber and that crystallization follows a Rayleigh fractionation law. At the end of appositional growth, the crystallites of the entire enamel tissue are in equilibrium with the enamel fluid because there should be a fully interconnected fluid network due to the low mineral density in enamel at this time. The highest Sr, Ba, MgO and Na<sub>2</sub>O concentrations at the EDJ are used to calculate the element concentrations in the enamel fluid at the beginning and during the course of maturation applying the

Rayleigh fractionation law. The observed and calculated distributions of Ba, Sr, MgO and Na<sub>2</sub>O in enamel are compared in Fig. 4 and Table 2. There is a very good agreement between model and observation assuming apatite-fluid partition coefficients ( $D_{Ap-Fl}$ ) of 1.25, 1.2 and 1.15 for Ba, Mg and Sr, respectively (Table 2). This sequence is consistent with that of the qualitative estimate. 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 variations (Table 2; Fig. 4). This agrees very well with the amount of mineral present in enamel after maturation.

Our estimated partition coefficients for bioapatite and enamel fluid are consistent with results from inorganic precipitation experiments and in vivo studies (Wells et al., 2000; Balter and Lécuyer, 2010) considering the principal uncertainties associated with low temperature experimental results and their application to biological processes and our idealized modeling approach. In reality, 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 impedes a detailed quantitative description. The absolute value of the partition coefficients may increase if the elements are continuously added to the tooth forming 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

At the scale of a specimen, i.e. habitat, the alkaline earth elements covary very well. Thus, element ratios such as Sr/Ca and Ba/Ca categorize hierarchical structures in a specific food web and information about the trophic, climatic and

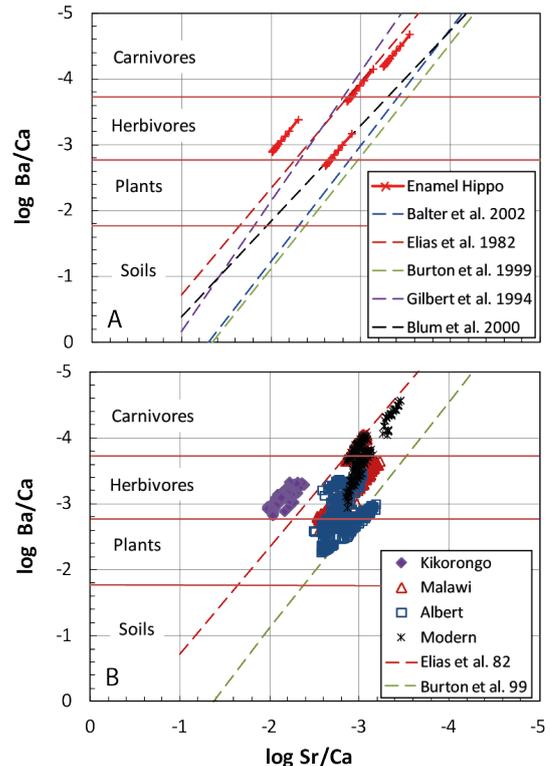


**Fig. 4.** Variation of MgO, Na<sub>2</sub>O, Sr and Ba in modern and fossil enamel from hippopotamid teeth. Note the large variation of Ba and Sr concentrations relative to MgO and Na<sub>2</sub>O. The coherent variation of all elements regardless of age, element concentrations and profile location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

geological background of a given environment can be obtained. However, on a regional scale this covariation is obliterated, because there are differences among sedimentary environments, and even systematic changes with geologic time can be observed.

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

There is an overall positive correlation between Sr/Ca and Ba/Ca of bone and tooth tissues (Fig. 5a). Hippopotamids are grazers; however, the variation of Ba/Ca and Sr/Ca in the studied enamel samples covers the entire herbivore array, including that of browsers, and even extends into the fields defined by plants and carnivores (Fig. 5b). Even so, the slopes of the Ba/Ca and Sr/Ca variation in 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 hippopotamid 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. If this suggestion is valid, it is apparent why Ba/Ca and Sr/Ca in bone and 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



**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 and Sr/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.

be alike during the formation of these tissues. Barium 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). For toxic elements,

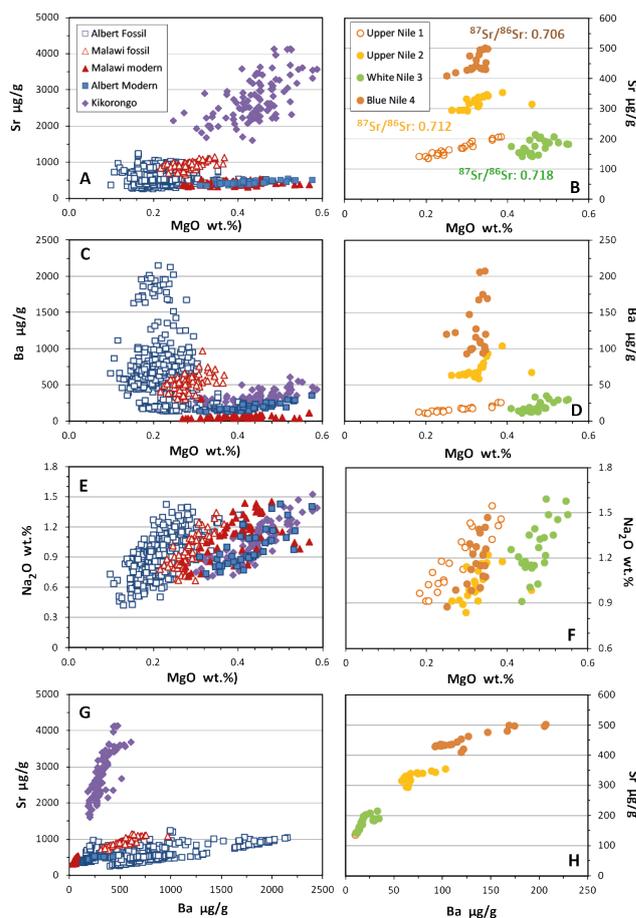
such as Pb, or essential elements (Cu, Zn) the discrimination relative to Ca may be subjected to additional metabolic controls and to significant incorporation in different organs, which also influence the element pathway from ingestion to incorporation into bioapatite. Therefore, different taxa may induce vital effects which significantly overprint the diet signal (Hirao and Patterson, 1974; Balter, 2004).

#### 4.2.2 Spatial variation of alkaline earth element concentrations: tracers of ecosystems

In the hippopotamid 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 ( $\sim 447 \mu\text{g g}^{-1}$ ). Enamel from Lake Kikorongo has extraordinary high Sr concentrations ( $> 1500 \mu\text{g g}^{-1}$ ) which are much higher than those in specimens from modern and fossil lakes and, in particular, rivers ( $< 1100 \mu\text{g g}^{-1}$ ; Fig. 6g). The natural environments of Lake Kikorongo and the Blue Nile are set apart by their association with basaltic volcanic rocks, whereas the remaining tooth specimens are from hippopotamids which lived in waters having Archaean-Proterozoic granite-gneiss terranes in their catchment area. Preliminary Sr isotopic compositions of the Nile specimens are given in Fig. 6b. Enamel from the Blue Nile has the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  of  $0.7056 \pm 0.0001$ . This isotope ratio is identical to that of dissolved Sr in the Blue Nile water and approaches values which are typical for the Ethiopian flood basalts (0.7035–0.7045; (Palmer and Edmond, 1989; Kieffer et al., 2004). Enamel from the basaltic crater of Lake Kikorongo also has relatively unradiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $\sim 0.708$ ; Brüggmann et al., 2008). This is within the range observed for the water in the crater lakes of the Katwe-Kikoronga area ( $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.706–0.717; Bahati et al., 2005) and is consistent with a habitat dominated by basaltic volcanic rocks. These rock types commonly have higher Sr contents than typical upper crustal rocks (Kieffer et al., 2004; Rudnick et al., 2003) and this may explain the relatively high Sr concentrations in enamel from the Blue Nile and Lake Kikorongo.

Enamel of the specimen from the White Nile has among the lowest Sr content of all specimens and its  $^{87}\text{Sr}/^{86}\text{Sr}$  is relatively radiogenic ( $0.7182 \pm 0.0004$ ; Fig. 6b). This signifies the presence of old continental crust along the watershed of the river because these lithologies have typically radiogenic Sr isotopic compositions with  $^{87}\text{Sr}/^{86}\text{Sr} > 0.71$ . The outlet lake of the White Nile is Lake Albert which lies within Archaean and Proterozoic crustal rocks and waters and sediments from the Albert and Victoria Nile River have radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7114 to 0.722 (Palmer and Edmond, 1989; Padoan et al., 2011).

The correlation of Ba with Sr in the enamel from the Nile River evokes that Ba concentrations also trace the water provenance (Fig. 6h). The low Ba concentration in enamel from the White Nile, however is unexpected, because



**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 (Brüggmann 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.

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.

A low Ba/Sr ( $< 1$ ) is a typical feature in watersheds of several modern rivers including such draining granitic source

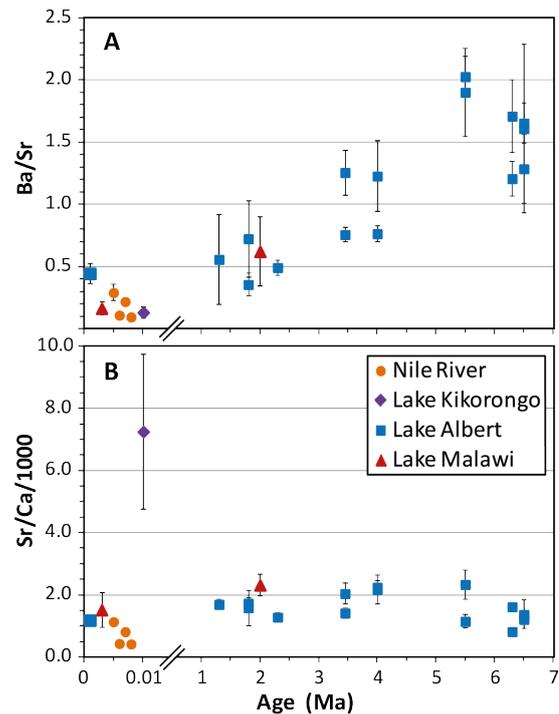
rocks (Dalai et al., 2002) and also East African lakes (Tanganyika, Malawi) have low Ba/Sr (Sako et al., 2007; Branchu et al., 2010). The reduced mobility of Ba relative to Sr in granite-gneiss watersheds is probably caused by scavenging of Ba by clay minerals and oxy-hydroxides or barite precipitation 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 MgO content in enamel is not exclusively controlled by the input from the source rock, but is modified by the local hydrological conditions. 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 that 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 indicated by the evaporation trend in Lake Albert since at least about 6.5 Ma as suggested by increasing  $\delta^{18}\text{O}$  of hippopotamid enamel during that time (Brachert et al., 2010).

#### 4.2.3 Temporal variation of alkaline earth element concentrations in enamel: tracers of environmental change

Another conspicuous feature is the highly variable Ba concentration in enamel from different stratigraphic units of the Lake Albert region. 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 than Pliocene, Pleistocene as well as Holocene and modern enamel, respectively (Fig. 7a). In contrast, Sr/Ca values 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 possible that the Ba increase with geological age is due to secondary addition during diagenetic alteration. No other major or trace element, however, shows such 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 (Brüggmann 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 represents a primary feature, which has been established during amelogenesis. Secondary overprint, therefore, is an unlikely process explaining the temporal Ba variation.



**Fig. 7.** Temporal variation of Ba/Sr and Sr/Ca in modern and fossil molar enamel from hippopotamids. Note the break along the axis of the abscissas; age of modern specimens is not to scale. (a) Ba/Sr in enamel versus geological age. Notice the systematic decrease of Ba/Sr with age which suggests limited Ba mobility relative to Sr in the Pleistocene (< 2.5 Ma) compared to the Pliocene and Miocene. (b) Sr/Ca in enamel versus geological age indicating no significant fractionation between Sr and Ca with time.

The alternative explanation is that the composition of the hippopotamid diet has changed, either because of a change of dietary preferences or a change of the diet's chemical composition. Indeed, our set of specimens includes different taxa; the modern teeth belong to the large-size species *Hippopotamus amphibius*, but the fossil teeth include 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 the samples do not reflect a systematic chronological distribution of the taxa populations.

Hence, the variation of these ratios with geological age indicates a systematic change of the diet composition, including that of drinking water. 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 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 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 watershed of Lake Albert 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 time (Brachert et al., 2010). Under arid conditions chemical weathering is less intense which should 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 which is related to 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, an 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

Bioapatite is in 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). These elements transport chemical information from the external environment into bone and tooth tissues, which contain, therefore, records of historical and ancient environmental change. The archive investigated here is premolar and molar hippopotamid tissue from lacustrine and fluvial environments (6.5 Ma to recent) of Eastern Africa. The variation of the concentrations of CaO ( $1\sigma \sim 1\%$ ), MgO ( $1\sigma \sim 38\%$ ), 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 externally, by the distribution of these elements in the habitats. 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 precludes the use of Ca concentrations as an environmental proxy. Magnesium is also an important essential nutritional element and 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 could in addition 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 distinction of saline and freshwater habitats or provenance signals using ratios such MgO/CaO or MgO/ $\text{Na}_2\text{O}$ .

In contrast, large variations of Ba and Sr concentrations in tooth tissues are possible due to 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 but for enamel it has no significant influence on the overall population statistics.

On the scale of a hippopotamid 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. Enamel formation, however, occurs in a semi-permeable open system, where element transport is physiologically mediated. These fluxes as well as the influence of the protein matrix on apatite precipitation are not well-known. Therefore, Rayleigh crystallization has to be

regarded as a simplified conceptual model describing the chemical variation in enamel.

On a regional scale, Ba and Sr variations in enamel can be related to variable diet compositions in different habitats which in turn reflect different water provenance and hydrochemical conditions. The large variations of Ba/Ca (2.4 log units), Sr/Ca (1.5 log units) and Ba/Sr (1.3 log units) in enamel imply that the plant signal entering the food chain is highly heterogeneous with regard to these elements. Enamel of each hippopotamid, however, shows a specific chemical signal which fingerprints the environmental setting of the animal's small territory. Thus, it is possible to estimate the Ba/Sr of the food ingested by hippopotamids by adjusting the observed ratio with that of the apatite-fluid partition coefficients of Ba and Sr. The catchment areas of lakes and rivers impose a dominant signature onto the hippopotamid habitats. 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. 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 scavenging 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.

Alkaline earth 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.net/9/4803/2012/bg-9-4803-2012-supplement.pdf>.**

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