Calcium isotopes in enamel of modern and Plio-Pleistocene East African mammals

J.E. E Martin, T. Tacail, T. E. Cerling, V. Balter

Calcium isotopes in enamel of modern and Plio-Pleistocene East African mammals

J.E.Martin[a], T.Tacail[a], T.E.Cerling[b], V.Balter[a]

[a]Laboratoire de Géologie de Lyon: Terre, Planète, Environnement, UMR CNRS 5276 (CNRS, ENS, Université Lyon1), Ecole Normale Supérieure de Lyon, 69364 Lyon cedex 07, France

[b]Department of Geology and Geophysics & Department of Biology, University of Utah, Salt Lake City, Utah 84112, USA

Abstract

Calcium isotope analyses show a depletion of heavy calcium isotopes in vertebrates, compared to food sources along each trophic step. Recent studies show considerable variability of the calcium isotopic composition of bone and teeth in modern mammals, leading to inconclusive interpretations regarding the utility of Ca isotopes for trophic inference in mammal-dominated terrestrial ecosystems. Here, we analyzed modern enamel samples from the Tsavo National Park (Kenya), and fossil enamel samples dated from *ca*. 4 Ma to 1.6 Ma from the Turkana Basin (Kenya). We found a constancy of taxa ordering between the modern and fossil datasets, suggesting that the diagenesis of calcium isotopes is minimal in fossils. In modern herbivore samples using similar digestive physiologies, browsers are enriched in ^{44}Ca compared to grazers. Both grazer and browser herbivore tooth enamel is enriched in ^{44}Ca relative to carnivores by about +0.30‰. Used together, carbon and calcium isotope compositions may help refine the structure of the C_3 and C_4 trophic chains in the fossil

record. Due to their high preservation potential, combining both carbon and calcium isotope systems represent a reliable approach to the reconstruction of the structure of past ecosystems.

1. Introduction

Calcium (Ca) is a major element (~40% weight) in carbonate hydroxylapatite (CHA): the inorganic phase of vertebrate phosphatic tissues (i.e., bone, enamel and dentine). Ca isotope ratios, $^{44}Ca/^{40}Ca$ (here expressed as $\delta^{44/42}Ca$, see details thereafter), in vertebrate phosphatic tissues were first measured by means of thermal ionization mass spectrometry (Russell et al., 1978; Skulan et al., 1997; Skulan et al., 1999; Clementz et al., 2003). Ca stable isotope ratios have not been measured routinely by means of multi collector inductively coupled plasma mass spectrometry (MC-ICPMS) due to a major isobaric interference on $^{40}Ca^+$ by $^{40}Ar^+$, and polyatomic and doubly charged interferences on $^{42}Ca^+$, $^{43}Ca^+$ and $^{44}Ca^+$ beams (Wieser et al., 2004; Valdes et al., 2014; Tacail et al., 2016). Subsequent improvements of the Ca purification chemistry and in MC-ICPMS analytics further encouraged the interest of Ca isotope systematics in recent and fossil vertebrate samples with an emphasis at understanding mammal, fish and reptile biology and reconstruction of associated trophic chains (Clementz et al. 2003; Chu et al., 2006, Reynard et al., 2010, 2011, 2013; Heuser et al., 2011; Melin et al., 2014; Martin et al., 2015, 2017a, 2017b; Tacail et al., 2017a; Hassler et al., 2018).

Two direct implications of the high Ca content in CHA stimulate the interest for the analysis of Ca isotopes. The first is that minute amount of phosphatic tissue, typically 100 μg, is necessary to process the measurement of Ca isotope ratios accurately. Such a small amount of sample opens perspectives for the use of sample

51 leftovers or the almost non-destructive sampling of precious fossils. The second is that
52 only extreme diagenesis, with more than 80% of reworked CHA, is predicted to have
53 an effect on the original Ca isotope composition (Martin et al., 2017a). These
54 calculations are made using water-rock interactions and assume that secondary
55 calcium carbonates are leached accordingly. Collagen nitrogen is rarely preserved in
56 fossils older than the Holocene or Late Pleistocene so that its potential as a trophic
57 indicator in the deep past is precluded. Therefore, measuring Ca isotope ratios have
58 the potential to allow reconstructing past trophic chains in vertebrate fossils of
59 Pleistocene age and older. So far, only trace elements, mainly the strontium-calcium
60 and barium-calcium ratios (Balter et al., 2001; Sponheimer and Lee-Throrp, 2006)
61 have been used to this end, but trace elements have the disadvantage to be potentially
62 altered by diagenetic processes (Reynard and Balter, 2014).
63 Trophic level reconstruction using Ca isotopes is based on the reasoning that
64 the whole body tissues of vertebrates are depleted in heavy Ca isotopes relative to
65 diet. The main observation is that bone Ca is depleted in heavy isotopes by -0.54‰ in
66 average (expressed as $\delta^{44/42}$Ca) when compared to dietary Ca in mammals (Skulan
67 and DePaolo 1999, Chu et al., 2006, Hirata et al., 2008, Tacail et al., 2014, Heuser et
68 al., 2016). This systematic and well-conserved offset argues in favor of a shared
69 physiological effect on Ca isotope fractionation in mammal tissues. The depletion in
70 heavy Ca isotopes is variable among organs, but taking blood as a baseline, Tacail et
71 al. (2017b), based on a compilation of available data in mammals (Skulan and
72 DePaolo 1999; Morgan et al. 2012; Tacail et al. 2014; Channon et al. 2015; and
73 Heuser et al. 2016) on various organisms including humans, calculated a Ca isotopic
74 offset $\delta^{44/42}$Ca between blood and diet of -0.30 ± 0.13‰ (1SD). The observed trophic

level effects in ecosystems could thus be explained by the propagation of this physiology-related isotopic fractionation from a trophic level to another.

Indeed, calcium isotope ratios were shown to decrease with trophic level position in marine ecosystems by Skulan et al. (1997) and this finding was later confirmed (Clementz et al. 2003; Martin et al., 2015; 2017b). Early work proposed a model to understand the relationship between dietary and mineralized calcium (Skulan and DePaolo, 1999) but subsequent studies raised some issues in interpreting calcium isotope values in terms of trophic fractionation, notably in terrestrial environments. Melin et al. (2014) studied calcium isotope ratios for terrestrial mammal ecosystems and concluded that while confirming the decrease in Ca isotope ratios in large carnivores, they also observed isotopic insensitivity to trophic levels between small faunivores and low trophic levels, suggesting limited applications of Ca isotopes in past ecosystems. Moreover the application of Ca isotopes for trophic level reconstruction in past continental ecosystems, including dinosaur fauna, was not conclusive (Heuser et al., 2011) although a recent study at regional scales permitted to distinguish between food sources between predatory dinosaurs (Hassler et al. 2018). Recent work offered encouraging perspectives in a Pleistocene mammalian fauna (Martin et al., 2017a) but some outliers remain difficult to interpret and may be so under the suspicion that physiological processes might be at play (Tacail et al. 2017a). Also, complexation of Ca with aqueous compounds (e.g. citrates, oxalates) potentially plays a role in isotopic fractionation between various plant or animal organs (Moynier and Fujii, 2017). Physiological differences have been previously discussed between fish and marine mammals (Martin et al. 2015) underlining the difficulty to interpret mammalian calcium isotope variability solely under the light of a trophic effect on

fractionation processes. Importantly, a comprehensive framework of Ca isotope distribution in modern terrestrial mammals is lacking.

In an effort to fill this gap, the present work reports Ca isotope ratios of modern enamel samples from the Tsavo National Park and from Turkana Basin (Kenya) (n = 64), and fossil enamel samples (n = 51) dated from *ca*. 4 Ma to 1.6 Ma from the Turkana Basin (Kenya). The $^{44/42}$Ca and $^{43/42}$Ca isotope ratios are compared with carbon isotope (^{13}C/^{12}C), oxygen isotope (^{18}O/^{16}O), strontium-calcium (Sr/Ca), and barium-calcium (Ba/Ca) ratios.

2. Methods

2.1. Samples

Tsavo National Park is situated in southern Kenya (*ca*. 3.4 S, 38.6 E, 550 m elevation) and has a mean annual temperature of 25 °C and 550 mm annual rainfall (Climatological Statistics for East Africa, 1975); it is a semi-desert bushland with riparian woodland (White, 1985). Samples of mammals were collected between 1997 and 2011 and include the long-term collections at the Tsavo Research Center near Voi; samples in this collection date back to the 1960s. Fossil samples from the Turkana Basin were collected from the National Museums of Kenya and the Turkana Basin Institute. Ages of fossils are based on the stratigraphic and geochronologic work of Brown and McDougall (2011). Both modern and fossil materials were collected as part of a paleoecology project reported earlier (Cerling et al., 2015). For all samples, powdered enamel was collected using a low-speed dental drill.

124 *2.2. Analytical techniques*

125

126 We compared samples that had undergone the standard pre-treatment used in light
127 stable isotope studies to remove organic matter and calcium carbonate (3% H_2O_2
128 followed by 0.1 M acetic acid as in Passey et al, 2002). Samples were analyzed for
129 $\delta^{13}C$ and $\delta^{18}O$ using digestion by 100% H_3PO_4 and analyzed on an isotope ratio mass
130 spectrometer using the standard ‰ notation where

131 $$\delta^{13}C(‰) = (R_{sample}/R_{standard} -1)*1000 \quad (1)$$

132 where R_{sample} and $R_{standard}$ are the $^{13}C/^{12}C$ ratios in the sample and standard,
133 respectively. An analogous equation defines $\delta^{18}O$. The isotope standard VPDB
134 (Vienna-PDB) is used for both carbon and oxygen isotopes.

135 The remaining powdered samples were treated in the clean lab at LGLTPE,
136 ENS de Lyon, France. For each dissolved sample, a fraction was taken for
137 concentration analyses and another fraction was kept for purification of calcium.
138 Concentration analyses were performed by means of inductively coupled plasma mass
139 spectrometer (ICP-MS Agilent Technologies 7500 Series) for trace elements such as
140 Sr, Ba, U, and major elements were measured on an inductively coupled plasma
141 atomic emission spectrometer ICP-AES (Thermo electron corporation ICAP 6000).
142 Measurements were controlled through a set of blanks and standards such as
143 SRM1486. Calcium was purified following the protocol described in previous work
144 using Eichrom Sr-specific resin (Sr-spec Eichrom®) and cation-exchange resin (AG-
145 50WX-12) with ultrapure solutions of nitric and hydrochloric acids as elution agents
146 (see details in Tacail et al. 2014; Martin et al. 2015; 2017a; 2017b). The purified
147 fraction was measured for Ca isotopes on a Thermo Neptune Plus MC-ICPMS at
148 medium resolution in static mode. Delta values were obtained using the standard

bracketing method using the *ICP Ca Lyon* standard issued from a Specpure calcium plasma standard solution (Alfa Aesar) (Tacail et al., 2014, 2016, 2017a; Martin et al., 2015, 2017a, 2017b; Hassler et al., 2018). SRM1486 was used as a secondary standard during each analytical sequence. Uncertainties are reported in Table S1 and represent 2 standard deviations of these analyses. $\delta^{44/42}$Ca values are defined as:

$$\delta^{44/42}Ca(‰) = (({}^{44}Ca/{}^{42}Ca_{sample})/({}^{44}Ca/{}^{42}Ca_{ICP\ Ca\ Lyon})-1)* 1000 \quad (2)$$

where $\delta^{44/42}$Ca is the normalized difference in per mil (‰) between a sample and our in-house *ICP Ca Lyon* standard. In this work, all measurements are expressed in $\delta^{44/42}$Ca (Table S1) and we invite the reader to refer to supplementary material (Figure S1, Table S2) for details regarding conversions of data from the literature. Calcium isotope values are often expressed as $\delta^{44/40}$Ca values in the literature. As a guideline, the magnitude of variations of $\delta^{44/42}$Ca is almost exactly half that of $\delta^{44/40}$Ca. SRM1486 yielded a value of –1.047 ± 0.013 2SE (± 0.13 2SD, n = 101), which is undistinguishable from all SRM1486 samples measured at LGLTPE, with an average value of -1.024 ± 0.006 ‰ (n = 404, 2SE, Tacail et al., 2014, 2016, 2017a, Martin et al., 2015, 2017a, 2017b, Hassler et al., 2018) and reported $\delta^{44/42}$Ca values in 5 other studies (-1.009 ± 0.026‰, 2SE, Heuser and Eisenhauer 2008, Heuser et al. 2011, Heuser et al. 2016). More details on the compositions of reference materials are available in Table S2. All measured samples plotted in a $\delta^{44/43}$Ca versus $\delta^{44/42}$Ca space fall on a line with a slope of 0.514 ± 0.026, 2SE, in good agreement with the 0.5067 slope predicted by the linear approximation of exponential mass-dependent fractionation (Fig. 1).

3. Results

Herbivores in both the modern and fossil samples range from browsers ($\delta^{13}C < -8‰$) to grazers ($\delta^{13}C > -1‰$; see discussion in Cerling et al 2015); hippos are mixed feeders in this modern Tsavo ecosystem. For the Turkana Basin fossil dataset, the time span sampled is from *ca*. 4 to 1 Myr. A few taxa change their diets through this time period and some taxa at the genus level are present only in the fossil record. The elephantids *Loxodonta* and *Elephas* were grazers in the fossil record, but modern *Loxodonta* is a browser in modern ecosystems in East Africa (see Table S1 and S2 and discussion in Cerling et al 1999, 2015) with *Elephas* being extinct in Africa today.

In the savanna mammals of the South African Kruger Park, Sponheimer and Lee-Thorp (2006) observed that grazers have higher Sr/Ca and Ba/Ca ratios than browsers. This observation is not confirmed here in the East African modern mammals of Tsavo (Fig S2). Noteworthy, we found that rhinos from this sample suite have extremely high Sr/Ca ratios with typical Sr contents that are one order of magnitude higher than in others animals (Fig S2). In agreement with the literature (Balter, 2004; Peek and Clementz, 2012), however, the Sr/Ca and Ba/Ca ratios are lower in carnivores than in herbivores in the modern dataset (Fig S2).

Fossil samples at Turkana are affected by diagenesis by the addition of trace metals: there is a strong positive correlation between Ba and Mn concentrations ($R^2 = 0.417$, $p^{***} < 10^{-}$; Fig S4C; Table 1) and between Sr and U (U; $R^2 = 0.247$, $p^{**} = 0.0004$; Fig S4D; Table 1). As a consequence, the Sr/Ca and Ba/Ca ratios do not discriminate carnivores from herbivores in this particular fossil assemblage (Fig S3). In addition, the Sr/Ca and Ba/Ca ratios are correlated at Turkana ($R^2=0.225$, $p^{**} = 0.0008$, Fig. S4B) while this correlation is not observed in the recent Tsavo fauna (Fig S4A).

That the Sr/Ca and Ba/Ca are correlated in fossil samples suggest a common diagenetic process for Sr and Ba. Likely, this diagenetic process involved the addition of a U and Mn-rich phase, which also contains Sr and Ba, explaining the overall increase by a factor of 1.7 and 3.3 of the Sr/Ca and Ba/Ca ratios, respectively, between modern and fossil samples. Mg/Ca ratios are not significantly different between modern and fossil samples. We conclude that our results show that diagenetic processes have altered the concentrations of Sr and Ba, and therefore the potential for isotopic alteration of the $^{87}Sr/^{86}Sr$ ratio in fossil materials must be evaluated carefully.

Inversely, the relative sensitivity of trace and major elements to diagenesis can be used to ascertain that little or no diagenesis has occurred for major elements if the trace elements normalized to calcium show ratios similar to modern samples. This is most probably the case for South African Plio-Pleistocene fossils for which original Sr/Ca and Ba/Ca patterns are apparently preserved (Sponheimer et al., 2006; Balter et al., 2012).

The $\delta^{44/42}Ca$ values range from –2.00‰ to –0.98‰ in the modern dataset of Tsavo/Turkana (Fig. 2A) and from –1.77‰ to –0.94‰ in the fossil dataset of Turkana (Fig. 3A). In both cases, carnivores exhibit the lowest $\delta^{44/42}Ca$ values, but hippos also have quite low values, between hyenas and felids. Equids have $\delta^{44/42}Ca$ values that fall in the variability of the felid carnivores, both in the modern and fossil datasets. In the modern dataset, suids exhibit similar $\delta^{44/42}Ca$ values to equids, while fossils suids have relatively high $\delta^{44/42}Ca$ values. Bovids, elephants and giraffes in the modern dataset have $\delta^{44/42}Ca$ values more positive than equids, carnivores and hippos, although one equid outlier shows a $\delta^{44/42}Ca$ value close to -1‰. The highest $\delta^{44/42}Ca$ values are from rhinos and some of the other herbivores such as one giraffe, one equid, a few elephants and bovids for the modern taxa analyzed (Fig. 2A). In the

223 fossil dataset, however, the fossil giraffes, bovids, rhinos and elephants have
224 undistinguishable $\delta^{44/42}$Ca values (Fig. 3A).
225 Therefore, diagenesis appears to affect some trace elements (Ba, Mn, possibly
226 Sr) but not for Ca-isotope ratios. The existence of a correlation between modern and
227 fossil $\delta^{44/42}$Ca values (Fig. S5) implies that diagenesis of the Ca isotope ratios at
228 Turkana is weak otherwise no correlation would have been obtained. Diagenesis of Ca
229 isotopes is expected to be minimal in most cases, because phosphatic tissues are so
230 rich in Ca that only extreme diagenesis (discussion above), which would modify the
231 stoichiometry of CHA, would be able to overprint the original Ca isotope composition
232 (Martin et al., 2017a).

4. Discussion

Recent data of calcium isotope compositions in enamel suggest a strong potential as a paleodietary indicator in marine settings (Skulan et al., 1997, Clementz et al., 2003; Martin et al., 2015; 2017b). On continents, however, data exhibit generally more complex patterning due, probably, to heterogeneous isotopic sources in soils and further fractionation in plants (Skulan and De Paolo, 1999; DePaolo 2004; Melin et al., 2014). Melin et al. (2014) analyzed the calcium isotope ratios of 21 bone samples from two modern mammalian communities in northern Borneo and northwestern Costa Rica: they observe a depletion of heavy calcium isotopes up the trophic chains involving two large vertebrate predators (one *Felis bengalensis* individual in Borneo and one *Panthera onca* individual in Costa Rica). Melin et al. (2014) concluded a lack of sensitivity of Ca isotopes to carnivory. Although tooth or bone samples from large predators are indeed difficult to secure, larger datasets including more of them are required to further explore this issue.

Our Ca isotope measurements arise from two modern datasets of mammals living at Tsavo National Park and at Turkana, both from Kenya; these datasets comprise 64 samples from individuals covering 9 different families of large mammals with 18 grazers, 21 browsers, 7 mixed feeders and 18 carnivores (Table 1). We considered several different digestive physiologies in the herbivore mammals of our dataset: ruminant foregut, non-ruminant foregut and hindgut. However, we found no statistically significant differences between groups. Although recent finds have highlighted that fractionation of calcium isotopes in the body mainly occurs from renal activity (Tacail et al. 2017b), it will be worth to expand the dataset and further explore potential links between digestive physiology and isotopic variability. Comparisons of $\delta^{44/42}$Ca values with respect to body mass are premature with our

current dataset; such studies should also include renal and digestive physiology as well as the C_3/C_4 mix of diet while also comparing for body mass. Here, 1) we discuss a Trophic Level Effect (TLE) as recorded in tooth enamel of modern mammals, underlining significant differences in Ca and C isotope values between some carnivores and herbivores; 2) we highlight that variability in mammal resource use such as plants, soils and waters needs to be considered to account for the observed variability in Ca isotope values of their tissues and may be related to differences in calcium isotope ratios between grazers and browsers; and 3) we infer fossil mammal Ca isotopic ecology in light of the knowledge derived from the modern samples.

4.1. $\delta^{44/42}$Ca and the Trophic Level Effect (TLE) in modern mammals

Carnivores exhibit an important variability of the Ca isotope composition being the lightest samples of the dataset but also overlapping with herbivore Ca isotope values, except some of the very large herbivores, i.e. rhinos, giraffes and elephants (Fig. 2A). We report a carnivore-prey offset of 0.24‰ when considering all carnivores versus herbivores of the modern dataset, and an offset of 0.33‰ when considering *Panthera leo* and *Crocuta crocuta* from Tsavo versus all modern herbivores. Therefore, a carnivore-prey offset of about 0.3‰ seems to characterize mammalian faunas. For the limited samples we have analyzed, the two modern felids from Tsavo, *Panthera leo* (n = 9) and *Panthera pardus* (n = 4) have differing $^{44/42}$Ca ratios, *P. leo* being the most depleted in heavy Ca isotopes (-1.63 ± 0.09‰, 1SD) similarly to the single hyenid *Crocuta crocuta* from Tsavo whereas *P. pardus* is enriched in heavy Ca isotopes (-1.46 ± 0.16‰, 1SD). In the modern dataset from Turkana, *C. crocuta* (n = 2) is also the most depleted in heavy Ca but in this ecosystem, *P. leo* (n = 2) is notably enriched in heavy Ca (-1.18 ± 0.01, 1SD), more so than *P. pardus* from Tsavo. Large

283 carnivores are flexible in their diet and their feeding habits may vary from one region
284 to another. Considering only *P. leo* and *C. crocuta* at Tsavo, carnivores possess
285 significant lower $\delta^{44/42}$Ca values than all herbivores, except the hippos (see discussion
286 below). Bone is often a significant component of the diet of hyenids but also of *P. leo*.
287 Across felid taxa, proportions of meat versus bone vary (Van Valkenburgh, 1996),
288 indicating bone consumption needs to be considered as a non-negligible supplier of
289 dietary calcium. Even a small amount of dietary bone ingested would shift the values
290 toward light Ca (Heuser et al. 2011), and could explain the low $\delta^{44/42}$Ca values
291 observed in our dataset for *P. leo* and *C. crocuta*. More calcium isotope data-points
292 are needed to test for a potential isotope scattering among carnivores according to
293 their feeding ecology. Based on behavioural observations, a dietary overlap exists
294 between *C. crocuta* and *P. leo* (Hayward, 2006) and may help explain that both taxa
295 display some of the most depleted Ca isotope values of the dataset. In the Pleistocene
296 of France, *C. crocuta* possesses the most $\delta^{44/42}$Ca-depleted value of the dataset
297 (Martin et al. 2017a), confirming our observations on *C. crocuta* from modern Kenya.
298 The δ^{13}C distribution clearly distinguishes C_4 from C_3 trophic chains (Fig. 2B)
299 and used with $\delta^{44/42}$Ca values provides further insights into niche partitioning.
300 Browsing herbivores, composed of a few bovids, giraffes, rhinos and elephants
301 exhibit high and low $\delta^{44/42}$Ca and δ^{13}C values, respectively. They are separated in the
302 $\delta^{44/42}$Ca versus δ^{13}C space from a group of predators, here represented by leopards,
303 which show similar δ^{13}C values but lower $\delta^{44/42}$Ca values (Fig. 2B). That *P. pardus*
304 avoids prey living in open habitats has been reported in the wild (Hayward et al.
305 2006b) and the isotopic distribution reported here indicates that some of the
306 herbivores mentioned above, especially small bovids, could represent potential prey
307 of the leopards. The preferred prey of the leopards have body masses not exceeding

25 kg (Hayward et al. 2006b) and therefore are not elephants, rhinos or giraffes. Further work is needed to sample and assess $\delta^{44/42}$Ca values for forest-dwelling small mammals such as small bovids (e.g., duikers, dik-diks, other neotragins) or primates, all of which are recognized prey of *P. pardus* and known to generally possess depleted δ^{13}C values (around -12 to -15‰) (Cerling et al. 2004). On the other hand, another group of herbivores comprising most of the larger bovids, suids and equids occupy a distinct δ^{13}C distribution indicating a C_4 source for predators represented by *P. leo*, as indicated by their lower $\delta^{44/42}$Ca values, corresponding to the expected dietary shift in $\delta^{44/42}$Ca values between consumer and prey.

Hippos do not follow the trends observed in other herbivores and have very low $\delta^{44/42}$Ca values typical of carnivores. Such measurements are difficult to reconcile with a TLE given their known grazing ecology (Cerling et al. 2008); however, hippos are semi-aquatic and thus have different physiological adaptations than all the other non-aquatic mammals; influences on bone density and associated bone mass balance may affect their $\delta^{44/42}$Ca values. Although hippos have been occasionally observed to exhibit carnivory (Dudley et al. 2016) the observations are so sparse to suggest that carnivory is unlikely to have an observable Ca-isotope effect in hippos.

4.2. Ca isotope variability in environmental sources

Drinking water represents a source of calcium for mammals with concentrations ranging between 15 and 150 ppm in modern-day streams (Tipper et al. 2016). Ca isotopes do not fractionate in a significant extent during geological processes leading to rather homogeneous isotope compositions in rocks, being sedimentary, metamorphic, plutonic or volcanic (Tipper et al., 2016). The Turkana modern and

333 fossil ecosystems are located around Lake Turkana and are comprised primarily of
334 fluvial Quaternary sediments derived primarily from Ethiopian Tertiary and
335 Quaternary volcanic rocks. The Tsavo ecosystem is located between Mombasa and
336 Nairobi and consists of metamorphic basement in the east (all of Tsavo East NP and
337 most of Tsavo West NP) with some Quaternary basalts in the western part of Tsavo
338 West NP. If local Ca-isotope variations are found between different substrates,
339 studies combining $\delta^{44/42}$Ca values with $^{87}Sr/^{86}Sr$ may be useful to study fossil
340 assemblages.

341 At the bottom of the trophic structure, mammalian herbivores source most of
342 their calcium from plants. Contrary to geological processes, reviewing the literature
343 shows that Ca isotopes fractionate in a significant extent between monocotyledons
344 (including grasses) and leaves of dicotyledons (Fig. 4), thus representing an important
345 source of isotopic variability. Roots of plants preferentially take up light Ca isotopes,
346 and there is a further fractionation in favor of heavy isotopes with variable amplitude
347 in leaves of dicotyledons, while this process is subdued or absent in monocotyledons
348 (Cenki-Tok et al. 2009, Holmden and Bélanger 2010). This leads to a difference of
349 +0.31‰ ($p^{***} < 10^{-4}$) between whole monocotyledon plant tissue and the leaves of
350 dicotyledons. This $\delta^{44/42}$Ca difference implies that grass and sedge consumers, i.e.
351 grazers, should have a $\delta^{44/42}$Ca value lower by about 0.3‰ compared to the browsing
352 leave-eaters; this is generally true for the modern Tsavo dataset (Fig. 2). If different
353 plant parts (i.e., roots, shoots, leaves) have different $\delta^{44/42}$Ca values, those differences
354 may be passed on to the consumer and this would be a useful tool for understanding
355 fossil diet partitioning.

356 This recognized isotopic difference between plant types, being passed on to
357 herbivores, eventually gets passed on to the next trophic level, i.e. carnivores. We

358 expect that carnivores feeding on grazers should exhibit different calcium isotopic
359 compositions than carnivores feeding on browsers and this is supported by our
360 modern dataset with lions and hyaenas showing more negative values (–1.65 ±
361 0.10‰, 1SD, n = 10) than leopards (–1.46 ± 0.16‰, 1SD, n = 4).
362 Despite some scattering in $\delta^{44/42}$Ca values among predators, it becomes clear
363 that in a modern ecosystem such as Tsavo, *P. pardus* feeds on prey with higher
364 $\delta^{44/42}$Ca values, and that *P. leo* and *C. crocuta* primarily feed on prey with lower
365 $\delta^{44/42}$Ca values. Remarkably, there is a tight $\delta^{44/42}$Ca versus δ^{13}C clustering of all the
366 taxa in the modern Tsavo panel, suggesting that Ca and C isotope ratios are driven, at
367 least partially by common processes. The concomitant use of $\delta^{44/42}$Ca and δ^{13}C values
368 provides for the first time an encouraging perspective on carnivore niche partitioning
369 between C_3 and C_4 prey. Certainly, more $\delta^{44/42}$Ca measurements covering specific
370 feeding ecologies among modern felids are required to further discuss the use of
371 calcium isotopes and decipher niche partitioning among large carnivores.
372
373 *4.3. Palaeoecological inferences using Ca isotopes*
374
375 The taxonomic distribution of the Ca isotope ratios have similar ordering for modern
376 and fossil East African faunas (Fig. 2A and Fig. 3A). Comparing the $\delta^{44/42}$Ca values
377 in modern Tsavo and fossil Turkana on a family taxon basis leads to a good
378 correlation ($R^2 = 0.621$, $p^* = 0.012$, Fig. 5) with an observed compression in the
379 $\delta^{44/42}$Ca range possibly due to differing feeding ecologies between fossil and modern
380 analogues, as evidenced by high $\delta^{44/42}$Ca values for fossil suids and saber-tooth cats.
381 Plio-Pleistocene assemblages from Turkana in northern Kenya are from ca. 4.1
382 Ma to 1.4 Ma, a period well after the rise of C_4 ecosystems (Cerling et al., 1997), but

383 in a time where there were significant changes in dietary guilds represented in the
384 fossil record (Cerling et al., 2015). The fossil Turkana ecosystem had similar
385 taxonomic lineages as the modern Turkana ecosystem: bovids, elephantids, giraffids,
386 equids, rhinocerotids. Fossil hyenids and felids were analyzed from Turkana; those
387 fossil carnivora taxa include those with no modern analogues such as saber tooth
388 felids.

389 The $\delta^{44/42}$Ca and δ^{13}C relationships are preserved for some taxonomic groups,
390 but not for all groups, when comparing the modern and fossil assemblages (Figure 2
391 and Figure 3). Most taxonomic groups have similar rankings for $\delta^{44/42}$Ca for fossil
392 versus modern samples (Figure 5) suggesting a conservative ecology and/or
393 physiology. Although most taxonomic groups have similar δ^{13}C values through time,
394 some notable exceptions, such as elephantids and rhinocerotids, show similar $\delta^{44/42}$Ca
395 values in spite of differing δ^{13}C values for the data considered here.

396 Bovids and equids have similar δ^{13}C and $\delta^{44/42}$Ca values for both modern and
397 fossil faunas although differences are noted. The fossil tragelaphins (*Taurotragus* and
398 *Tragelaphus*) had higher grass components in their diets than the modern ones from
399 Tsavo, and likewise the fossil alcelaphins (*Megalotragus*) had a slightly higher
400 browse content than do modern alcelaphins from East Africa (see Cerling et al.,
401 2015). Equids had similar δ^{13}C values for both modern and fossil samples. Fossil and
402 modern bovids have similar $\delta^{44/42}$Ca values, but modern equids have $\delta^{44/42}$Ca values
403 slightly different than fossil equids.

404 The comparison between modern and fossil elephantids and rhinocerotids is
405 noted here. Although the $\delta^{44/42}$Ca values are comparable, the diets of the studied
406 samples are quite different, unlike all other fossil-modern comparisons in this study.
407 Both elephantid fossil *Elephas* and *Loxodonta* were grazers, but modern *Loxodonta* is

408 primarily a browser (Cerling et al. 2015). The abundant fossil rhinocerotid
409 *Ceratotherium* was a grazer and was analyzed as part of this study; the modern
410 rhinocerotid *Diceros* was a browser (Cerling et al., 2015) and was analyzed as well.
411 For these lineages, $\delta^{44/42}$Ca values are similar for fossil and modern comparisons, in
412 spite of the dietary (grazing versus browsing) differences. Clearly, further
413 comparison within the elephantid and rhinocerotids for both modern and fossil faunas
414 is needed to understand why $\delta^{44/42}$Ca values in these groups appears to be
415 conservative across dietary differences.

416 Modern suids, represented by *Phacochoerus aethiopicus*, have $\delta^{44/42}$Ca values
417 (-1.48 ± 0.04‰, 1SD, n = 3) significantly different from fossil suids (-1.09 ± 0.11‰,
418 1SD, n = 3). The fossil dataset includes three genera (*Kolpochoerus*, *Metridiochoerus*
419 and *Notochoerus*) and there is little variation in their respective Ca isotope values.
420 Modern *P. aethiopicus* are mostly herbivorous, feeding on grass. More specimens of
421 fossil suids, especially contemporaneous lineages is needed to determine if Ca-
422 isotopes can distinguish different feeding strategies, such as using underground
423 storage organs, versus grass stems or leaves (Fig. 4).

424 It is noteworthy that the ^{44}Ca-enrichment observed for carnivores between
425 Turkana fossils and modern Tsavo samples is linked to five out of fourteen fossil
426 samples (Fig. 5), with $\delta^{44/42}$Ca values above -1.2‰, which represent very high values
427 even considering the modern Tsavo carnivores. Excluding these five samples, it can
428 be noted that fossil and recent carnivores have identical $\delta^{44/42}$Ca values (Fig. 5)
429 implying that those hyaenids and felids already occupied similar niches as modern *C.*
430 *crocuta* and *P. leo*. There are no pure C_3 carnivores in this dataset of fossil Turkana
431 carnivores that fill the niche of extent leopards. All the fossil Turkana carnivores

examined in this paper relied on herbivores with a mixed C_3-C_4 diet and cover a wide time range.

The group (n = 5) of fossil carnivores with extremely ^{44}Ca-enriched values (Fig. 3) includes four felids with two individuals of the genus *Dinofelis* (-1.17 ± 0.10% and -1.03 ± 0.22‰), one machairodontid of the genus *Homotherium* (-1.08 ± 0.15‰) and one indeterminate felid (-1.09 ± 0.12 ‰). Three of them are characterized by saber-shaped canines, the function of which has been interpreted to deliver a weaker bite force than *P. leo* (McHenry et al. 2007). According to our carbon isotope data, this group of felids fed on herbivores that consumed a mixture of C_3-C_4 plants or the diet was a mix of grazers and browsers. The high $\delta^{44/42}$Ca values of Turkana saber-tooth cats imply an absence of bone consumption, probably reflecting adaptation to exclusive flesh-eating. Even considering such a derived feeding preference toward meat-based diet, the $\delta^{44/42}$Ca values for this group of felids remain high and applying an offset of about +0.3‰ (see 4.1) indicates a prey source with a $\delta^{44/42}$Ca enamel value around -0.8‰, i.e. not measured in our dataset. A provocative explanation would be that these carnivores relied mainly on an unanalyzed group of prey. As tempting as it may seem, two outliers may contradict such hypotheses and are represented by a machairodontine (saber-tooth) with low $\delta^{44/42}$Ca value (-1.53 ± 0.12‰) as well as a hyenid with a particularly high $\delta^{44/42}$Ca value (-0.93 ± 0.13‰), both of which should be expected to respectively display high and low $\delta^{44/42}$Ca values instead. Alternatively, the model of Skulan and DePaolo (1999) could explain high $\delta^{44/42}$Ca values in some carnivores if a large proportion of ingested calcium ends up mineralized, in other words resulting in no fractionation between mineral and diet. Clearly, more data are needed to fully cover the range of $\delta^{44/42}$Ca variations in modern mammals, but the present study already gives encouraging grounds for first order

457 paleoecological reconstructions. Tighter time intervals for the fossil record would be
458 beneficial for understanding past relationships in $\delta^{44/42}$Ca space, and additional studies
459 of modern ecosystems are also needed.

Acknowledgements

We thank the Government of Kenya for permission to sample modern and fossil samples, the Kenya Wildlife Service for assistance in the field, and the National Museums of Kenya. Samples were collected with grants from the US National Science Foundation, the Packard Foundation, and the LSB Leakey Foundation. We also thank CNRS (Tellus-Rift) and ENS-Lyon for support of this project. We thank two anonymous reviewers for their insightful comments on the last version of this work.

References

Bagard, M.L., Schmitt, A.D., Chabaux, F., Pokrovsky, O.S., Viers, J., Stille, P., Labolle, F. and Prokushkin, A.S., 2013. Biogeochemistry of stable Ca and radiogenic Sr isotopes in a larch-covered permafrost-dominated watershed of Central Siberia. *Geochimica et Cosmochimica Acta*, *114*, 169-187.

Balter, V., Person, A., Labourdette, N., Drucker, D., Renard, M., & Vandermeersch, B. (2001). Les Néandertaliens étaient-ils essentiellement carnivores? Résultats préliminaires sur les teneurs en Sr et en Ba de la paléobiocénose mammalienne de Saint-Césaire. *Comptes Rendus de l'Académie des Sciences-Series IIA-Earth and Planetary Science*, *332*(1), 59-65.

Balter, V. (2004). Allometric constraints on Sr/Ca and Ba/Ca partitioning in terrestrial mammalian trophic chains. *Oecologia*, *139*(1), 83-88.

485 Balter, V., Braga, J., Télouk, P., & Thackeray, J. F. (2012). Evidence for dietary
486 change but not landscape use in South African early hominins. *Nature*, *489*(7417),
487 558-560.
488
489 Brown FH, Mcdougall I (2011) Geochronology of the Turkana depression of northern
490 Kenya and southern Ethiopia. *Evolutionary Anthropology* 20.6: 217-227.

491 Cenki-Tok, B., Chabaux, F., Lemarchand, D., Schmitt, A. D., Pierret, M. C., Viville,
492 D., Bagard, M.-L., & Stille, P. (2009). The impact of water–rock interaction and
493 vegetation on calcium isotope fractionation in soil-and stream waters of a small,
494 forested catchment (the Strengbach case). *Geochimica et Cosmochimica Acta*, *73*(8),
495 2215-2228.
496
497 Cerling, T. E., Harris, J. M., MacFadden, B. J., Leakey, M. G., Quade, J., Eisenmann,
498 V., & Ehleringer, J. R. (1997). Global vegetation change through the
499 Miocene/Pliocene boundary. Nature, 389(6647), 153-158.
500
501 Cerling TE, JM Harris, and MG Leakey (1999) Browsing and grazing in modern and
502 fossil proboscideans. *Oecologia* 120: 364–374.

503 Cerling, T. E., Hart, J. A., Hart, T.B. 2004. Stable isotope ecology in the Ituri Forest.
504 Oecologia 138:5–12.
505
506 Cerling, T. E., Harris, J. M., Hart, J. A., Kaleme, P., Klingel, H., Leakey, M. G.,
507 Levin, N.E. Lewison, R.L. & Passey, B. H. (2008). Stable isotope ecology of the
508 common hippopotamus. *Journal of Zoology*, *276*(2), 204-212.

509

510 Cerling TE, Andanje SA, Blumenthal SA, Brown FH, Chritz KL, Harris JM, Hart JA,
511 Kirera FM, Kaleme P, Leakey LN, Leakey MG, Levin NE, Manthi FK, Passey BH,
512 Uno KT (2015) Dietary changes of large herbivores in the Turkana Basin, Kenya
513 from 4 to 1 million years ago. *Proceedings of the National Academy of Sciences.* 112:
514 11467-11472.

515

516 Channon, M. B., Gordon, G. W., Morgan, J. L., Skulan, J. L., Smith, S. M., & Anbar,
517 A. D. (2015). Using natural, stable calcium isotopes of human blood to detect and
518 monitor changes in bone mineral balance. *Bone*, *77*, 69-74.

519

520 Chu, N. C., Henderson, G. M., Belshaw, N. S., & Hedges, R. E. (2006). Establishing
521 the potential of Ca isotopes as proxy for consumption of dairy products. *Applied*
522 *geochemistry*, *21*(10), 1656-1667.

523

524 Clementz, M. T., Holden, P., & Koch, P. L. (2003). Are calcium isotopes a reliable
525 monitor of trophic level in marine settings?. *International Journal of*
526 *Osteoarchaeology*, *13*(1-2), 29-36.

527

528 Climatological Statistics for East Africa (1975) *Climatological Statistics for East*
529 *Africa*. East African Meteorological Department, Nairobi.

530

531 DePaolo, D. J. (2004). Calcium isotopic variations produced by biological, kinetic,
532 radiogenic and nucleosynthetic processes. *Reviews in mineralogy and geochemistry*,
533 *55*(1), 255-288.

534

535 Dudley, J. P., Hang'Ombe, B. M., Leendertz, F. H., Dorward, L. J., Castro, J.,
536 Subalusky, A. L., & Clauss, M. (2016). Carnivory in the common hippopotamus
537 *Hippopotamus amphibius*: implications for the ecology and epidemiology of anthrax
538 in African landscapes. *Mammal Review*, *46*(3), 191-203.

539

540 Farkaš, J., Déjeant, A., Novák, M. and Jacobsen, S.B., 2011. Calcium isotope
541 constraints on the uptake and sources of Ca2+ in a base-poor forest: a new concept of
542 combining stable (δ44/42Ca) and radiogenic (εCa) signals. *Geochimica et*
543 *Cosmochimica Acta*, *75*:7031-7046.

544

545 Gussone, N., and A. Heuser. "Biominerals and biomaterial." In *Calcium Stable*
546 *Isotope Geochemistry*, pp. 111-144. Springer, Berlin, Heidelberg, 2016.

547

548 Hassler, A., Martin, J.E., Amiot, R., Tacail, T., Arnaud Godet, F., Allain, R., Balter,
549 V. 2018. Calcium isotopes offer clues on resource partitioning among Cretaceous
550 predatory dinosaurs. Proceedings of the Royal Society B. 285: 20180197.

551

552 Hayward, M. W. (2006). Prey preferences of the spotted hyaena (Crocuta crocuta) and
553 degree of dietary overlap with the lion (*Panthera leo*). *Journal of Zoology*, *270*(4),
554 606-614.

555

556 Hayward, M. W., Henschel, P., O'brien, J., Hofmeyr, M., Balme, G., & Kerley, G. I.
557 H. (2006b). Prey preferences of the leopard (*Panthera pardus*). *Journal of Zoology*,
558 *270*(2), 298-313.
559
560 Heuser, A., & Eisenhauer, A. (2008). The calcium isotope composition (δ44/40Ca) of
561 NIST SRM 915b and NIST SRM 1486. Geostandards and Geoanalytical Research,
562 32(3), 311-315.
563
564 Heuser, A., Tütken, T., Gussone, N., & Galer, S. J. (2011). Calcium isotopes in fossil
565 bones and teeth—Diagenetic versus biogenic origin. *Geochimica et Cosmochimica*
566 *Acta*, *75*(12), 3419-3433.
567
568 Heuser, A., Eisenhauer, A., Scholz-Ahrens, K. E., & Schrezenmeir, J. (2016).
569 Biological fractionation of stable Ca isotopes in Göttingen minipigs as a physiological
570 model for Ca homeostasis in humans. *Isotopes in environmental and health studies*,
571 *52*(6), 633-648.
572
573 Heuser, A., A.-D. Schmitt, N. Gussone, and F. Wombacher. "Analytical methods." In
574 *Calcium Stable Isotope Geochemistry*, pp. 23-73. Springer, Berlin, Heidelberg, 2016.
575
576 Hindshaw, R. S., B. C. Reynolds, J. G. Wiederhold, M. Kiczka, R. Kretzschmar, and
577 B. Bourdon. (2013). Calcium isotope fractionation in alpine plants. *Biogeochemistry*
578 112, no. 1-3:373-388.
579

580 Hirata, T., Tanoshima, M., Suga, A., Tanaka, Y. K., Nagata, Y., Shinohara, A., &
581 Chiba, M. (2008). Isotopic analysis of calcium in blood plasma and bone from mouse
582 samples by multiple collector-ICP-mass spectrometry. *Analytical Sciences*, *24*(11),
583 1501-1507.
584
585 Holmden, C., & Bélanger, N. (2010). Ca isotope cycling in a forested ecosystem.
586 *Geochimica et Cosmochimica Acta*, *74*(3), 995-1015.
587
588 Martin, J. E., Tacail, T., Adnet, S., Girard, C., & Balter, V. (2015). Calcium isotopes
589 reveal the trophic position of extant and fossil elasmobranchs. *Chemical Geology*,
590 *415*, 118-125.
591
592 Martin, J. E., Tacail, T., & Balter, V. (2017a). Non-traditional isotope perspectives in
593 vertebrate palaeobiology. *Palaeontology*. 60 :485–502.
594
595 Martin, J. E., Vincent, P., Tacail, T., Khaldoune, F., Jourani, E., Bardet, N., & Balter,
596 V. (2017b). Calcium Isotopic Evidence for Vulnerable Marine Ecosystem Structure
597 Prior to the K/Pg Extinction. *Current Biology*. 27: 1641-1644.
598
599 McHenry, C.R., Wroe, S., Clausen, P.D., Moreno, K., Cunningham, E. 2007.
600 Supermodeled sabercat, predatory behavior in *Smilodon fatalis* revealed by high-
601 resolution 3D computer simulation. *Proceedings of the National Academy of Sciences.*
602 104: 16010-16015.
603

Melin, A. D., Crowley, B. E., Brown, S. T., Wheatley, P. V., Moritz, G. L., Yu, Y., Bernard, H., DePaolo, D.J., Jacobson, A.D. & Dominy, N. J. (2014). Calcium and carbon stable isotope ratios as paleodietary indicators. *American journal of physical anthropology*, *154*(4), 633-643.

Moore, J., Jacobson, A.D., Holmden, C. and Craw, D., 2013. Tracking the relationship between mountain uplift, silicate weathering, and long-term CO2 consumption with Ca isotopes: Southern Alps, New Zealand. *Chemical Geology*, *341*,110-127.

Morgan, J. L., Skulan, J. L., Gordon, G. W., Romaniello, S. J., Smith, S. M., & Anbar, A. D. (2012). Rapidly assessing changes in bone mineral balance using natural stable calcium isotopes. *Proceedings of the National Academy of Sciences*, *109*(25), 9989-9994.

Moynier, F., and T. Fujii. (2017). Calcium isotope fractionation between aqueous compunds relevant to low-temperature geochemistry, biology and medicine. *Scientific Reports*, 7, 44255.

Page, B., D., Thomas D. Bullen, and Myron J. Mitchell. (2008). Influences of calcium availability and tree species on Ca isotope fractionation in soil and vegetation. *Biogeochemistry* 88, no:1-13.

627 Passey BH, ME Perkins, MR Voorhies, TE Cerling, JM Harris, and ST Tucker, 2002,
628 Timing of C_4 biomass expansion and environmental change in the Great Plains: an
629 isotopic record from fossil horses. *Journal of Geology* 110: 123–140.
630
631 Peek, S., & Clementz, M. T. (2012). Sr/Ca and Ba/Ca variations in environmental and
632 biological sources: A survey of marine and terrestrial systems. *Geochimica et*
633 *Cosmochimica Acta*, *95*, 36-52.
634
635 Reynard, L. M., Henderson, G. M., & Hedges, R. E. M. (2010). Calcium isotope
636 ratios in animal and human bone. *Geochimica et Cosmochimica Acta*, *74*(13), 3735-
637 3750.
638
639 Reynard, L. M., Henderson, G. M., & Hedges, R. E. M. (2011). Calcium isotopes in
640 archaeological bones and their relationship to dairy consumption. *Journal of*
641 *Archaeological Science*, *38*(3), 657-664.
642
643 Reynard, L. M., Pearson, J. A., Henderson, G. M., & Hedges, R. E. M. (2013).
644 Calcium isotopes in juvenile milk-consumers. *Archaeometry*, *55*(5), 946-957.
645
646 Reynard, B., & Balter, V. (2014). Trace elements and their isotopes in bones and
647 teeth: Diet, environments, diagenesis, and dating of archeological and paleontological
648 samples. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *416*, 4-16.
649

650 Russell, W. A., & Papanastassiou, D. A. (1978). Calcium isotope fractionation in ion-
651 exchange chromatography. *Analytical Chemistry*, *50*(8), 1151-1154.
652
653 Schmitt, A.D., Chabaux, F. and Stille, P., (2003). The calcium riverine and
654 hydrothermal isotopic fluxes and the oceanic calcium mass balance. *Earth and*
655 *Planetary Science Letters*, *213*, 503-518.
656
657 Skulan, J., DePaolo, D. J., & Owens, T. L. (1997). Biological control of calcium
658 isotopic abundances in the global calcium cycle. *Geochimica et Cosmochimica Acta*,
659 *61*(12), 2505-2510.
660
661 Skulan, J., & DePaolo, D. J. (1999). Calcium isotope fractionation between soft and
662 mineralized tissues as a monitor of calcium use in vertebrates. *Proceedings of the*
663 *National Academy of Sciences*, *96*(24), 13709-13713.
664
665 Sponheimer, M., & Lee-Thorp, J. A. (2006). Enamel diagenesis at South African
666 Australopith sites: Implications for paleoecological reconstruction with trace
667 elements. *Geochimica et Cosmochimica Acta*, *70*(7), 1644-1654.
668
669 Tacail, T., Albalat, E., Télouk, P., & Balter, V. (2014). A simplified protocol for
670 measurement of Ca isotopes in biological samples. *Journal of Analytical Atomic*
671 *Spectrometry*, *29*(3), 529-535.
672

673 Tacail, T., Télouk, P., & Balter, V. (2016). Precise analysis of calcium stable isotope
674 variations in biological apatites using laser ablation MC-ICPMS. *Journal of*
675 *Analytical Atomic Spectrometry*, *31*(1), 152-162.
676
677 Tacail T, Thivichon-Prince B, Martin JE, Charles C, Viriot L, Balter V. 2017a.
678 Assessing human weaning practices with calcium isotopes in tooth enamel.
679 *Proceedings of the National Academy of Sciences*. 27: 1641–1644.

680 Tacail T, Balter V, Pelletier S, Barbesier M, Hernandez J-A, Jaouen K, Lafage-
681 Proust M-H, Lamboux A, Soulage C, Télouk P, Wegrzyn J, Albarède F & Fouque D.
682 2017b. A Comprehensive Box-Model for Calcium Isotopes in Humans. Goldschmidt
683 Conference, August 13-18, Paris.

684 Tipper, E. T., Schmitt, A. D., Gussone, N. (2016). Global Ca Cycles: Coupling of
685 Continental and Oceanic Processes. In *Calcium Stable Isotope Geochemistry* (pp.
686 173-222). Springer Berlin Heidelberg.
687
688 Valdes, M. C., Moreira, M., Foriel, J., Moynier, F. (2014). The nature of Earth's
689 building blocks as revealed by calcium isotopes. Earth and Planetary Science Letters,
690 394:135–145.
691
692 Van Valkenburgh, B. 1996. Feeding behavior in free-ranging, large African
693 carnivores. Journal of Mammalogy. 77:240–254.
694

White F (1983) *The vegetation of Africa: a descriptive memoir to accompany the UNESCO/AETFAT/UNSO vegetation map of Africa by F White*. Natural Resources Research Report XX, UNESCO, Paris, France.

Wiegand, B.A., Chadwick, O.A., Vitousek, P.M. and Wooden, J.L., 2005. Ca cycling and isotopic fluxes in forested ecosystems in Hawaii. *Geophysical Research Letters*, *32*(11).

Wieser, M. E., Buhl, D., Bouman, C., & Schwieters, J. (2004). High precision calcium isotope ratio measurements using a magnetic sector multiple collector inductively coupled plasma mass spectrometer. *Journal of Analytical Atomic Spectrometry*, *19*(7), 844-851.

Figure captions.

Figure 1. Three-isotope-plot for all data measured in this study, with $\delta^{43/42}$Ca (‰) as a function of $\delta^{44/42}$Ca (‰) relative to *ICP Ca Lyon* bracketing standard. The samples and standards fall on a line with a slope of 0.518 ± 0.028 (2SE), indistinguishable from the 0.507 slope predicted by the exponential mass-dependent fractionation law (red stippled line). Error bars correspond to 2SD. The blue line corresponds to the regression line. The red shaded area corresponds to the 95% confidence interval on the regression line.

Figure 2. A, $\delta^{44/42}$Ca variability by taxonomic groups (‰, rel. *ICP Ca Lyon*), arranged by increasing average values, as measured in tooth enamel of a mammalian assemblage from the modern ecosystem of Tsavo, Kenya. **B**, $\delta^{44/42}$Ca as a function of

720 $\delta^{13}C$ measured from tooth enamel from the same modern assemblage. Note the spatial
721 distinction between Hyenidae + *P. leo* and *P. pardus*. Abbreviations: t, tragelaphine
722 bovids.
723
724 **Figure 3. A**, Calcium isotope variability by taxonomic grouping of fossil assemblage
725 of Turkana Basin, Kenya. **B**, $\delta^{44/42}Ca$ as a function of $\delta^{13}C$ measured from tooth
726 enamel from the same fossil assemblage. Abbreviations: a, alcelaphine bovids.
727
728 **Figure 4.** Calcium isotope variability compared between soils, browser and grazer
729 tooth enamel and their potential source foods, i.e. plant parts including roots, shoots,
730 leaves/fruits and whole Poacea (data for soils and plants derived from Bagard et al.
731 2013; Chu et al. 2006; Farkas et al. 2011; Gussone and Heuser, 2016; Heuser et al.,
732 2016; Hindshaw et al. 2013; Holmden et al. 2010; Moore et al. 2013; Page et al. 2008;
733 Schmitt et al. 2003; Skulan and DePaolo, 1999; Tacail et al. 2014; Wiegand et al.
734 2005). Student t-test P values are indicated: **P = 0.001–0.01; and ***P<0.001.
735
736 **Figure 5.** $\delta^{44/42}Ca$ in fossil tooth enamel from Turkana Basin compared to $\delta^{44/42}Ca$ of
737 modern tooth enamel from Tsavo for similar taxonomic groups.
738
739
740
741
742
743
744

Supplementary data

Conversion of literature data to ICP Ca Lyon

All standards and datasets from the literature expressed in $\delta^{44/40}Ca$ values were converted to $\delta^{44/42}Ca$ by dividing by 2.048, as calculated using the exponential mass-dependent fractionation law (e.g. Russell et al., 1978, Maréchal et al., 1999).

The measured $\delta^{44/42}Ca$ values of 4 international Ca isotope standards expressed with respect to SRM915a standard were compared to 71 values from the literature as compiled from 52 publications. The constant difference of – 0.518 ± 0.025 ‰ between standards measured against SRM915a *versus* ICP Ca Lyon (Figure S1) was used to calculate the corresponding isotope compositions of international standards from the literature with respect to *ICP Ca Lyon*, as well as to compare our dataset to literature dataset published against SRM915a, Seawater, SRM915b, SRM1486, CaF2 GEOMAR, BSE and the CaCO3 standard described in Skulan et al. (1997). All the measured and compiled $\delta^{44/42}Ca$ values of Ca standards and reference materials are summarized in Table S2.

Table S1. Modern and fossil samples analyzed in this study for calcium isotope values (expressed as $\delta^{44/42}Ca$ and $\delta^{43/42}Ca$ in ‰ relative to standard ICP Ca-Lyon), carbon and oxygen isotope values as well as concentrations and concentration ratios for some major and trace elements.

Table S2. Table summarizing the isotope compositions of all 7 standards or reference materials measured or converted to *ICP Ca Lyon.* Underlined values are the values

used to convert literature datasets from a given reference material to ICP Ca Lyon when necessary.

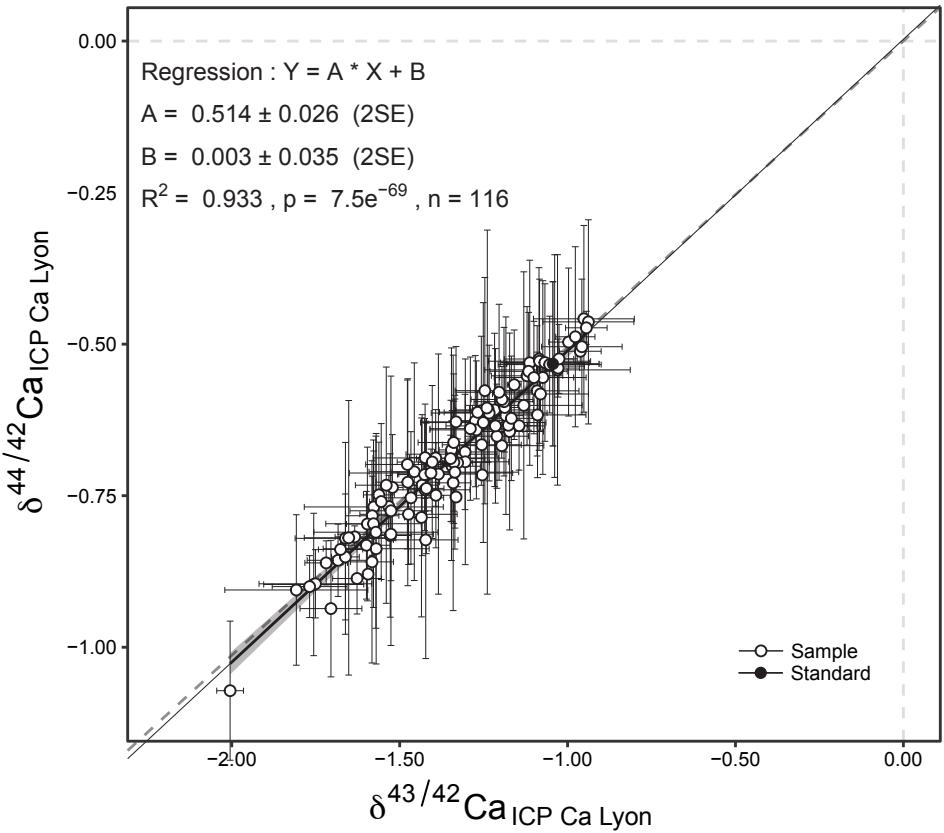
Supp. Figure 1. Literature $\delta^{44/42}$Ca average values (‰, rel. *SRM915a*) as a function of measured $\delta^{44/42}$Ca average values (‰, rel. *ICP Ca Lyon*) of 4 international Ca isotope standards (Seawater, SRM915a, SRM915b and SRM1486). This value is thus used to convert literature datasets expressed against *SRM915a* to *ICP Ca Lyon*. The blue line is the regression line for which the equation is given in blue. The dotted line is the identity line (y = x); the dotted grey line is the line with slope 1 and y-intercept of 0.518‰. The 0.518‰ value is the one used for conversions of datasets initially expressed relative to SRM915a. Error bars are 2SE (95% confidence interval from the Student's t-test).

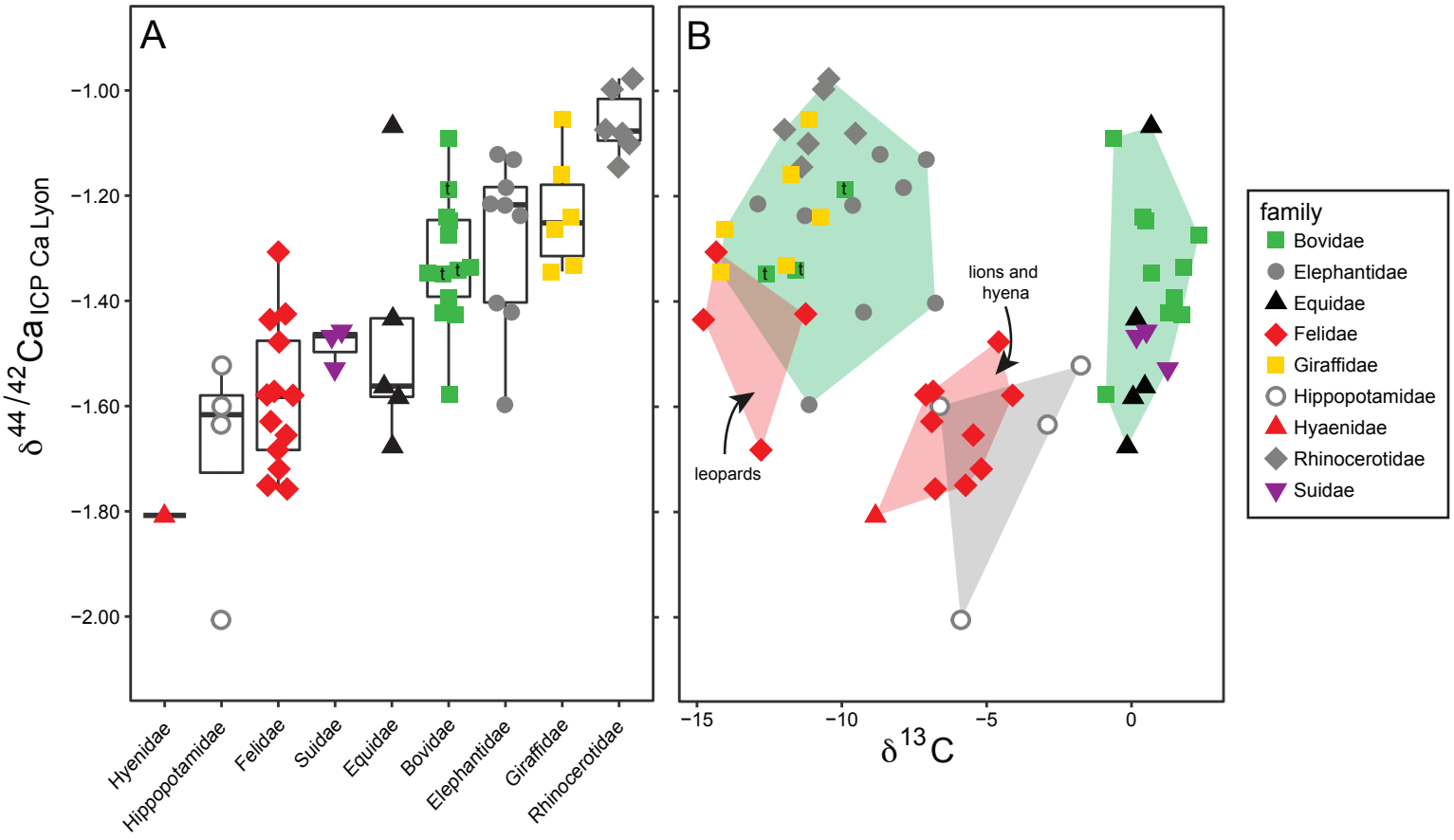
Supp. Figure 2. Log10(Sr/Ca) ratios in the modern mammal assemblage of Tsavo, Kenya represented by **A**, family groups and by **B**, ecological groups. Log10(Ba/Ca) ratios in the modern mammal assemblage of Tsavo, Kenya represented by **C**, family groups and by **D**, ecological groups.

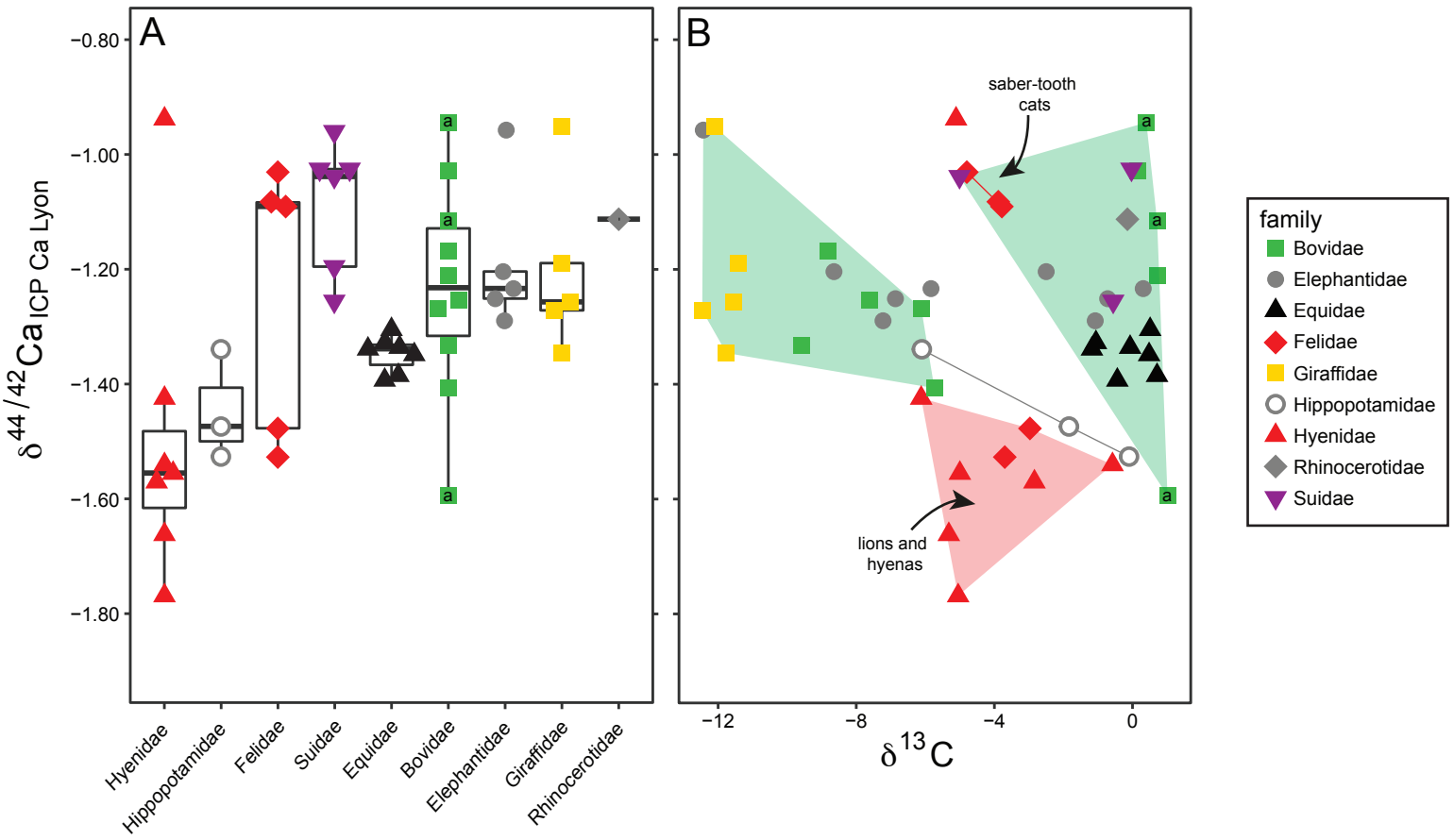
Supp. Figure 3. A, Log10(Sr/Ca) and **B**, Log10(Ba/Ca) ratios in the fossil mammal assemblage of Turkana Basin, Kenya represented by family.

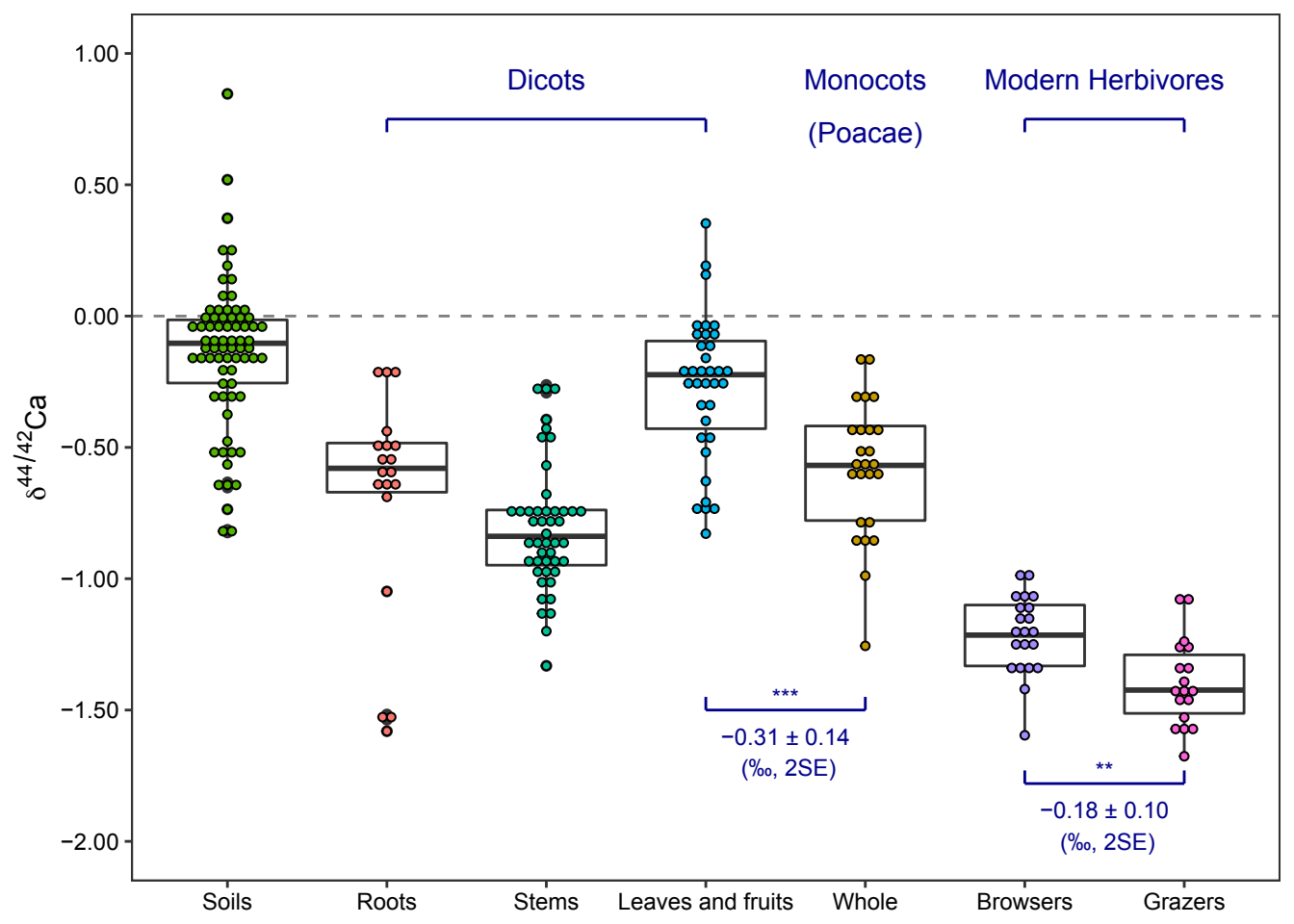
Supp. Figure 4. Trace element concentrations measured from tooth enamel samples from modern and fossil mammals analyzed in this study. Green corresponds to herbivores and red corresponds to carnivores. **A**, Ba/Ca ratios as a function of Sr/Ca ratios from the modern mammalian assemblage; **B**, Ba/Ca ratios as a function of

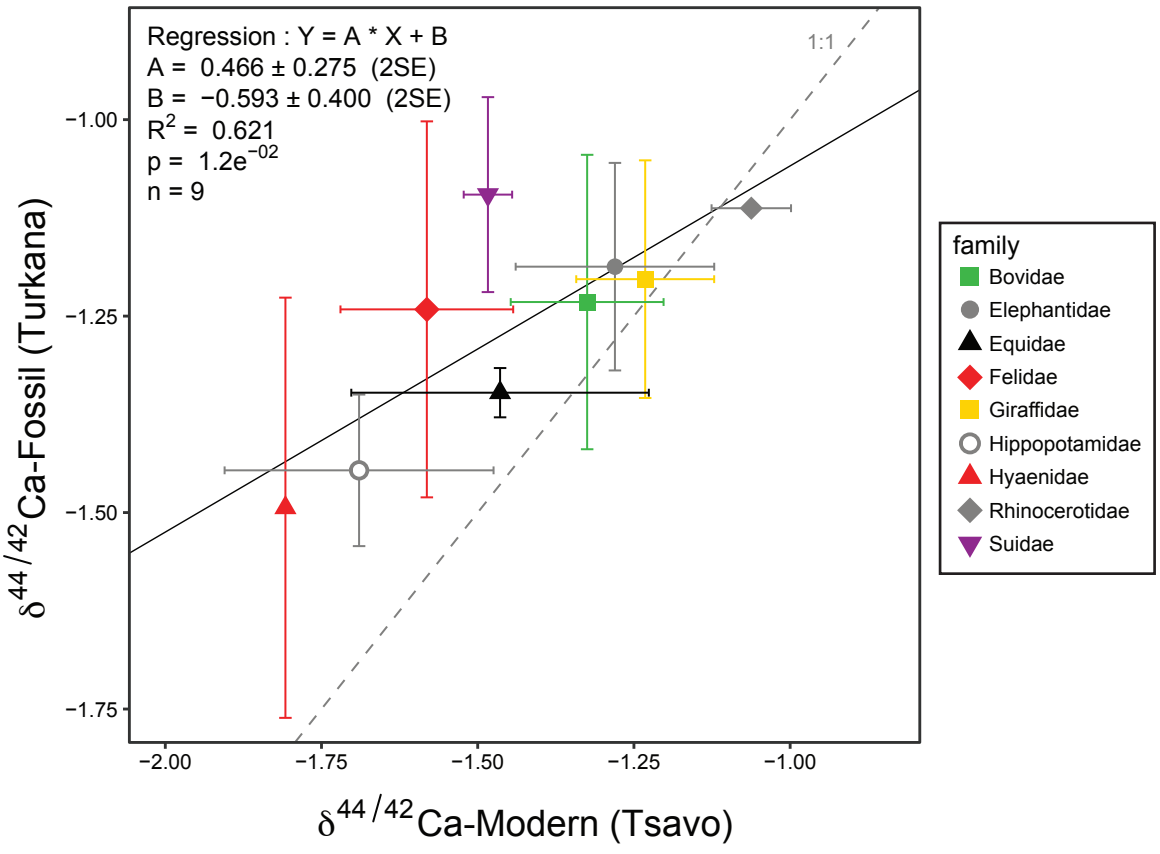
820 Sr/Ca ratios from the fossil mammalian assemblage of Turkana Basin; **C**, Mn as a
821 function of Ba from the fossil mammalian assemblage of Turkana Basin; **D**, U as a
822 function of Sr from the fossil mammalian assemblage of Turkana Basin.
823
824 **Supp. Figure 5**. Comparison of $\delta^{44/42}$Ca values measured on pairs of treated versus
825 untreated samples (in ‰, relative to *ICP Ca Lyon* standard). The blue line is the
826 identity line. Error bars are 2SD.


Regression : Y = A * X + B
A = 0.514 ± 0.026 (2SE)
B = 0.003 ± 0.035 (2SE)
R2 = 0.933 , p = 7.5e−69 , n = 116
Sample
Standard
0.00
−0.25
−0.50
−0.75
−1.00
−2.00
−1.50
−1.00
−0.50
0.00
δ44/42CaICP Ca Lyon
δ43/42CaICP Ca Lyon


A
B
−1.00
−1.20
−1.40
−1.60
−1.80
−2.00
δ44/42Ca ICP Ca Lyon
Hyenidae
Hippopotamidae
Felidae
Suidae
Equidae
Bovidae
Elephantidae
Giraffidae
Rhinocerotidae
−15
−10
−5
0
δ13C
lions and hyena
leopards
family
Bovidae
Elephantidae
Equidae
Felidae
Giraffidae
Hippopotamidae
Hyaenidae
Rhinocerotidae
Suidae


A
B
−0.80
−1.00
−1.20
−1.40
−1.60
−1.80
δ44/42Ca ICP Ca Lyon
Hyenidae
Hippopotamidae
Felidae
Suidae
Equidae
Bovidae
Elephantidae
Giraffidae
Rhinocerotidae
a
saber-tooth cats
lions and hyenas
−12
−8
−4
0
δ13C
family
Bovidae
Elephantidae
Equidae
Felidae
Giraffidae
Hippopotamidae
Hyenidae
Rhinocerotidae
Suidae


Dicots
Monocots
(Poacae)
Modern Herbivores
1.00
0.50
0.00
−0.50
−1.00
−1.50
−2.00
δ44/42Ca
***
−0.31 ± 0.14
(‰, 2SE)
**
−0.18 ± 0.10
(‰, 2SE)
Soils
Roots
Stems
Leaves and fruits
Whole
Browsers
Grazers

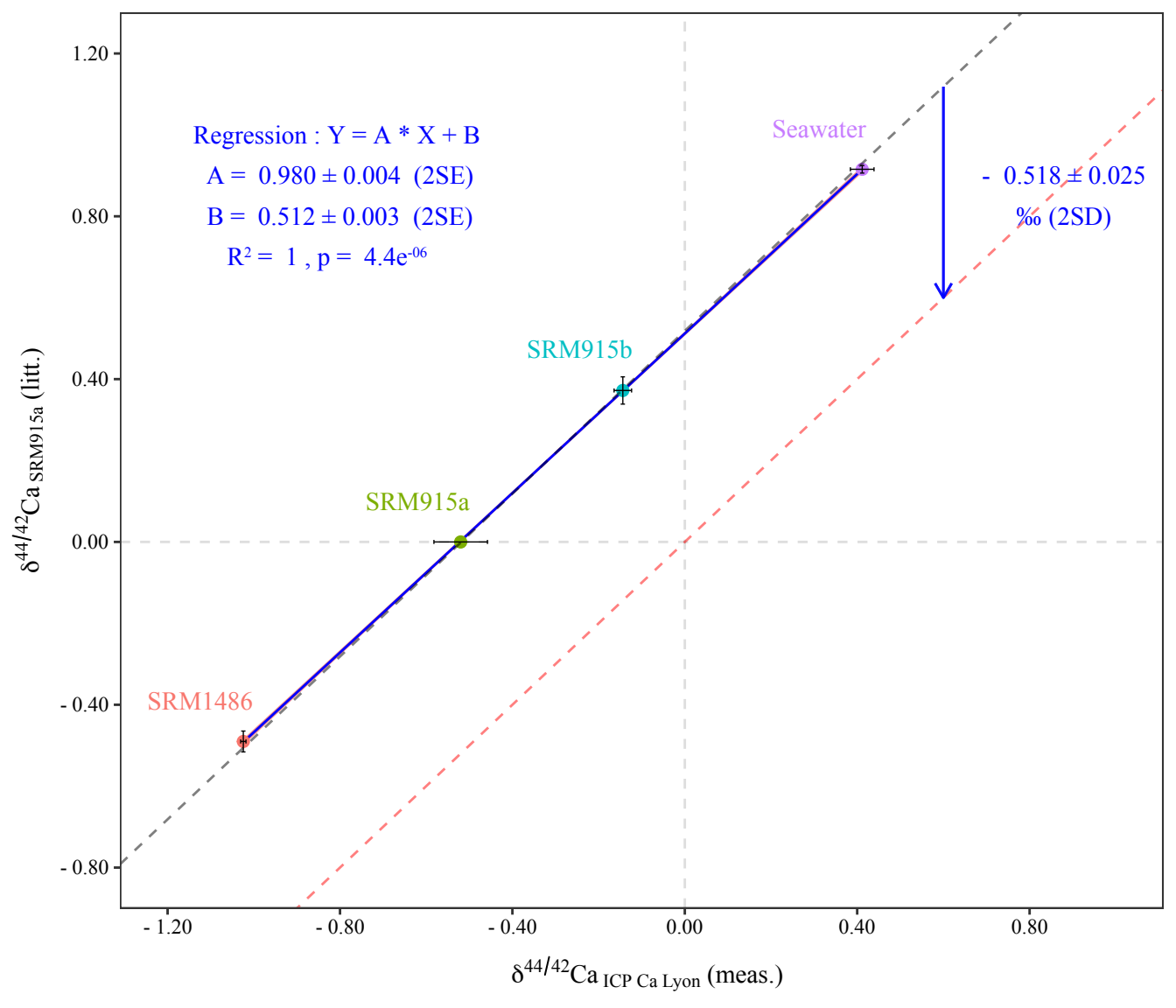

Regression : Y = A * X + B
A = 0.466 ± 0.275 (2SE)
B = −0.593 ± 0.400 (2SE)
R2 = 0.621
p = 1.2e−02
n = 9
1:1
−1.00
−1.25
−1.50
−1.75
−2.00
−1.75
−1.50
−1.25
−1.00
δ44/42Ca-Fossil (Turkana)
δ44/42Ca-Modern (Tsavo)
family
Bovidae
Elephantidae
Equidae
Felidae
Giraffidae
Hippopotamidae
Hyaenidae
Rhinocerotidae
Suidae

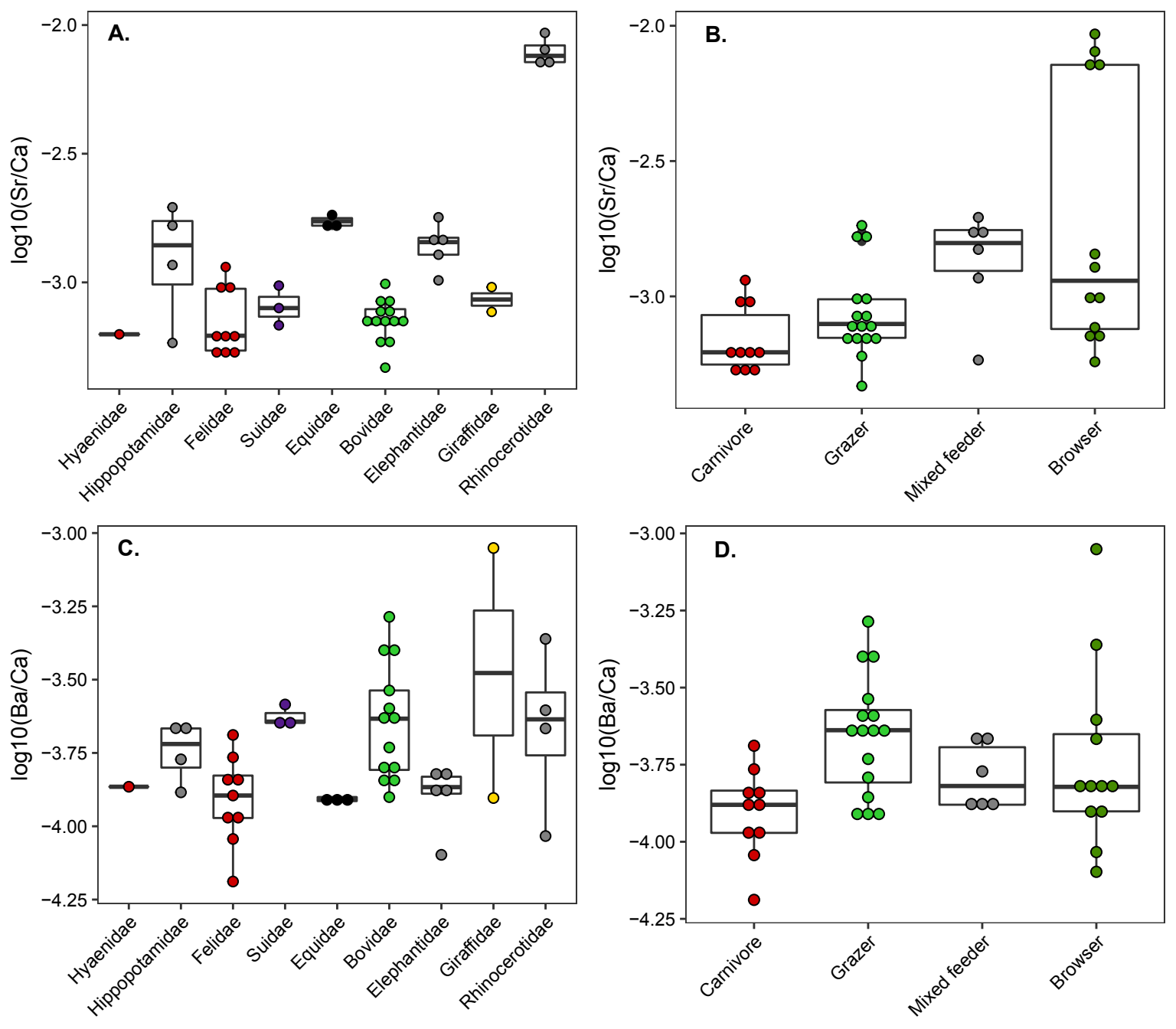
TSAVO_TURKANA	family	genus_species	DIGESTIVE.PHYSIOLOGY	ecology__δ13C	MOD_FOSS	sample_ID	treat_untreat	geol_fm	DATE_MY_BF	AGE_RANGE	tooth_type	δ13C	δ18O	δ44/42Ca (‰)	2SD	δ43/42Ca (‰)	2SD	δ44/42Ca_AV_SRM915a	n	Ca/P (AES)	Mg/Ca (AES)	Sr/Ca	Ba/Ca	Ca (%)	Mn (ppm)	U (ppm)
TSAVO	Rhinocerotidae	Diceros_bicornis	HINDGUT	browser	MODERN	K98-Tsv-128	untreated	NaN	NA	NaN	m3	-12	-0.4	-1.07	0.13	-0.56	0.16	-0.56	3	2.1	0.003842	0.007178	0.000216	33.9	20.5	NA
TSAVO	Rhinocerotidae	Diceros_bicornis	HINDGUT	browser	MODERN	K98-Tsv-129	untreated	NaN	NA	NaN	m3	-11.4	2.8	-1.14	0.05	-0.63	0.07	-0.63	3	2.1	0.005383	0.00932	0.000093	36.1	9	NA
TSAVO	Rhinocerotidae	Diceros_bicornis	HINDGUT	browser	MODERN	K98-Tsv-130	untreated	NaN	NA	NaN	m3	-10.6	-0.6	-1	0.06	-0.5	0.12	-0.48	3	2.1	0.003225	0.007169	0.000435	37.6	15.6	NA
TSAVO	Rhinocerotidae	Diceros_bicornis	HINDGUT	browser	MODERN	K98-Tsv-131	untreated	NaN	NA	NaN	m3	-10.5	-0.5	-0.98	0.06	-0.49	0.15	-0.46	3	2.1	0.00409	0.008029	0.000249	36.2	14.8	NA
TSAVO	Giraffidae	Giraffa_camelopardalis	RUMINANT_FOREGUT	browser	MODERN	K99-136-Tsv	untreated	NaN	NA	NaN	M3	-14.2	3.3	-1.34	0.08	-0.7	0.09	-0.83	3	2.1	0.008442	0.000959	0.000889	25.7	12.3	NA
TSAVO	Giraffidae	Giraffa_camelopardalis	RUMINANT_FOREGUT	browser	MODERN	K08-Tsv-209e	untreated	NaN	NA	NaN	NaN	-14.1	-0.2	-1.26	0.07	-0.63	0.02	-0.74	3	2	0.006951	0.000768	0.000125	35.1	8.4	NA
TSAVO	Elephantidae	Loxodonta_africana	HINDGUT	browser	MODERN	K98-Tsv-112	untreated	NaN	NA	NaN	m3	-8.7	0	-1.12	0.11	-0.55	0.11	-0.6	3	2.1	0.006215	0.001281	0.000154	33.1	9.5	NA
TSAVO	Elephantidae	Loxodonta_africana	HINDGUT	browser	MODERN	K98-Tsv-113	untreated	NaN	NA	NaN	m3	-9.6	0.2	-1.22	0.12	-0.61	0.13	-0.7	3	2.1	0.006053	0.00102	0.00008	35	7.1	NA
TSAVO	Elephantidae	Loxodonta_africana	HINDGUT	browser	MODERN	K08-Tsv-214e	untreated	NaN	NA	NaN	NaN	-11.3	0.4	-1.24	0.06	-0.61	0.09	-0.72	3	2.1	0.006064	0.001434	0.000148	32.8	35.7	NA
TSAVO	Bovidae	Taurotragus_oryx	RUMINANT_FOREGUT	browser	MODERN	K00-Tsv-121	untreated	NaN	NA	NaN	M2	-9.9	3.4	-1.19	0.05	-0.6	0.07	-0.67	4	2.1	0.004164	0.000727	0.000156	34.9	24.4	NA
TSAVO	Bovidae	Tragelaphus_imberbis	RUMINANT_FOREGUT	browser	MODERN	K00-Tsv-126	untreated	NaN	NA	NaN	P4	-11.6	5.1	-1.34	0.05	-0.73	0.21	-0.82	6	2	0.005805	0.0007	0.000126	35.1	37.8	NA
TSAVO	Bovidae	Tragelaphus_imberbis	RUMINANT_FOREGUT	browser	MODERN	K00-Tsv-232	untreated	NaN	NA	NaN	m3	-12.6	1.6	-1.35	0.04	-0.69	0.1	-0.83	4	2.1	0.003952	0.000573	0.000147	32.5	58.3	NA
TSAVO	Elephantidae	Loxodonta_africana	NaN	browser	MODERN	K98-tsv-114	untreated	NaN	NA	NaN	m2	-11.1	5.3	-1.6	0.06	-0.8	0.13	-1.08	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Elephantidae	Loxodonta_africana	NaN	browser	MODERN	K98-tsv-118	untreated	NaN	NA	NaN	m3	-12.9	0.6	-1.21	0.15	-0.63	0.13	-0.7	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Elephantidae	Loxodonta_africana	NaN	browser	MODERN	K98-tsv-115	untreated	NaN	NA	NaN	m5 (=m2)	-9.3	0.3	-1.42	0.05	-0.74	0.11	-0.9	2	NA	NA	NA	NA	NA	NA	NA
TSAVO	Rhinocerotidae	Diceros_NaN	NaN	browser	MODERN	K99-tsv-137	untreated	NaN	NA	NaN	M2	-11.2	0	-1.1	0.12	-0.56	0.09	-0.58	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Rhinocerotidae	Diceros_NaN	NaN	browser	MODERN	K99-tsv-138	untreated	NaN	NA	NaN	m3	-9.5	0.2	-1.08	0.14	-0.58	0.06	-0.56	4	NA	NA	NA	NA	NA	NA	NA
TSAVO	Giraffidae	Giraffa_camelopardalis	NaN	browser	MODERN	K00-tsv-111	untreated	NaN	NA	NaN	p2	-11.8	5.5	-1.16	0.02	-0.57	0.09	-0.64	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Giraffidae	Giraffa_camelopardalis	NaN	browser	MODERN	K00-tsv-112	untreated	NaN	NA	NaN	p2	-11.9	3.7	-1.33	0.09	-0.63	0.12	-0.81	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Giraffidae	Giraffa_camelopardalis	NaN	browser	MODERN	K00-tsv-131	untreated	NaN	NA	NaN	p2	-10.8	3.9	-1.24	0.04	-0.61	0.01	-0.72	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Giraffidae	Giraffa_camelopardalis	NaN	browser	MODERN	K00-tsv-147	untreated	NaN	NA	NaN	p2	-11.1	3.9	-1.05	0.15	-0.53	0.08	-0.53	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Hyaenidae	Crotuta _crotuta	CARNIVORE	carnivore	MODERN	K00-Tsv-120	untreated	NaN	NA	NaN	P2	-8.8	-2	-1.81	0.21	-0.91	0.12	-1.29	3	2.1	0.00507	0.000628	0.000136	34.6	21.7	NA
TSAVO	Felidae	Panthera_pardus	CARNIVORE	carnivore	MODERN	dII-sophia (8-	untreated	NaN	NA	NaN	C	-11.3	-3.7	-1.42	0.13	-0.74	0.01	-0.91	3	1.9	0.043991	0.000527	0.000149	21.2	5.9	NA
TSAVO	Felidae	Panthera_pardus	CARNIVORE	carnivore	MODERN	08-Tsv-203-m	untreated	NaN	NA	NaN	m3	-12.8	-2.3	-1.68	0.09	-0.86	0.06	-1.16	3	2.1	0.007102	0.001148	0.000107	36.7	14.9	NA
TSAVO	Felidae	Panthera_pardus	CARNIVORE	carnivore	MODERN	K08-Tsv-204-(	untreated	NaN	NA	NaN	C	-14.3	-2.1	-1.31	0.09	-0.68	0.1	-0.79	4	2.1	0.007232	0.000966	0.00014	35.1	35.8	NA
TSAVO	Felidae	Panthera_pardus	CARNIVORE	carnivore	MODERN	K08-Tsv-205-(	untreated	NaN	NA	NaN	c	-14.8	-1.6	-1.44	0.05	-0.79	0.16	-0.92	6	2.1	0.008222	0.000945	0.000091	33.5	11.6	NA
TSAVO	Felidae	Panthera_leo	CARNIVORE	carnivore	MODERN	K00-Tsv-119	untreated	NaN	NA	NaN	I	-6.8	1	-1.76	0.15	-0.9	0.12	-1.24	5	2.1	0.005356	0.000623	0.000172	34.6	32.5	NA
TSAVO	Felidae	Panthera_leo	CARNIVORE	carnivore	MODERN	08-Tsv-202-2	untreated	NaN	NA	NaN	C	-6.9	-1.7	-1.63	0.07	-0.89	0.06	-1.11	4	2.1	0.006446	0.000543	0.000107	36.9	10.1	NA
TSAVO	Felidae	Panthera_leo	CARNIVORE	carnivore	MODERN	K00-Tsv-801	untreated	NaN	NA	NaN	m1	-4.1	1	-1.58	0.08	-0.78	0.07	-1.06	3	2	0.00651	0.000613	0.000127	29.3	24	NA
TSAVO	Felidae	Panthera_leo	CARNIVORE	carnivore	MODERN	K00-Tsv-802	untreated	NaN	NA	NaN	m1	-5.8	-0.2	-1.75	0.17	-0.9	0.06	-1.23	5	2.1	0.005895	0.00062	0.000065	34.9	56.9	NA
TSAVO	Felidae	Panthera_leo	CARNIVORE	carnivore	MODERN	K00-Tsv-803	untreated	NaN	NA	NaN	m1	-5.2	1.4	-1.72	0.06	-0.86	0.04	-1.2	6	2.1	0.006015	0.000526	0.000205	33.3	28.1	NA
TURKANA	Felidae	Panthera_leo	NaN	carnivore	MODERN	MK-OM 8976	untreated	NaN	NA	NaN	lt C	-3.7	1.7	-1.2	0.13	-0.67	0.02	-0.68	3	2.1	0.009893	0.00127	0.000089	34.2	61.4	0
TURKANA	Felidae	Panthera_leo	NaN	carnivore	MODERN	MK-OM 8976	treated	NaN	NA	NaN	lt C	-3.7	1.7	-1.18	0.06	-0.63	0.03	-0.66	2	2.1	0.011012	0.001494	0.000117	29.2	42.9	0
TURKANA	Hyaenidae	Crocuta_crocuta	NaN	carnivore	MODERN	MK-OM 8997	untreated	NaN	NA	NaN	lt P4	-7.9	-1.9	-1.66	0.15	-0.82	0.16	-1.14	4	2.1	0.0069	0.00151	0.00006	36	37.5	0
TURKANA	Hyaenidae	Crocuta_crocuta	NaN	carnivore	MODERN	MK-OM 8997	treated	NaN	NA	NaN	lt P4	-7.9	-1.9	-1.7	0.09	-0.94	0.11	-1.19	3	2.1	0.007144	0.00156	0.00007	35.7	44.1	NA
TSAVO	Felidae	Panthera_leo	NaN	carnivore	MODERN	K00-tsv-800	untreated	NaN	NA	NaN	P4	-4.6	0.5	-1.48	0.09	-0.73	0.17	-0.96	4	NA	NA	NA	NA	NA	NA	NA
TSAVO	Felidae	Panthera_leo	NaN	carnivore	MODERN	K00-tsv-806	untreated	NaN	NA	NaN	m1	-5.5	0.8	-1.65	0.13	-0.82	0.23	-1.13	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Felidae	Panthera_leo	NaN	carnivore	MODERN	K00-tsv-808	untreated	NaN	NA	NaN	m1	-7.1	0.1	-1.58	0.14	-0.8	0.14	-1.06	5	NA	NA	NA	NA	NA	NA	NA
TSAVO	Felidae	Panthera_leo	NaN	carnivore	MODERN	K00-tsv-810	untreated	NaN	NA	NaN	dm1	-6.9	1.3	-1.57	0.18	-0.81	0.16	-1.05	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Equidae	Equus_burchelli	HINDGUT	grazer	MODERN	K98-Tsv-139	untreated	NaN	NA	NaN	M3	0.5	6	-1.56	0.05	-0.75	0.09	-1.04	3	2	0.005642	0.001728	0.000125	35.3	6.5	NA
TSAVO	Equidae	Equus_burchelli	HINDGUT	grazer	MODERN	K98-Tsv-141	untreated	NaN	NA	NaN	M3	0.1	5.9	-1.58	0.06	-0.86	0.17	-1.06	3	2	0.005131	0.001828	0.000119	34.4	8.6	NA
TSAVO	Equidae	Equus_burchelli	HINDGUT	grazer	MODERN	K98-Tsv-142	untreated	NaN	NA	NaN	P4	0.2	3.8	-1.43	0.05	-0.73	0.12	-0.91	3	2.1	0.00843	0.001597	0.000127	29.4	18.3	NA
TSAVO	Bovidae	Kobus_ellisiprymnus	RUMINANT_FOREGUT	grazer	MODERN	K00-Tsv-122	untreated	NaN	NA	NaN	M3	1.8	2.4	-1.34	0.04	-0.7	0.11	-0.82	3	2	0.006465	0.000787	0.000518	30.8	39.6	NA
TSAVO	Bovidae	Kobus_ellisiprymnus	RUMINANT_FOREGUT	grazer	MODERN	K00-Tsv-123	untreated	NaN	NA	NaN	M3	-0.9	2.6	-1.58	0.21	-0.77	0.09	-1.06	6	2.1	0.005541	0.000466	0.000252	34.2	42.7	NA
TSAVO	Bovidae	Kobus_ellisiprymnus	RUMINANT_FOREGUT	grazer	MODERN	K00-Tsv-127	untreated	NaN	NA	NaN	P4	0.5	2.8	-1.25	0.09	-0.58	0.19	-0.73	3	2.1	0.004594	0.000688	0.000398	35.7	17.7	NA
TSAVO	Bovidae	Oryx_beisa	RUMINANT_FOREGUT	grazer	MODERN	K98-Tsv-156	untreated	NaN	NA	NaN	m3	-0.6	5.1	-1.09	0.14	-0.62	0.1	-0.57	3	2.1	0.006751	0.000601	0.00029	35.5	11.3	NA
TSAVO	Bovidae	Oryx_beisa	RUMINANT_FOREGUT	grazer	MODERN	K98-Tsv-162	untreated	NaN	NA	NaN	M2	0.4	1.5	-1.24	0.14	-0.61	0.3	-0.72	3	2.1	0.006125	0.000832	0.000235	35.1	8.4	NA
TSAVO	Suidae	Phacochoerus_aethiopicus	HINDGUT	grazer	MODERN	K98-Tsv-165	untreated	NaN	NA	NaN	M3	0.2	0.7	-1.47	0.1	-0.75	0.11	-0.95	3	2.1	0.006251	0.000972	0.000227	35.1	20.3	NA
TSAVO	Suidae	Phacochoerus_aethiopicus	HINDGUT	grazer	MODERN	08-Tsv-215-1	untreated	NaN	NA	NaN	c	0.5	2.1	-1.46	0.13	-0.71	0.18	-0.94	3	2	0.015824	0.000681	0.000223	31.9	21.7	NA
TSAVO	Suidae	Phacochoerus_aethiopicus	HINDGUT	grazer	MODERN	K08-Tsv-216e	untreated	NaN	NA	NaN	NaN	1.2	0.1	-1.53	0.06	-0.82	0.13	-1.01	6	2	0.004893	0.000795	0.00026	29.7	208.2	NA
TSAVO	Bovidae	Syncerus_caffer	RUMINANT_FOREGUT	grazer	MODERN	K00-Tsv-133	untreated	NaN	NA	NaN	P2	0.7	0.9	-1.35	0.14	-0.68	0.18	-0.83	5	2.1	0.004325	0.000987	0.000186	36.2	15.9	NA
TSAVO	Bovidae	Syncerus_caffer	RUMINANT_FOREGUT	grazer	MODERN	K98-Tsv-144	untreated	NaN	NA	NaN	P2	1.3	2.1	-1.42	0.1	-0.82	0.2	-0.9	3	2.1	0.006029	0.000756	0.000399	35.2	7.3	NA
TSAVO	Bovidae	Syncerus_caffer	RUMINANT_FOREGUT	grazer	MODERN	K98-Tsv-145	untreated	NaN	NA	NaN	M3	1.7	2.4	-1.43	0.08	-0.72	0.09	-0.91	3	2.1	0.005238	0.000708	0.000139	36.5	3.9	NA
TSAVO	Bovidae	Syncerus_caffer	RUMINANT_FOREGUT	grazer	MODERN	K98-Tsv-146	untreated	NaN	NA	NaN	M3	2.3	1.3	-1.27	0.05	-0.63	0.11	-0.76	3	2.1	0.005762	0.000859	0.000233	35.5	6.3	NA
TSAVO	Bovidae	Syncerus_caffer	RUMINANT_FOREGUT	grazer	MODERN	K98-Tsv-152	untreated	NaN	NA	NaN	P4	1.5	1.9	-1.39	0.06	-0.75	0.09	-0.87	3	2.1	0.005008	0.000717	0.000162	34.8	13.3	NA
TSAVO	Equidae	Equus_burchelli	NaN	grazer	MODERN	K00-tsv-115	untreated	NaN	NA	NaN	I	0.7	2.5	-1.07	0.13	-0.53	0.13	-0.55	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Equidae	Equus_burchelli	NaN	grazer	MODERN	K00-tsv-116	untreated	NaN	NA	NaN	p3	-0.2	1.7	-1.68	0.07	-0.84	0.03	-1.16	3	NA	NA	NA	NA	NA	NA	NA
TSAVO	Hippopotamidae	Hippopotamus_amphibius	NON_RUMINANT_FOREGUT	mixed_feeder	MODERN	9-133-Tsv-RM	untreated	NaN	NA	NaN	M2	-1.8	-2.6	-1.52	0.03	-0.74	0.09	-1	3	2.1	0.003997	0.000582	0.000217	35.4	88.4	NA
TSAVO	Hippopotamidae	Hippopotamus_amphibius	NON_RUMINANT_FOREGUT	mixed_feeder	MODERN	K00-Tsv-200	untreated	NaN	NA	NaN	m3	-5.9	-1.8	-2	0.04	-1.07	0.11	-1.49	3	2.1	0.00636	0.001959	0.000215	35	122.8	NA
TSAVO	Hippopotamidae	Hippopotamus_amphibius	NON_RUMINANT_FOREGUT	mixed_feeder	MODERN	-Tsv-201 460/	untreated	NaN	NA	NaN	C	-6.6	-4.4	-1.6	0.07	-0.83	0.09	-1.08	4	2.1	0.0053	0.001169	0.000169	35.2	46.7	NA
TSAVO	Hippopotamidae	Hippopotamus_amphibius	NON_RUMINANT_FOREGUT	mixed_feeder	MODERN	K08-Tsv-208e	untreated	NaN	NA	NaN	NaN	-2.9	-3.8	-1.63	0.06	-0.82	0.02	-1.12	3	2	0.007425	0.001662	0.000131	33.5	14.3	NA
TSAVO	Elephantidae	Loxodonta_africana	HINDGUT	mixed_feeder	MODERN	K98-Tsv-110	untreated	NaN	NA	NaN	p2	-7.1	0.7	-1.13	0.17	-0.6	0.22	-0.61	4	2.1	0.006221	0.001491	0.000136	36.2	10	NA
TSAVO	Elephantidae	Loxodonta_africana	HINDGUT	mixed_feeder	MODERN	K98-Tsv-111	untreated	NaN	NA	NaN	m2	-7.9	0.7	-1.18	0.05	-0.62	0.16	-0.67	4	2.1	0.006152	0.001791	0.000129	26.9	3.5	NA
TSAVO	Elephantidae	Loxodonta_africana	NaN	mixed_feeder	MODERN	K98-tsv-119	untreated	NaN	NA	NaN	m6	-6.8	1	-1.4	0.1	-0.69	0.13	-0.88	3	NA	NA	NA	NA	NA	NA	NA
TURKANA	Giraffidae	Giraffa_cf. jumae	NaN	browser	FOSSIL	KNM-ER 6344	treated	Lonyumon	NA	4.1	lt M	-11.6	2.1	-1.26	0.08	-0.61	0.12	-0.74	3	2	0.004442	0.002708	0.000351	36.4	35.4	6.4
TURKANA	Giraffidae	Giraffa_stillei	NaN	browser	FOSSIL	KNM-ER 932	treated	KBS	NA	1.89-1.64	rUM3	-11.4	3.2	-1.19	0.09	-0.59	0.12	-0.67	3	2.2	0.004884	0.001867	0.010412	34.4	775	7.6
TURKANA	Giraffidae	Giraffa_pygmaea	NaN	browser	FOSSIL	KNM-ER 1489	treated	Lokochot	NA	3.40-3.2	LM3	-11.8	4.8	-1.35	0.04	-0.67	0.05	-0.83	3	2.1	0.007599	0.001848	0.000625	33.9	502	6.3
TURKANA	Giraffidae	Giraffa_stillei	NaN	browser	FOSSIL	KNM-ER 1488	treated	Lokochot	NA	3.40-3.2	m frag	-12.5	4	-1.27	0.14	-0.64	0.11	-0.75	4	2.1	0.004964	0.002146	0.000739	32.2	721	4.6
TURKANA	Giraffidae	Giraffa_stillei	NaN	browser	FOSSIL	KNM-ER 932	treated	KBS	NA	1.89-1.64	lUM3	-12.1	3.8	-0.95	0.15	-0.46	0.15	-0.43	4	2.1	0.004343	0.003405	0.000704	39.8	393	31
TURKANA	Bovidae	NaN_NaN	NaN	browser	FOSSIL	KNM-ER 499	untreated	Okote	NA	1.64-1.39	m2	-8.8	-1.7	-1.17	0.09	-0.62	0.1	-0.65	4	2.1	0.0064	0.002921	0.001363	22.3	945	8.8
TURKANA	Bovidae	NaN_NaN	NaN	browser	FOSSIL	f14432	untreated	KBS	NA	1.89-1.64	NaN	-9.6	-1	-1.33	NA	-0.75	NA	-0.81	1	2.1	0.010559	0.001464	0.000357	18.3	276.9	6.2
TURKANA	Deinotheridae	Deinotherium_bozasi	NaN	browser	FOSSIL	WT 3617	treated	Kanapoi	NA	4.1	m or M	-12.4	-1.8	-0.96	0.12	-0.5	0.11	-0.44	3	2.2	0.005198	0.003281	0.000417	34.8	432.6	19.9
TURKANA	Felidae	NaN_NaN	NaN	carnivore	FOSSIL	KNM-ER 6096	untreated	KBS	NA	1.89-1.64	P4 or p4	-3	-2.2	-1.53	0.01	-0.77	0.05	-1.01	3	2.2	0.008406	0.002552	0.000884	41.5	691.3	3.4
TURKANA	Felidae	NaN_NaN	NaN	carnivore	FOSSIL	KNM-ER 6096	treated	KBS	NA	1.89-1.64	P4 or p4	-3	-2.2	-1.48	0.12	-0.7	0.14	-0.96	3	2.2	0.007729	0.002346	0.000919	36.8	715.1	3.5
TURKANA	Felidae	Dinofelis?_NaN	NaN	carnivore	FOSSIL	KNM-ER 6295	untreated	Upper Burgi	NA	2-1.89	m frag	-4.8	0	-1.17	0.1	-0.64	0.16	-0.65	3	2.2	0.00875	0.005764	0.001183	38.3	759.1	13.2
TURKANA	Felidae	Dinofelis?_NaN	NaN	carnivore	FOSSIL	KNM-ER 6295	treated	Upper Burgi	NA	2-1.89	m frag	-4.8	0	-1.03	0.22	-0.54	0.19	-0.51	5	2.2	0.007527	0.005231	0.001138	37.6	770	14.6
TURKANA	Hyaenidae	NaN_NaN	NaN	carnivore	FOSSIL	KNM-ER 6096	untreated	NaN	NA	KBS or UBM	rt P4	-5.1	-2.2	-0.94	0.14	-0.46	0.17	-0.42	3	2.3	0.003954	0.005221	0.001499	32.4	1102.3	44.7
TURKANA	Hyaenidae	NaN_NaN	NaN	carnivore	FOSSIL	KNM-ER 6094	untreated	KBS	NA	1.89-1.64	rt p3	-5	-5.5	-1.55	0.03	-0.76	0.13	-1.04	3	2.2	0.004267	0.002246	0.000544	29.6	793.5	3.3
TURKANA	Hyaenidae	cf. Crocuta_NaN	NaN	carnivore	FOSSIL	KNM-ER 6093	treated	KBS	NA	1.89-1.64	lt P4	-2.8	0.4	-1.57	0.16	-0.84	0.19	-1.05	4	2.1	0.00518	0.003676	0.001065	32.9	915	1.7
TURKANA	Hyaenidae	Crocuta_ultra	NaN	carnivore	FOSSIL	KNM-ER 4041	treated	KBS or Okote	NA	1.5 to 1.8	p3	-0.6	-2.7	-1.54	0.09	-0.73	0.19	-1.02	3	2.2	0.004161	0.003745	0.000724	27.1	646.1	12.6
TURKANA	Felidae	Machairodontinae_NaN	NaN	carnivore	FOSSIL	KNM-ER 6096	treated	Upper Burgi	NA	2-1.89	rt C	-3.7	-1.1	-1.53	0.12	-0.77	0.22	-1.01	3	2.1	0.005375	0.00171	0.00054	36.3	672.1	7.8
TURKANA	Felidae	NaN_NaN	NaN	carnivore	FOSSIL	NM-ER 60971	treated	NaN	NA	NaN	rt P4	-3.8	1.4	-1.09	0.12	-0.58	0.11	-0.57	4	2.1	0.00532	0.002336	0.000861	34	1420.9	1.5
TURKANA	Felidae	Homotherium_NaN	NaN	carnivore	FOSSIL	KNM-ER 6100	treated	Upper Burgi	NA	2-1.89	rt m1	-3.9	-3.7	-1.08	0.15	-0.53	0.14	-0.57	4	2.2	0.006449	0.002944	0.000431	41.5	231.4	9.3
TURKANA	Hyaenidae	Parahyaena_howelli	NaN	carnivore	FOSSIL	KNM-KP 3255	treated	Kanapoi	NA	4.1	lt p3	-6.1	-0.4	-1.42	0.05	-0.69	0.09	-0.91	3	2.2	0.005	0.002109	0.000352	42.5	887.2	2.8
TURKANA	Hyaenidae	cf. Crocuta_NaN	NaN	carnivore	FOSSIL	NM-WT 1684	treated	ower Lomekw	NA	3.1 to 2.8	lt C	-5.1	-4.9	-1.77	0.11	-0.9	0.05	-1.25	3	2.2	0.004794	0.003484	0.000714	36.6	872.5	43
TURKANA	Hyaenidae	Crocuta_sp.	NaN	carnivore	FOSSIL	NM-WT 1685	treated	iddle Lomekw	NA	3.4 to 3.1	lt p2	-5.3	-2.5	-1.66	0.04	-0.85	0.1	-1.14	3	2.2	0.00392	0.002298	0.000895	36.1	2114.7	15.4
TURKANA	Elephantidae	Elephas_NaN	NaN	grazer	FOSSIL	WT 4124 kk-1	treated	Kanapoi	NA	4.1	m or M	-0.7	-0.2	-1.25	0.19	-0.63	0.2	-0.73	5	2.2	0.00418	0.002088	0.000263	36.2	527	15.9
TURKANA	Rhinocerotidae	Ceratotherium_NaN	NaN	grazer	FOSSIL	f6038 control	treated	Upper Burgi	NA	2-1.89	m frag	-0.1	-2.6	-1.11	0.08	-0.53	0.17	-0.59	3	2.1	0.003248	0.003013	0.001156	39.6	1890.4	4.3
TURKANA	Suidae	Notochoerus_jaegeri	NaN	grazer	FOSSIL	NM-WT 6428	untreated	NaN	NA	NaN	M3	NA	NA	-1.2	0.09	-0.59	0.05	-0.68	2	2.1	0.008014	0.002241	0.001588	16.5	508.7	17.2
TURKANA	Suidae	Notochoerus_euilus	NaN	grazer	FOSSIL	NM-WT 6425	untreated	NaN	NA	NaN	M3	NA	NA	-0.96	0.06	-0.51	0.02	-0.44	3	2.1	0.004405	0.003616	0.001187	22.2	489.3	8.1
TURKANA	Equidae	Equus_grevyi?	NaN	grazer	FOSSIL	KNM-ER 2680	treated	Okote	NA	1.64-1.39	UP3 or UP4	0.5	-1	-1.3	0.13	-0.69	0.17	-0.79	5	2.2	0.007466	0.00546	0.00072	31.3	686.8	5.6
TURKANA	Hippopotamidae	Hippopotamus_karumensis	NaN	grazer	FOSSIL	KNM-ER 4887	treated	Upper Burgi	NA	2-1.89	LM3	-0.1	-4.5	-1.53	0.13	-0.81	0.08	-1.01	5	2.2	0.005395	0.001894	0.000535	35.8	1311.5	8.4
TURKANA	Equidae	Equus_grevyi?	NaN	grazer	FOSSIL	KNM-ER 2066	treated	Okote	NA	1.64-1.39	UM1 or UM2	0.7	1.6	-1.38	0.12	-0.71	0.2	-0.87	3	2.1	0.006616	0.004028	0.000749	30.5	671	17.9
TURKANA	Bovidae	Megalotragus_isaaci	NaN	grazer	FOSSIL	KNM-ER 1035	untreated	Okote	NA	1.64-1.39	M	1	2.2	-1.59	NA	-0.88	NA	-1.08	1	2.1	0.004688	0.002806	0.000717	27.2	112	4.9
TURKANA	Bovidae	NaN_NaN	NaN	grazer	FOSSIL	KNM-ER 4354	untreated	Okote	NA	1.64-1.39	M2	0.1	2.1	-1.03	0.06	-0.54	0.05	-0.51	3	2.2	0.004442	0.002604	0.000804	17.6	406.6	5.9
TURKANA	Bovidae	NaN_NaN	NaN	grazer	FOSSIL	f11046	untreated	UBM	NA	2-1.89	NaN	0.7	-0.6	-1.21	0.09	-0.65	0.09	-0.69	3	2.2	0.004337	0.001331	0.000493	22.4	273.8	2.8
TURKANA	Bovidae	Megalotragus_isaaci	NaN	grazer	FOSSIL	KNM-ER 515	untreated	KBS	NA	1.89-1.64	M	0.4	3.8	-0.94	0.06	-0.47	0.03	-0.43	3	2.2	0.004988	0.004386	0.000987	30.9	788.1	21.3
TURKANA	Bovidae	Megalotragus_isaaci	NaN	grazer	FOSSIL	KNM-ER 2543	untreated	Okote	NA	1.64-1.39	M2	0.7	5.1	-1.12	0.11	-0.54	0.1	-0.6	4	2.2	0.004102	0.00282	0.000633	30.7	683.6	6.3
TURKANA	Equidae	Equus_Koobiforensis	NaN	grazer	FOSSIL	KNM-ER 1242	treated	KBS	NA	1.89-1.64	UM3	0.5	3.7	-1.35	0.1	-0.69	0.04	-0.83	3	2.1	0.003958	0.002449	0.000315	35.5	632.5	8.8
TURKANA	Equidae	Equus_Koobiforensis	NaN	grazer	FOSSIL	KNM-ER 1271	treated	Upper Burgi	NA	2-1.89	UM1 or UM2	-0.1	2.7	-1.34	0.19	-0.71	0.13	-0.82	5	2.1	0.00649	0.002187	0.000705	28.5	1172.1	4
TURKANA	Suidae	Notochoerus_euilis	NaN	grazer	FOSSIL	KNM-ER 225	treated	Lokochot	NA	3.40-3.2	m frag	-0.6	-1.1	-1.26	0.12	-0.67	0.05	-0.74	4	2.2	0.003573	0.002102	0.000232	37.1	806.4	3.2
TURKANA	Elephantidae	Elephas recki_recki	NaN	grazer	FOSSIL	KNM-ER 5871	treated	Upper Burgi	NA	2-1.89	m or M	0.3	-1	-1.23	0.17	-0.61	0.11	-0.72	4	2.2	0.00468	0.002368	0.000201	38.9	279.8	19.1
TURKANA	Equidae	Hipparion _sp.	NaN	grazer	FOSSIL	KNM-ER 5359	treated	KBS	NA	1.89-1.64	UM1 or UM2	-0.4	7.1	-1.39	0.19	-0.69	0.08	-0.87	4	2.2	0.004891	0.003493	0.000836	34.8	610.2	3.9
TURKANA	Suidae	Metridiochoerus_andrewsi	NaN	grazer	FOSSIL	KNM-ER 3696	treated	Upper Burgi	NA	2-1.89	M3	0	2	-1.03	0.05	-0.52	0.06	-0.51	3	2.2	0.005307	0.002931	0.001043	38.3	1540.8	12.2
TURKANA	Suidae	Kolpochoerus_heseloni	NaN	mixed_feeder	FOSSIL	KNM-ER 6150	untreated	Lonyumon	NA	4.1	M3	-5	-3.7	-1.09	0.1	-0.52	0.15	-0.57	3	2.2	0.0048	0.002163	0.000788	30.5	745.9	8.6
TURKANA	Suidae	Kolpochoerus_heseloni	NaN	mixed_feeder	FOSSIL	KNM-ER 6150	treated	Lonyumon	NA	4.1	M3	-5	-3.7	-1.04	0.09	-0.54	0.18	-0.52	3	2.1	0.004601	0.001913	0.000765	35.6	963.1	10.1
TURKANA	Elephantidae	Loxodonta_adaurora	NaN	mixed_feeder	FOSSIL	WT 3833	treated	Kanapoi	NA	4.1	m or M	-1.1	2.2	-1.29	0.12	-0.64	0.12	-0.77	5	2	0.005159	0.002133	0.000599	36.7	563	13.9
TURKANA	Hippopotamidae	Hippopotamus_protoamphibius	NaN	mixed_feeder	FOSSIL	KNM-ER 4119	treated	Lokochot	NA	3.40-3.2	m frag	-6.1	-3.1	-1.34	0.11	-0.66	0.11	-0.82	3	2.2	0.003917	0.001957	0.000628	37.7	1340	9.6
TURKANA	Equidae	Equus_grevyi?	NaN	mixed_feeder	FOSSIL	KNM-ER 2672	treated	Okote	NA	1.64-1.39	UM1 or UM2	-1.1	2.8	-1.33	0.04	-0.7	0.04	-0.81	3	2.2	0.005695	0.003552	0.000335	26.6	463.5	29.1
TURKANA	Hippopotamidae	Hippopotamus_karumensis	NaN	mixed_feeder	FOSSIL	KNM-ER 2186	treated	KBS	NA	1.89-1.64	m frag	-1.8	-4.1	-1.47	0.14	-0.78	0.08	-0.96	3	2.1	0.004337	0.00154	0.00035	35.4	349.9	6.8
TURKANA	Bovidae	NaN_NaN	NaN	mixed_feeder	FOSSIL	KNM-ER 4350	untreated	Okote	NA	1.64-1.39	m1	-6.1	-2.4	-1.27	0.1	-0.61	0.04	-0.75	2	2.1	0.005908	0.002162	0.0006	24.7	359.7	2.2
TURKANA	Equidae	Hipparion_hasumense	NaN	mixed_feeder	FOSSIL	KNM-ER 2788	untreated	ulu Bor - Low	NA	3-2.52	LM	-1.2	-2.7	-1.34	0.11	-0.69	0.1	-0.82	3	2.2	0.00467	0.002867	0.000489	23.7	363.7	15
TURKANA	Bovidae	NaN_NaN	NaN	mixed_feeder	FOSSIL	f7075	untreated	Okote	NA	1.64-1.39	m	-5.7	-1.8	-1.41	0.24	-0.71	0.04	-0.89	2	2.1	0.003941	0.001497	0.000454	22.9	227.3	6.1
TURKANA	Bovidae	NaN_NaN	NaN	mixed_feeder	FOSSIL	f12085	untreated	UBM	NA	2-1.89	NaN	-7.6	-1.2	-1.25	NA	-0.72	NA	-0.74	1	2.1	0.013293	0.001703	0.00043	21.8	256	2.4
TURKANA	Elephantidae	Elephas_ekorensis	NaN	mixed_feeder	FOSSIL	WT 3614	treated	Kanapoi	NA	4.1	m or M	-2.5	1.1	-1.2	0.13	-0.58	0.15	-0.69	4	2.2	0.004856	0.002546	0.000397	33.6	475.2	14.1

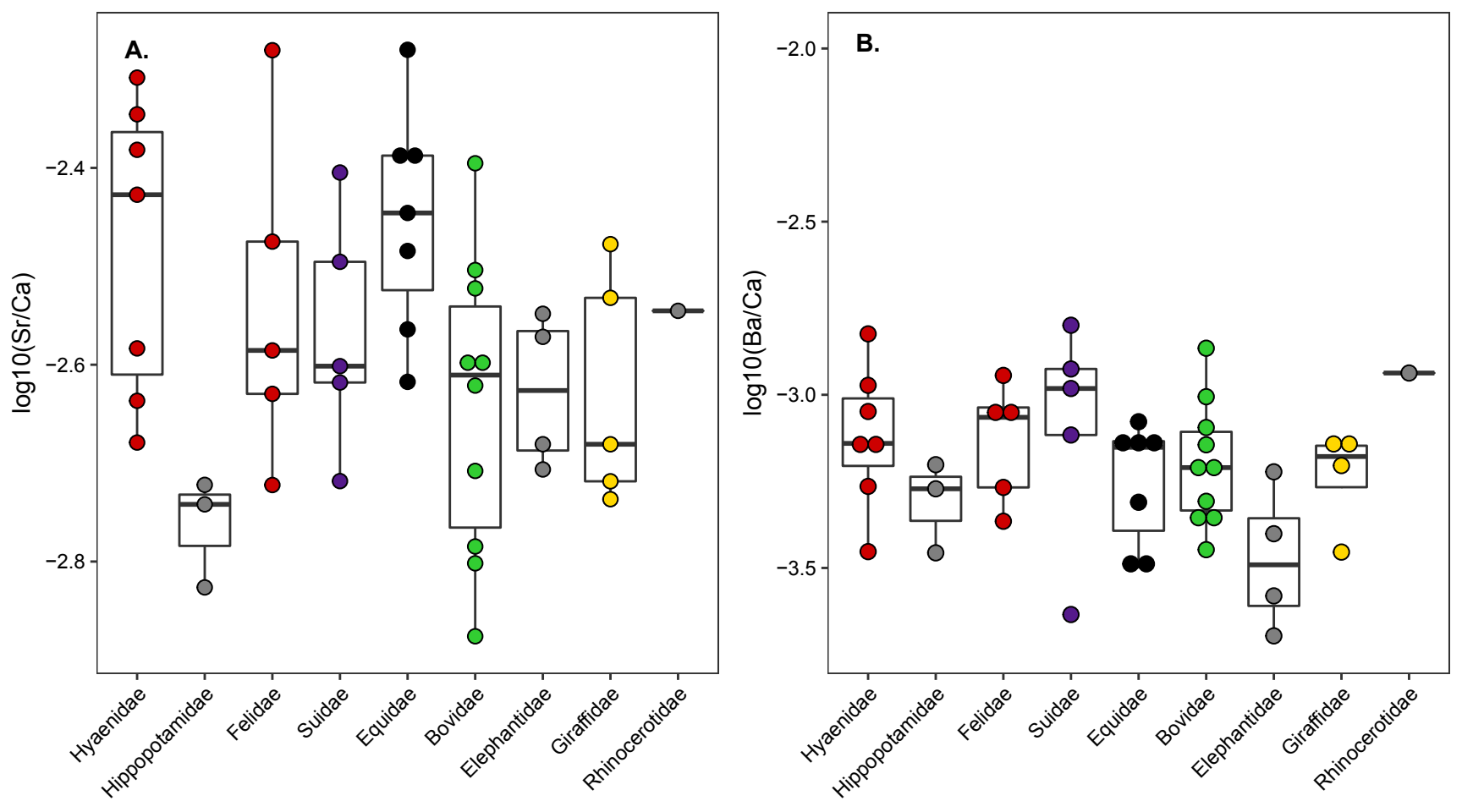
Standard as sample	Method	*n*	$\delta^{44/42}$Ca (‰) rel. *ICP Ca Lyon*	2SD	2SE	$\delta^{44/42}$*Ca (‰)* *rel. Literature Ref. Mat.*		Conv. to *ICP Ca Lyon* by adding :	References
Seawater	*Measured*	*17 meas.*	**0.412**	0.107	0.027	**-**	-	-	32, 51, 52
	Converted	*39 ref.*	**0.397**	0.057	0.009	**0.916**	*rel. SRM915a*	-0.518	1-5, 8-11, 13, 20-30, 36, 40, 41, 43, 44, 45, 49, 50, 54, 55, 57, 59
SRM915b	*Measured*	*26 meas.*	**-0.144**	0.101	0.020	**-**	-	-	32, 51-53
	Converted	*7 refs.*	**-0.146**	0.073	0.034	**0.372**	*rel. SRM915a*	-0.518	6, 11, 15, 20, 40, 42, 58
SRM915a	*Measured*	*5 meas.*	**-0.520**	0.100	0.062	**-**	-	-	53
	Used for conversion	-	**-0.518**	**-**	**-**	**0.000**	*rel. SRM915a*	-0.518	-
SRM1486	*Measured*	*101 meas.*	**-1.047**	0.130	0.013	**-**	-	-	This study
	Measured	*404 meas.*	**-1.024**	0.125	0.006	**-**	-	-	14, 33-34, 51-53
	Converted	*5 refs.*	**-1.009**	0.041	0.026	**-0.490**	*rel. SRM915a*	-0.518	15, 18, 19, 31
CaF2 GEOMAR	*Converted*	*13 refs.*	**0.180**	0.041	0.013	**0.698**	*rel. SRM915a*	-0.518	5, 12, 13, 16, 17, 22, 36, 39, 44, 45, 54
BSE	*Converted*	*5 refs.*	**-0.036**	0.021	0.013	**0.482**	*rel. SRM915a*	-0.518	7, 35, 37, 38, 46
CaCO3 *(Skulan et al. 1997)*	*Converted*	*2 refs.*	**-0.023**	0.041	NA	**-0.435**	*rel. Seawater*	+0.412	47, 48

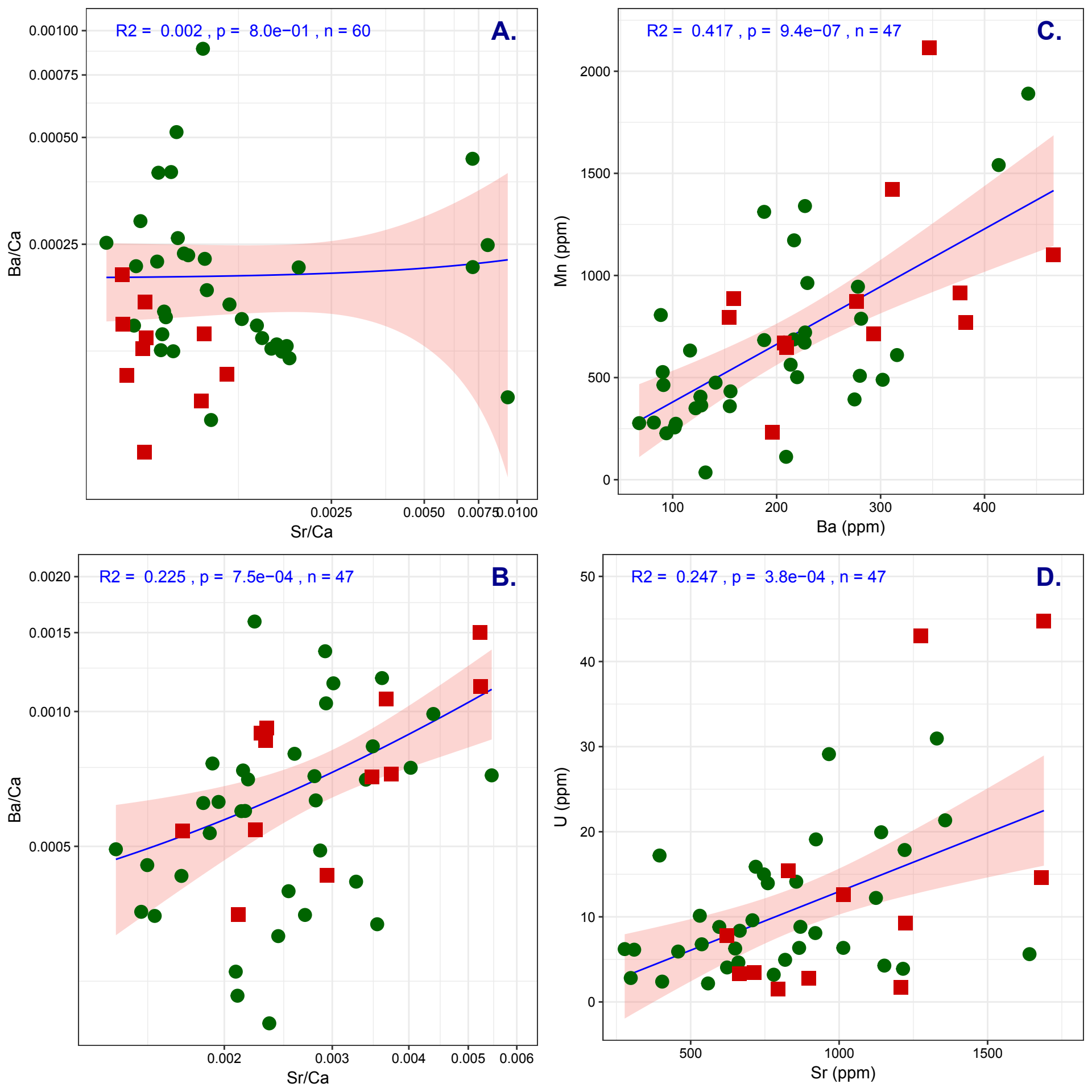
References

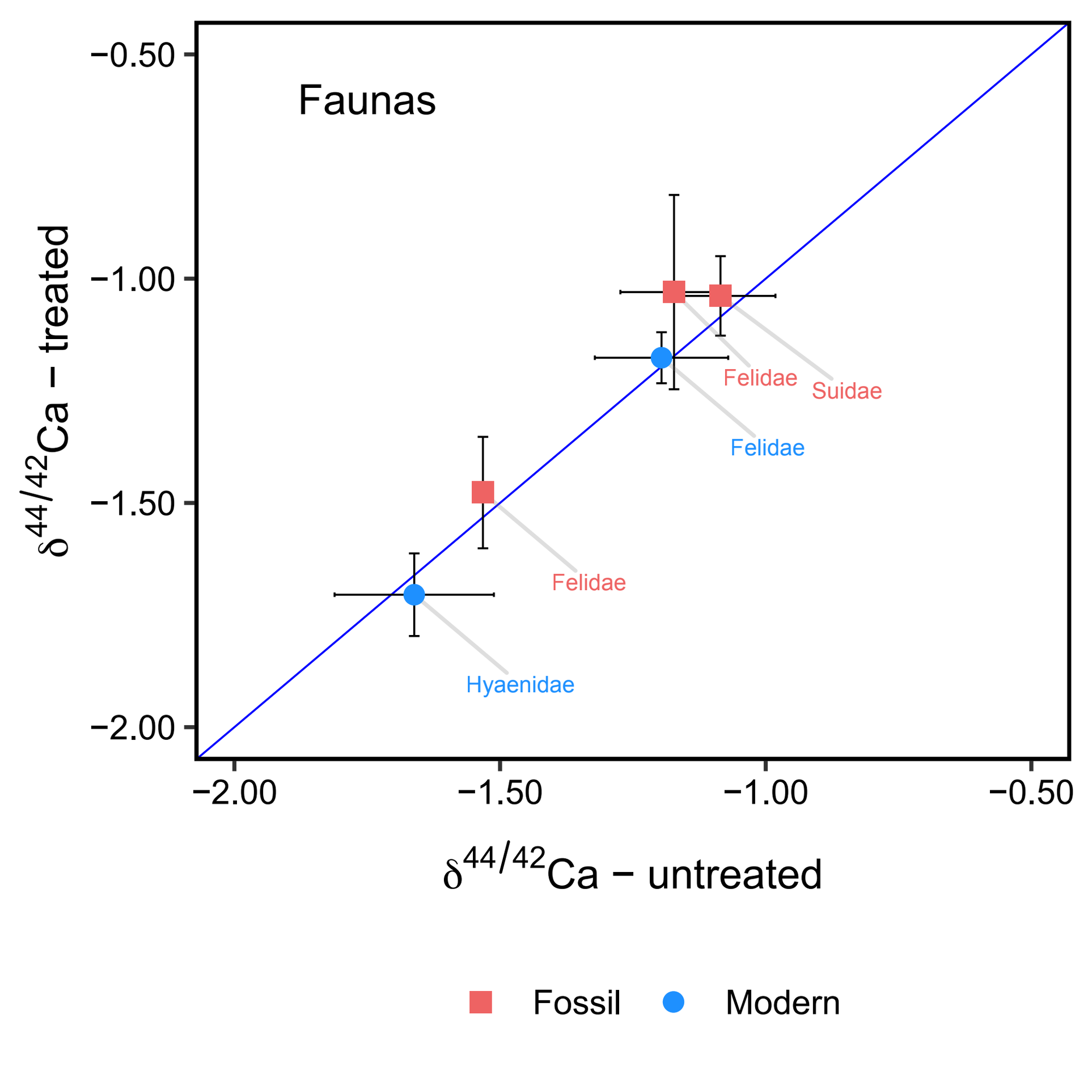
1 Amini et al. 2008 Geoch. Cosm. Acta. 72(16), 4107-4122.
2 Amini et al. 2009 Geostand. Geoanal. Res. 33(2), 231-247.
3 Böhm et al. 2006 Geoch. Cosm. Acta. 70(17), 4452-4462.
4 Chang et al. 2004 Biochem. Biophys. Res. Comm. 323(1), 79-85.
5 Cobert et al. 2011 Rapid Comm. Mass Spec. 5(19), 2760-2768.
6 Colla et al. 2013 Geoch. Cosm. Acta. 121, 363-373.
7 Fantle 2015 Geoch. Cosm. Acta. 148, 378-401.
8 Farkas et al. 2007 Earth. Planet. Sci. Lett. 253(1-2), 96-111.
9 Farkas et al. 2007 Geoch. Cosm. Acta. 71(21), 5117-5134.
10 Farkas et al. 2011 Geoch. Cosm. Acta. 75(22), 7031-7046.
11 Feng et al. 2016 Geostand. Geoanal. Res. 41(1)
12 Gussone et al. 2003 Geoch. Cosm. Acta. 67(7), 1375-1382.
13 Harouaka et al. 2014 Geoch. Cosm. Acta. 184, 114-131.
14 Hassler et al. 2018 Proc. Roy. Soc. B 285(1876), 20180197.
15 Heuser and Eisenhauer 2008 Geostand. Geoanal. Res. 32(3)
16 Heuser et al. 2002 Int. J. Mass. Spec. 220(3), 385-397.
17 Heuser et al. 2005 Paleoceano. Paleoclim. 20(2).
18 Heuser et al. 2011 Geoch. Cosm. Acta. 75(12), 3419-3433.
19 Heuser et al. 2016 Isotopes. Environ. Health Stud. 52(6), 633-648.
20 Hindshaw et al. 2011 Geoch. Cosm. Acta. 75(1), 106-118.
21 Hindshaw et al. 2013 Earth. Planet. Sci. Lett. 374, 173-184.
22 Hippler et al. 2003 Geostand. Newslett. 27(1), 13-19.
23 Holmden et al. 2010 Geoch. Cosm. Acta. 74(3), 995-1015.
24 Holmden et al. 2012 Geoch. Cosm. Acta. 83, 179-194.
25 Huang et al. 2010 Earth. Planet. Sci. Lett. 292(3-4), 337-344.
26 Huang et al. 2012 Geoch. Cosm. Acta. 77, 252-265.
27 Jacobson and Holmden 2008 Earth. Planet. Sci. Lett.
28 Jacobson et al. 2015 Earth. Planet. Sci. Lett. 416, 132-142.
29 Kasemann et al. 2008 Earth. Planet. Sci. Lett. 270(3-4), 349-353.
30 Lehn and Jacobson 2015 J. Anal. At. Spec. 30(7), 1571-1581.
31 Li et al. 2015 Chem. Geol. 422, 1-12.
32 Martin et al. 2015 Chem. Geol.415, 118-125
33 Martin et al. 2017a Curr. Biol. 27,1641-1644.
34 Martin et al. 2017b Palaeontology 60, 485-502.
35 Melin et al. 2014 American J. Phys. Anthr. 154(4), 633-643.
36 Mueller et al. 2011 Geoch. Cosm. Acta. 75(8), 2088-2102.
37 Nielsen et al. 2012 Handbook Environ. Isotope. Geochem. 105-124
38 Nielsen and DePaolo 2013 Geoch. Cosm. Acta. 118, 276-294.
39 Ockert et al. 2013 Geoch. Cosm. Acta. 112, 374-388.
40 Reynard et al. 2011 Geoch. Cosm. Acta. 75(13), 3726-3740.
41 Romaniello et al. 2015 J. Anal. At. Spec. 30(9), 1906-1912.
42 Schiller et al. 2012 J. Anal. At. Spec. 27(1), 38-49.
43 Schmitt et al. 2003 Geoch. Cosm. Acta. 67(14), 2607-2614.
44 Schmitt et al. 2009 J. Anal. At. Spec. 24(8), 1089-1097.
45 Schmitt et al. 2013 Geoch. Cosm. Acta. 110, 70-83.
46 Simon and DePaolo 2010 Earth. Planet. Sci. Lett. 289(3-4), 457-466.
47 Skulan and DePaolo 1999 Proc. Nat. Acad. Sci. 96(24), 13709-13713.
48 Skulan et al. 1997 Geoch. Cosm. Acta. 61(12), 2505-2510.
49 Skulan et al. 2007 Clin. Chem. 53(6), 1155-1158.
50 Steuber and Buhl 2006 Geoch. Cosm. Acta. 70(22), 5507-5521.
51 Tacail et al. 2014 J. Anal. At. Spec. 29(3), 529-535.
52 Tacail et al. 2016 J. Anal. At. Spec. 31(1), 152-162.
53 Tacail et al. 2017 Proc. Nat. Acad. Sci. 201704412.
54 Teichert et al. 2009 Earth. Planet. Sci. Lett. 279(3), 373-382.
55 Tipper et al. 2010 Global Biogeochem. Cycles 24(3).
56 Used for conversion
57 Wieser et al. 2004 J. Anal. At. Spec. 19(7), 844-851.
58 Wombacher et al. 2009 J. Anal. At. Spec. 24(5), 627-636.
59 Zhu et al. 2015 Geostand. Geoanal. Res. 40(2).


Regression : Y = A * X + B
A = 0.980 ± 0.004 (2SE)
B = 0.512 ± 0.003 (2SE)
R² = 1 , p = 4.4e-06
Seawater
- 0.518 ± 0.025
‰ (2SD)
SRM915b
SRM915a
SRM1486
1.20
0.80
0.40
0.00
- 0.40
- 0.80
- 1.20
- 0.80
- 0.40
0.00
0.40
0.80
δ44/42Ca SRM915a (litt.)
δ44/42Ca ICP Ca Lyon (meas.)


A.
B.
C.
D.
log10(Sr/Ca)
log10(Ba/Ca)
−2.0
−2.5
−3.0
−3.00
−3.25
−3.50
−3.75
−4.00
−4.25
Hyaenidae
Hippopotamidae
Felidae
Suidae
Equidae
Bovidae
Elephantidae
Giraffidae
Rhinocerotidae
Carnivore
Grazer
Mixed feeder
Browser


A.
log10(Sr/Ca)
−2.4
−2.6
−2.8
B.
log10(Ba/Ca)
−2.0
−2.5
−3.0
−3.5
Hyaenidae
Hippopotamidae
Felidae
Suidae
Equidae
Bovidae
Elephantidae
Giraffidae
Rhinocerotidae


R2 = 0.002 , p = 8.0e−01 , n = 60
A.
Ba/Ca
Sr/Ca
0.00100
0.00075
0.00050
0.00025
0.0025
0.0050
0.0075
0.0100
R2 = 0.417 , p = 9.4e−07 , n = 47
C.
Mn (ppm)
Ba (ppm)
2000
1500
1000
500
0
100
200
300
400
R2 = 0.225 , p = 7.5e−04 , n = 47
B.
Ba/Ca
Sr/Ca
0.0020
0.0015
0.0010
0.0005
0.002
0.003
0.004
0.005
0.006
R2 = 0.247 , p = 3.8e−04 , n = 47
D.
U (ppm)
Sr (ppm)
50
40
30
20
10
0
500
1000
1500


Faunas
−0.50
−1.00
−1.50
−2.00
δ44/42Ca − treated
−2.00
−1.50
−1.00
−0.50
δ44/42Ca − untreated
Felidae
Suidae
Felidae
Felidae
Hyaenidae
Fossil
Modern