

Enamel diagenesis at South African Australopith sites: Implications for paleoecological reconstruction with trace elements

M. Sponheimer^{a,b,*}, J.A. Lee-Thorp^{b,c}

^a Department of Anthropology, University of Colorado at Boulder, Boulder, CO 80309, USA

^b Department of Archaeology, University of Cape Town, Rondebosch 7701, South Africa

^c Department of Archaeological Sciences, University of Bradford, Bradford BD7 1DP, UK

Received 27 October 2005; accepted in revised form 27 December 2005

Abstract

Elemental ratio data from archaeological and paleontological bone have often been used for paleoecological reconstruction, but recent studies have shown that, even when solubility profiling techniques are employed in an attempt to recover biogenic signals, bone is an unreliable material. As a result, there has been renewed interest in using enamel for such studies, as it is known to be less susceptible to diagenesis. Nevertheless, enamel is not immune from diagenetic processes, and several studies have suggested that paleoecologically relevant elements may be altered in fossil enamel. Here, we investigate Sr, Ba, Zn, and Pb compositions of enamel from South African karstic cave sites in an effort to ascertain whether or not this material provides reliable paleoecological information. We compared enamel data for mammals from three fossil sites aged 1.8–3.0 Ma, all of which are on dolomites, with data from modern mammals living on dolomitic and granitic substrates. Sr/Ca and Ba/Ca are about three times higher in enamel from modern mammals on granites than those living on dolomites, stressing the need for geologically appropriate modern/fossil comparisons. After pretreatment with dilute acid, we found no evidence of increased Sr/Ca, Ba/Ca, or Pb/Ca in fossil enamel. In contrast, Zn/Ca increased by over five times at one site (Makapansgat), but much more subtly elsewhere. Ecological patterning in Sr/Ca, Ba/Ca, and Sr/Ba ratios was also retained in fossil enamel. This study suggests that Sr/Ca, Ba/Ca, and Pb/Ca data likely preserve paleoecological information from these sites, but also demonstrates that geologically similar sites can differ in the degree to which they impart certain elements (Zn in this case) to fossils. Thus, screening is probably necessary on a site-by-site basis. Lastly, further investigation of elemental distributions in modern foodwebs is necessary before elemental ratio analysis can become a common tool for paleoecological reconstruction.

© 2006 Elsevier Inc. All rights reserved.

1. Introduction

Elemental analysis of archaeological and paleontological bone has been a widely used tool for paleoecological reconstruction based upon the premise that systematic variations in elemental ratio data (e.g., Sr/Ca and Ba/Ca) are related to differences in trophic behavior (e.g., Toots and Voorhies, 1965; Brown, 1974; Schoeninger, 1979; Sillen, 1981; Klepinger, 1984; Lambert et al., 1984; Price et al., 1985; Sillen, 1992; Safont et al., 1998; Balter et al., 2002; Palmqvist et al., 2003). Such applications have been questioned, however, due to growing concerns about

diagenesis as well as problems of interpretation (e.g., Sillen, 1981; Nelson et al., 1986; Dauphin, 1989; Tuross et al., 1989; Price et al., 1992; Burton and Wright, 1995; Sponheimer et al., 2005a). In order to circumvent the problems of elemental diagenesis, Sillen developed a sophisticated “solubility profiling” technique that aimed to extract a near-original biogenic component based on the differing solubility properties of various apatites and carbonates (Sillen, 1981, 1992). Several studies have shown, however, that even when these painstaking techniques are used, diagenetic strontium often cannot be eradicated from bone and dentine (Sillen, 1981, 1986; Budd et al., 2000; Hoppe et al., 2003; Trickett et al., 2003; Lee-Thorp and Sponheimer, 2003). This has led to recent attempts to investigate paleoecology using elemental ratios in modern enamel

* Corresponding author. Fax: +1 916 313 3226.

E-mail address: msponheimer@yahoo.com (M. Sponheimer).

(Sponheimer et al., 2005a), which as a denser, far more crystalline and ordered apatitic tissue (LeGeros, 1991; Elliot, 1994), is more resistant to post-mortem alteration than bone (e.g., Lee-Thorp and van der Merwe, 1987, 1991; Ayliffe et al., 1994; Wang and Cerling, 1994; Michel et al., 1995, 1996; Sponheimer and Lee-Thorp, 1999a; Hoppe et al., 2003; Lee-Thorp and Sponheimer, 2003).

Nevertheless, enamel is not immune from diagenetic processes. It may be structurally and isotopically altered (Michel et al., 1995; Sponheimer and Lee-Thorp, 1999a; Schoeninger et al., 2003) and become enriched in rare-earth elements (Grandjean and Albarède, 1989; Toyoda and Tokonami, 1990; Kohn et al., 1999; Trueman and Tuross, 2002) during fossilization, although these changes are very small compared to those in poorly crystalline bone and dentine (e.g., Lee-Thorp and van der Merwe, 1991; Michel et al., 1996; Kohn et al., 1999; Budd et al., 2000; Trueman and Tuross, 2002; Trickett et al., 2003; Dauphin and Williams, 2004). More significantly for our purposes here, however, is that a few studies have suggested that elements used for investigating paleoecology—both paleodiets (Sr, Ba, Zn; Sillen and Kavanagh, 1982; Klepinger, 1984; Gilbert et al., 1994; Safont et al., 1998) and paleolandscapes (Sr, Pb; Hoppe et al., 1999; Montgomery et al., 2000; Müller et al., 2003)—may also be altered in enamel, to one extent or another, over geological time. For example, Dauphin and Williams (2004) noted that fossil enamel from a variety of African fossil sites was enriched in Sr (as well as Fe) compared to modern enamel; and Kohn et al. (1999) argued that Ba, and possibly Sr, were diagenetically enriched in enamel from the Kenyan early hominin site Allia Bay.

Nonetheless, the degree to which these findings can be generalized to enamel at other fossil sites remains uncertain. Others have found little or no evidence that enamel is enriched in either Sr or Zn even after more than 60 million years (Wyckoff and Doberenz, 1968; Bocherens et al., 1994), or that enamel Sr-isotope compositions are significantly altered over time (Budd et al., 2000; Montgomery et al., 2000; Hoppe et al., 2003; Lee-Thorp and Sponheimer, 2003; Trickett et al., 2003). This highlights the importance of the taphonomic history, burial environment, and surrounding sediment in determining the nature of alteration in any given set of fossils (e.g., Sillen, 1986, 1989; Dauphin and Williams, 2004). Of particular interest here is the degree to which previous studies of enamel diagenesis pertain to enamel from large mammals interred in South African early hominin sites, as material from such sites has been used in a series of elemental paleodietary studies (Sillen, 1992; Sillen et al., 1995; Sponheimer et al., 2005a), and because much of our previous work has focused on reconstructing the diets of hominins from these sites using stable carbon isotopes (Lee-Thorp et al., 1994; Sponheimer et al., 1999, 2005b). So the question we are asking here is: what evidence is there that paleoecologically relevant enamel elemental compositions are altered during fossilization at these sites?

In fact, there have been very few studies of alteration in the enamel elemental concentrations of terrestrial mammals in general, much less in the karstic environments that typify the South African early hominin sites. The most comprehensive mammalian study focused largely (but not entirely) on rodent teeth (Dauphin and Williams, 2004), and while suggestive, might not prove illustrative of the changes that occur in the enamel of large-bodied mammals, as fossil rodent teeth have often been altered by gastric acids in the alimentary tracts of avian predators (Brain, 1981; Andrews, 1990). And even though Kohn et al. (1999) examined large mammal teeth from the early hominin site Allia Bay, it is on the shores of highly alkaline Lake Turkana which favors recrystallization to fluorapatite (Schoeninger et al., 2003), and we cannot assume that diagenetic processes at the South African karstic caves are similar. Indeed, there is limited evidence suggesting that this is not the case, as rodent bones from alkaline lake sites in East Africa are highly enriched in Sr and Ba (Denys et al., 1996), while rodent bones from karstic cave sites in South Africa are not (Dauphin and Denys, 1992). Hence, there is good reason to believe that enamel diagenesis in these two regions is generally dissimilar.

There are also a few methodological issues that make previous studies of enamel diagenesis difficult to interpret from a paleoecological context. Firstly, few multiple-element studies pretreated fossil enamel to remove diagenetic contaminants, which is standard procedure for paleoecological studies using fossil enamel (e.g., Lee-Thorp and van der Merwe, 1987, 1991; Lee-Thorp et al., 1994; Koch et al., 1994; Cerling et al., 1999; Sponheimer et al., 1999; Schoeninger et al., 2003). Hence, even if exogenous ions were present either within inclusions or incorporated within the apatite itself, this might not tell us about the levels of diagenetic contaminants post-pretreatment. We have found, for instance, that up to 50% of the carbonate in fossil enamel specimens can be diagenetic, but that even under these extreme circumstances, it is usually bound in secondary carbonate minerals or in highly soluble apatitic domains that are completely removed with 0.1 M acetic acid (Sponheimer, 1999). Similarly, Kohn et al. (1999) suggest that the principle elemental contamination in their fossil samples was in the form of oxyhydroxides, which are likely removed using standard pretreatment protocols (Price et al., 1992; Balter et al., 2002).

A second, and we believe, crucial issue is that the inherent variability in trace element distributions in calcified tissues has been largely unappreciated. Sillen (1988) reported coefficients of variation (CVs) for Sr/Ca for a single species in a single location (Nagapande, Zimbabwe) of up to 71%, although CVs of 30–40% are more typical for individual species in any given area (Price et al., 1985; Sillen, 1988; Sponheimer et al., 2005a). In fact, even in controlled-feeding studies intraspecific CVs tend to be about 20% (Schoeninger, 1979; Price et al., 1986). Hence, the natural variation in mammalian elemental compositions is such that large numbers of samples are required to adequately characterize

a species, much less entire mammalian communities. Yet, most previous studies looked at very small numbers of modern and fossil mammals. Kohn et al. (1999), for instance, examined only five modern and five fossil teeth.

Lastly, there are often problems of geographic comparability between the modern and fossil samples. Dauphin and Williams (2004) compared modern rodent enamel from France, Morocco, Algeria, and Tanzania to fossil rodent enamel from South Africa (as well as other places). While this study had large sample sizes, it is not at all clear that comparisons between disparate locations are appropriate given the importance of local geology in governing mammalian elemental concentrations (e.g., Wyckoff and Doberenz, 1968; Sillen and Kavanagh, 1982; Burton et al., 2003).

Here, we provide new elemental ratio data for modern and fossil enamel from South Africa in an effort to address the above concerns, and in so doing, better our understanding of diagenesis at South African early hominin sites. As it is our aim to investigate enamel diagenesis as it directly pertains to paleoecological reconstruction, we have limited our analysis to four elements (Sr, Ba, Zn, and Pb) that others have suggested provide paleoecological information (e.g., Elias et al., 1982; Sillen and Kavanagh, 1982; Klepinger, 1984; Gilbert et al., 1994; Safont et al., 1998; Montgomery et al., 2000; Müller et al., 2003; Palmqvist et al., 2003).

2. Materials and methods

2.1. Samples

Modern teeth from two areas were analyzed. We sampled 39 teeth from animals on granitic substrates in the Greater Kruger National Park (KNP), South Africa, as well as 12 teeth from animals on dolomitic substrates around the well-known South African early hominin sites. We also sampled fossil teeth from Swartkrans (Member 1, 1.8 Ma; 29 teeth), Sterkfontein (Member 4, 2.5 Ma; 19 teeth), and Makapansgat Limeworks (Member 3, 3.0 Ma; 50 teeth), all of which are karstic cave sites formed in the 2.5–2.6 Ga Malmani Dolomites of South Africa. Some of the first australopith specimens were discovered in these caves (more than a decade before similar finds were unearthed in East Africa), and they are also among the world's most fossiliferous hominin sites with hundreds of thousands of specimens retrieved to date (Brain, 1981). Hence, they are very important sites for students of human evolution. All of the specimens were sampled at either the Transvaal Museum or the Bernard Price Institute for Palaeontological Research, both of which are located in Gauteng, South Africa. We restricted this study to late-forming teeth, as enamel from early-forming teeth is formed partially during infancy when mammals may not have fully developed their capacity to discriminate against strontium (Lengeman, 1963; Lough et al., 1963; McClellan, 1964; Rivera and Harley, 1965).

2.2. Analytical and statistical methods

Enamel powder (~3 mg) was removed from permanent, late-forming teeth (e.g., bovid M₃s) using a rotary drill with a diamond-tipped dental burr. Enamel was collected from as large an area of the tooth as possible to ensure that the sample contained enamel laid down over many months, and in some cases years. The enamel powder was pre-treated with 0.1 M acetic acid for 10 min to remove contaminants and rinsed to neutrality with triply distilled, deionized water (Sponheimer, 1999). The remaining sample was then dissolved in 1 ml of 40% HF: 65% HNO₃ (4:1) in closed teflon beakers. After complete dissolution the beakers were opened and the samples evaporated to dryness on a hotplate. The residue was then dissolved in 0.5 ml of 65% HNO₃ and evaporated to dryness. After further dissolution in 0.5 ml of 65% HNO₃, the samples were dried and dissolved in 10 ml of 5% HNO₃ solution and finally analyzed along with several multi-element standard solutions for Sr, Ba, Zn, Pb, and Ca on a Perkin-Elmer Elan 6000 ICP-MS. The precision of this instrument for these elements is better than 3%. Elemental data are presented as ratios (e.g., (Ba/Ca) * 1000) as is typical for paleoecological applications (e.g., Sillen, 1992; Sillen et al., 1995; Balter et al., 2002; Palmqvist et al., 2003; Balter, 2004).

We looked for differences in Sr/Ca, Ba/Ca, Zn/Ca, and Pb/Ca between sites/areas using analysis of variance (ANOVA), and where significant differences were found we performed pairwise comparisons using Fisher's PLSD test. All data were log-transformed to obtain normal distributions prior to statistical analysis, but non-transformed data are presented in the tables and figures to maximize comparability between this and previous studies (e.g., Price et al., 1985; Sillen, 1992; Gilbert et al., 1994; Sillen et al., 1995; Safont et al., 1998; Palmqvist et al., 2003).

3. Results

3.1. Modern and fossil elemental ratio data

ANOVA reveals highly significant differences in Sr/Ca, Ba/Ca, and Zn/Ca between sites/areas ($P < 0.0001$) (Table 1; Fig. 1; all data discussed herein can be found in [electronic annex EA-1](#)). Pairwise comparisons show that most of these differences are between the mammals on granitic substrates (KNP) and those on dolomites (all others), with mean Sr/Ca and Ba/Ca at least 2.5 times higher on the granitic substrates. This observation demonstrates, again, the importance of local geology in determining mammalian elemental compositions. In contrast, there are no significant differences in the Pb/Ca of the modern or fossil sites except between the modern granites and the fossil site Swartkrans ($P < 0.01$). Notably, Pb/Ca for animals on the modern dolomites and all three fossil sites are statistically indistinguishable ($P > 0.48$); thus, there is no evidence that Pb has been altered in any way through time at these fossil sites. This fidelity, or consistency, is significant for

Table 1

Elemental ratio means, standard errors, and sample sizes for modern tooth enamel from two geological substrates and from three fossil sites in South Africa

| Site | Age | <i>n</i> | Sr/Ca | SE | Ba/Ca | SE | Zn/Ca | SE | Pb/Ca | SE |
|--------------|--------|----------|-------|------|-------|------|-------|------|-------|------|
| Granites | Modern | 39 | 2.10 | 0.21 | 0.85 | 0.12 | 1.80 | 0.73 | 0.17 | 0.03 |
| Dolomites | Modern | 12 | 0.83 | 0.14 | 0.27 | 0.06 | 1.27 | 0.20 | 0.10 | 0.02 |
| Swartkrans | 1.8 Ma | 29 | 0.74 | 0.04 | 0.32 | 0.05 | 1.97 | 0.26 | 0.06 | 0.01 |
| Sterkfontein | 2.5 Ma | 19 | 0.81 | 0.09 | 0.22 | 0.04 | 2.39 | 0.30 | 0.20 | 0.11 |
| Makapansgat | 3.0 Ma | 50 | 0.35 | 0.03 | 0.18 | 0.02 | 7.11 | 0.49 | 0.11 | 0.02 |

The data distributions are shown in Fig. 1. We did not obtain Pb data for some teeth, so the Pb/Ca sample sizes for the modern granites and Makapansgat are reduced to 25 and 41, respectively.

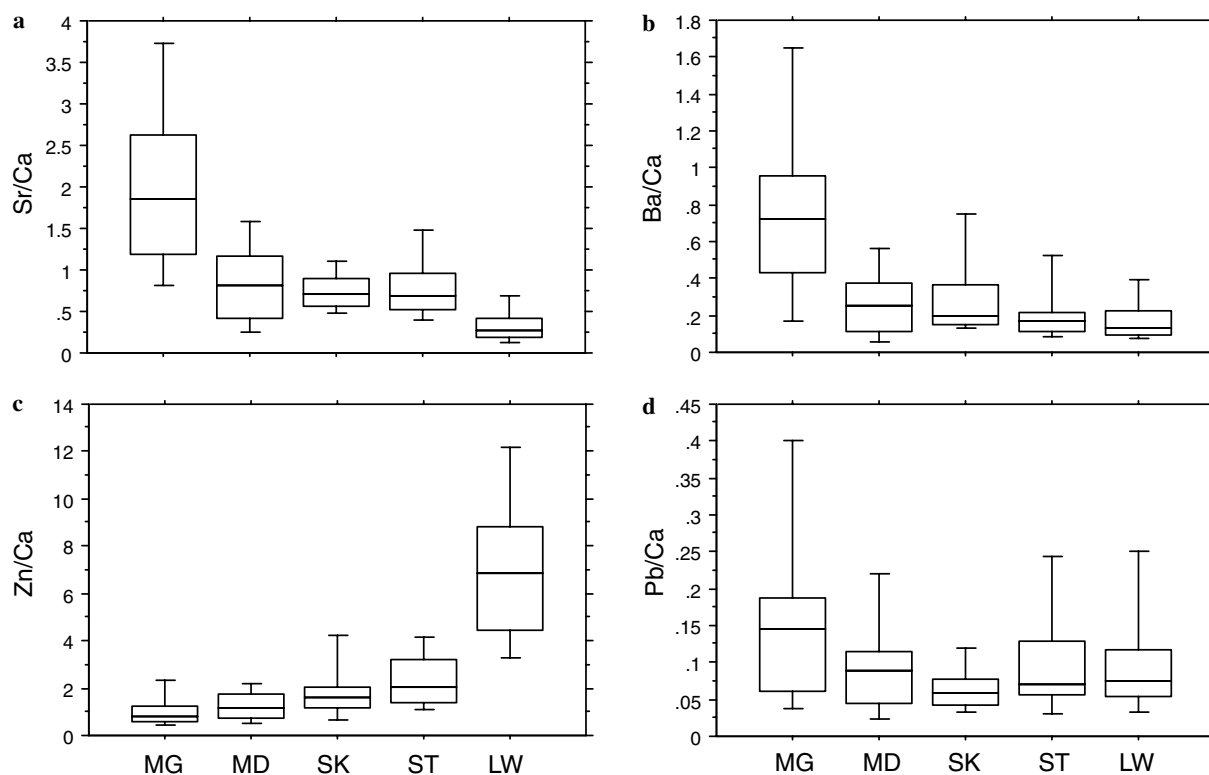


Fig. 1. Sr/Ca (a), Ba/Ca (b), Zn/Ca (c), and Pb/Ca (d) for mammals from the granites of Kruger National Park (MG), dolomites in the vicinity of fossil hominin sites (MD), Swartkrans Member 1 (SK), Sterkfontein Member 4 (ST), and Makapansgat Limeworks Member 3 (LW). The boxes represent the 25th–75th percentiles (with the medians as horizontal lines) and the whiskers show the 10th–90th percentiles.

although Pb/Ca ratios are not generally believed to reveal much about paleodiet (but see Elias et al., 1982), lead isotopes can be important for determining “local” and “immigrant” individuals at archaeological and paleontological sites (e.g., Montgomery et al., 2000; Müller et al., 2003), and thus can help answer questions about distances traveled by species across the paleolandscape.

Likewise, there is no evidence that diagenetic Sr or Ba have become structurally incorporated within the fossil enamel analyzed here. None of the fossil fauna are significantly different from fauna from the modern dolomites in Ba/Ca ($P > 0.16$). Moreover, the Sr/Ca of the Swartkrans and Sterkfontein fauna is not different from that of fauna on the modern dolomites ($P > 0.81$). Makapansgat, in contrast, has lower Sr/Ca ($P < 0.001$); however, this result is at

least partly due to the preponderance of browsing taxa at the site, since they tend to have low Sr/Ca (see below and Sponheimer et al., 2005a). It is also possible that the geology in the immediate vicinity of the site supports vegetation with anomalously low Sr/Ca. Regardless, there is no evidence that exogenous Sr ions have become incorporated to a significant/detectable extent in fossil enamel at this site.

It is not the case, however, that *no* elemental concentrations have increased at these sites. At Makapansgat, enamel Zn/Ca ratios are nearly six times greater than those from the modern dolomites ($P < 0.0001$), and at least three times greater than those from the other fossil sites ($P < 0.0001$). In fact, linear regression reveals a significant temporal trend with Zn/Ca becoming greater over time

($P < 0.0001$; $R^2 = 0.48$); this is at least partially an artifact of the exceptional values at Makapansgat, however, as Swartkrans enamel Zn/Ca is not significantly different from that of the modern dolomites ($P = 0.12$). It may be that Zn contamination is a common problem at these sites, but it appears to be particularly egregious at Makapansgat. This is not surprising, for fossils from Makapansgat (particularly Member 3) are commonly stained by manganese (Brink and Partridge, 1980; Maguire, 1998), also a transition metal with a smaller ionic radius (0.46 Å) than calcium (0.99 Å). Our data cannot be used to pinpoint the location in which the diagenetic Zn resides in the Makapansgat fossils (within the apatite itself or within secondary minerals), but Zn²⁺ substitution for larger Ca²⁺ ions within the crystal lattice is known to occur in synthetic apatites (LeGeros, 1991), so incorporation of exogenous Zn within enamel apatite due to dissolution/precipitation phenomena at crystal surfaces and in highly soluble microdomains is to be expected (Rey et al., 1991; Sponheimer and Lee-Thorp, 1999a). Zn substitution for Sr at Ca-sites might also contribute to the lower Sr/Ca at this site, and might signal moderate leaching of native Sr from enamel therein.

3.2. Modern and fossil ecological patterning

Given that the traditional paleodietary elements (Ba and Sr) have been minimally altered at these sites, we should then expect the same ecological patterning of elemental ratios in the modern and fossil faunas. This cannot be tested using our modern dolomite specimens as they are too few, or with our 3 Ma Makapansgat specimens, as they are dominated by one ecological type (browsing herbivores); however, we do have sufficient numbers of specimens and

ecological diversity from the KNP, and from the combined Sterkfontein Valley sites (Swartkrans and Sterkfontein are only 1 km from each other and are on identical geological substrates), to attempt such an analysis.

Yet, we must first address the question of what type of ecological patterning to expect? Mammals discriminate against Ba and Sr with respect to Ca in the digestive tract and kidneys (Walser and Robinson, 1963; Kostial et al., 1969; Spencer et al., 1973; Kobayashi and Suzuki, 1990; Leggett, 1992; Sips et al., 1997), and as a result herbivore tissues have lower Ba/Ca and Sr/Ca ratios than the plants that they eat, and carnivores in turn have lower Ba/Ca and Sr/Ca than the herbivores they consume (e.g., Elias et al., 1982; Burton et al., 1999; Blum et al., 2000). Systematic variation in Ba/Ca and Sr/Ca within trophic levels is also known to occur (Sealy and Sillen, 1988; Sillen, 1988; Gilbert et al., 1994; Burton et al., 1999; Balter et al., 2002; Sponheimer et al., 2005a), although the exact nature of the distributions and the mechanisms responsible for them remain poorly understood. Our data for plants and animals in the KNP might exemplify and clarify these patterns. Although there is a great deal of inter- and intraspecific variation in plant Ba/Ca ratios in KNP, there is a systematic difference in the Ba/Ca of grasses and browse plants (forbs and trees), with the former having higher Ba/Ca than the latter ($P < 0.01$) (Table 2). This distinction is ultimately passed down to the herbivores within KNP, as Ba/Ca is significantly higher in grazers than in browsers ($P = 0.01$), and as expected, carnivore Ba/Ca is lower than that of both herbivore groups ($P < 0.02$) (Fig. 2a; Table 2; see observed ratios in Table 2). A similar pattern is also evident in the Sr/Ca of plants and animals in Kruger, although the distinctions between groups are not always

Table 2
Elemental ratio means, standard errors, and sample sizes of grazers, browsers, carnivores, molarats, browse plants, and graze plants in the Kruger National Park

| Group | <i>n</i> | Sr/Ca | SE | Ba/Ca | SE | Sr/Ba | SE |
|-----------------------------|----------|-------|------|-------|------|-------|-------|
| KNP mammals | | | | | | | |
| Browsers | 9 | 1.12 | 0.12 | 0.62 | 0.08 | 2.12 | 0.37 |
| Carnivores | 7 | 1.37 | 0.20 | 0.36 | 0.11 | 4.98 | 0.92 |
| Grazers | 14 | 2.61 | 0.28 | 1.41 | 0.27 | 2.38 | 0.36 |
| <i>C. hottentotus</i> | 3 | 4.18 | 1.54 | 0.41 | 0.28 | 33.15 | 17.35 |
| KNP plants | | | | | | | |
| Browse | 7 | 8.63 | 1.38 | 4.36 | 1.45 | 3.45 | 0.65 |
| Graze | 11 | 11.35 | 1.30 | 14.56 | 3.03 | 1.22 | 0.41 |
| Sterkfontein valley mammals | | | | | | | |
| Browsers | 7 | 0.47 | 0.07 | 0.25 | 0.03 | 1.84 | 0.18 |
| Carnivores | 8 | 0.66 | 0.07 | 0.16 | 0.02 | 4.42 | 0.60 |
| Grazers | 9 | 0.92 | 0.10 | 0.68 | 0.08 | 1.43 | 0.16 |
| <i>A. africanus</i> | 7 | 1.10 | 0.15 | 0.15 | 0.02 | 7.60 | 1.10 |

The same data are also provided for fossil browsers, carnivores, and grazers from the Sterkfontein Valley. Data distributions are shown in Figs. 2–5. Zn/Ca and Pb/Ca data are not included as they manifest no ecological patterning in our modern and fossil datasets. Observed Ratio_{enamel-diet} (OR) values for the KNP browsers, grazers, and carnivores are 0.13, 0.23 (herbivore mean = 0.18), and 0.53, respectively, for Sr, and 0.14, 0.10 (herbivore mean = 0.12), and 0.26 for Ba. We caution, however, that given the massive inter- and intraseasonal variability in plant elemental compositions (e.g., Razic et al., 2003), our small dry season plant sample is only sufficient to show general patterns, not properly calculate OR values. Carnivore OR values were estimated assuming grazers were their principle foods (Sponheimer, unpublished data). Once again, however, these numbers mean little except when calculated using known prey species, which was not possible in this case.

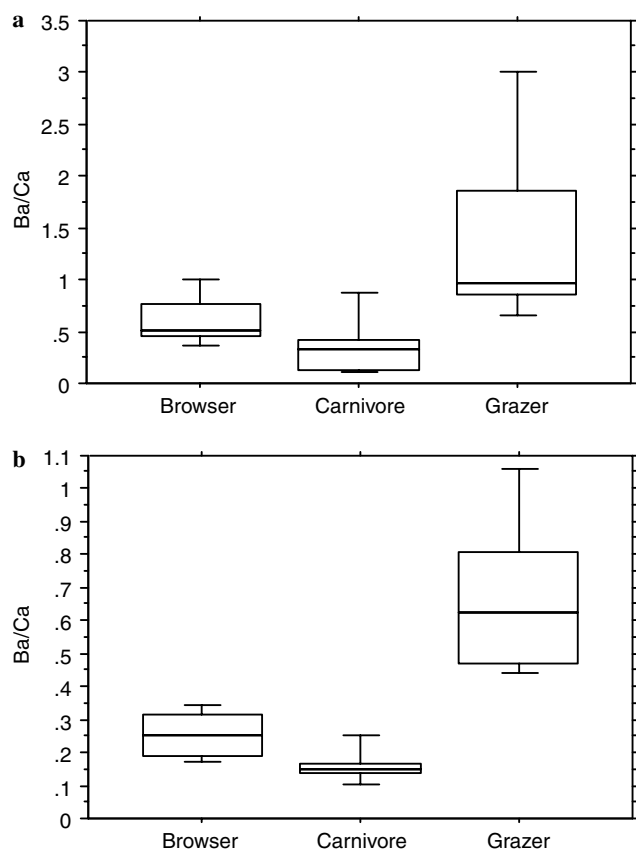


Fig. 2. Ba/Ca patterns for modern (a) and fossil (b) mammals. The boxes represent the 25th–75th percentiles (with the medians as horizontal lines) and the whiskers show the 10th–90th percentiles. Note the nearly identical ecological patterning for both datasets. Absolute values are expected to differ for the modern and fossil specimens because they are from different geological substrates.

statistically significant (Table 2; Fig. 3a). The KNP browse plants have slightly, but not significantly lower Sr/Ca than grasses ($P = 0.14$), and, concomitantly, browsers have lower Sr/Ca than grazers ($P < 0.01$); however, the Sr/Ca ratios of the KNP browsers and carnivores are indistinguishable ($P = 0.40$). Thus, Ba/Ca may be a more sensitive paleodietary indicator than Sr/Ca (Sillen and Kavanagh, 1982; Gilbert et al., 1994). (We do not discuss Zn/Ca or Pb/Ca in this section as they display no statistically significant ecological patterning in our modern or fossil datasets.)

Can we identify the Ba/Ca pattern of grazers > browsers > carnivores in the Sterkfontein Valley fossil fauna? The data in Table 2 and Fig. 2 demonstrate that the observed modern ecological pattern is indeed preserved in the Sterkfontein Valley fossils. The Sterkfontein Valley grazers have higher Ba/Ca than browsers ($P < 0.01$), which are in turn significantly elevated compared to carnivores ($P < 0.01$). Furthermore, the magnitudes of change in both the modern and fossil faunas are similar. For instance, in both the modern and fossil datasets, browser Ba/Ca is about 40% of grazer Ba/Ca (44% and 37%, respectively). The Sr/Ca patterning is also the same for the modern and fossil faunas, although the concordance

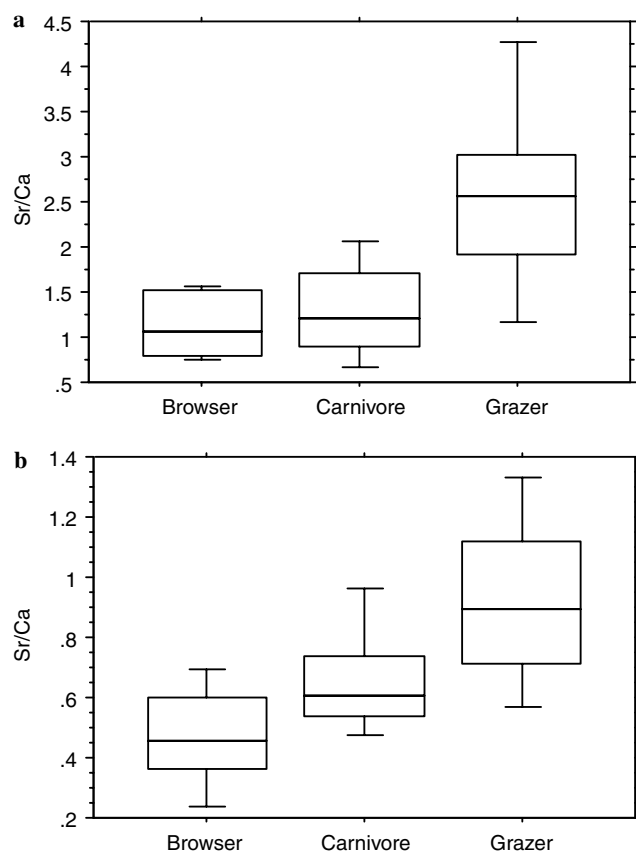


Fig. 3. Sr/Ca patterns for modern (a) and fossil (b) mammals. The boxes represent the 25th–75th percentiles (with the medians as horizontal lines) and the whiskers show the 10th–90th percentiles. Note the similar ecological patterning for both datasets. Absolute values are expected to differ for the modern and fossil specimens because they are from different geological substrates.

is not as exact as that for Ba/Ca (Table 2; Fig. 3). In both cases, grazers have higher Sr/Ca than browsers ($P < 0.01$), which are in turn slightly elevated compared to carnivores (but only significantly so for the fossils, $P = 0.04$); and once again the magnitude of change is similar, as browser Sr/Ca is 43% and 51% of grazer Sr/Ca for the modern and fossil datasets, respectively.

Given the above, it is not surprising that Sr/Ba ratios are also patterned similarly in modern and fossil enamels. Although rarely used, this ratio strongly distinguishes between herbivorous and carnivorous fauna. As Sr and Ba concentrations tend to covary in foodwebs (Elias et al., 1982; Gilbert et al., 1994; Burton et al., 1999; Balter, 2004), grazing and browsing herbivores in Kruger, despite having very different Sr/Ca and Ba/Ca, have similar Sr/Ba ratios ($P = 0.66$) (Table 2; Fig. 4a). Carnivores, in contrast, have higher Sr/Ba than both grazers and browsers ($P < 0.01$). The same pattern holds for the Sterkfontein Valley fossils (Table 2; Fig. 4b), as grazer and browser Sr/Ba are indistinguishable ($P = 0.09$), but carnivore Sr/Ba is significantly higher than both herbivore groups ($P < 0.01$). This trophic level effect is a natural consequence of the higher bioapatite/diet observed ratio (OR) for Sr

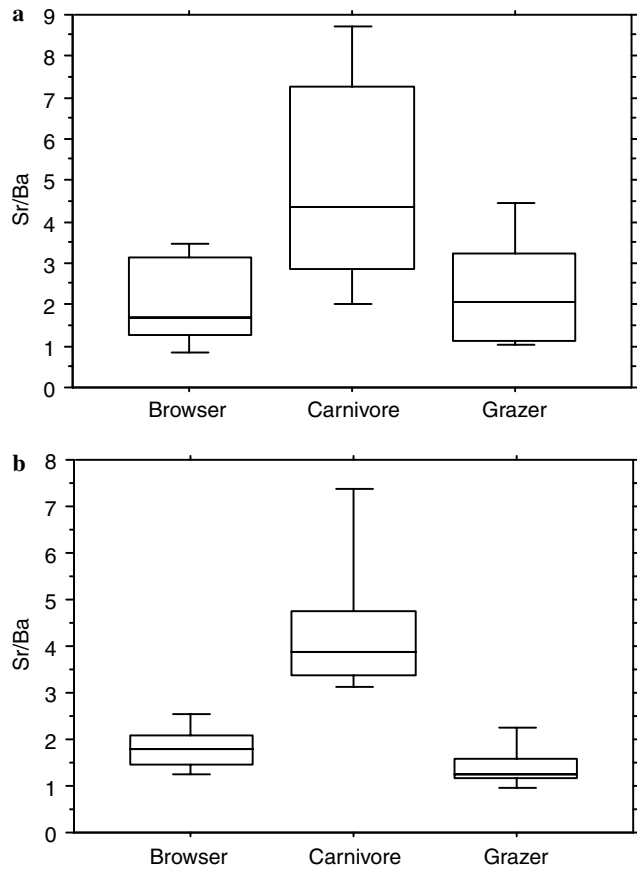


Fig. 4. Sr/Ba patterns for modern (a) and fossil (b) mammals. The boxes represent the 25th–75th percentiles (with the medians as horizontal lines) and the whiskers show the 10th–90th percentiles. Note the nearly identical ecological patterning for both datasets.

(~0.25) than Ba (~0.15) (Comar et al., 1957; Elias et al., 1982; Balter, 2004). Put another way, mammals discriminate more strongly against dietary Ba than Sr, and thus Ba must become relatively less abundant every step up the food chain. Therefore, Sr/Ba provides further support for trophic level differences, but more importantly for our purposes here, confirms that modern ecological patterning has not been obscured by diagenesis in the Sterkfontein Valley fossils. We have also found it particularly useful for increasing ecological resolution when plotted against Ba/Ca ratios.

4. Discussion

4.1. Enamel diagenesis at South African *Australopith* sites

This study has shown that although enamel Zn levels have increased dramatically at the 3 Ma Makapansgat Member 3, there is no evidence for such an increase in Sr/Ca, Ba/Ca, or Pb/Ca at any of the three fossil sites, aged 1.8–3 Ma. This does not rule out the possibility of significant alteration of any given fossil (which might be profitably investigated using other tools including electron microprobe analysis and scanning electron microscopy as

in Kohn et al. (1999) and Dauphin and Williams (2004)), but it does show that the assemblages on the whole, especially those from Swartkrans and Sterkfontein, appear to have maintained much of their paleoecological integrity. We have also shown that grazers, browsers, and carnivores can be distinguished using alkaline earth ratio data in both modern and fossil savanna ecosystems in South Africa, which further suggests that diagenesis has not obscured the relevant paleoecological signal. We stress, however, that this ecological patterning may not be relevant in all ecosystems, as each of these broad dietary categories subsume animals with quite different diets and habitat preferences. For instance, some browsers eat nothing but tree leaves and forbs, while others may eat a great deal of fruit; and some grazers are found in sere grasslands, while others feed exclusively near the water's edge. Such dietary and habitat differences may well influence mammalian trace element compositions, so ecological patterning may often be more complicated than is apparent here. Nonetheless, the congruence here in modern and fossil ecological patterning suggests that paleoecological studies using Sr, Ba, or Pb, whether investigating paleodiets or paleolandscape use, are likely to prove fruitful at these and karstic cave sites of similar age elsewhere.

It is possible that these promising results may not pertain under the very different depositional and chemical circumstances of the East African early hominin sites. However, while it is likely that previous reports of increases in metals, alkaline earths, and other elements at these sites are correct (Kohn et al., 1999; Dauphin and Williams, 2004), there remains at least some grounds to surmise that useful trace element distribution data might yet be obtainable from these fossil enamel specimens. For instance, while it was argued that fossil enamel exhibited increased Ba at Allia Bay (Kohn et al., 1999), the entire range of Ba concentrations in that study, for modern and fossil specimens combined ($n = 10$), falls comfortably within the range of modern herbivores from the KNP. Thus, it is probably premature to make strong statements about increases in alkaline earth concentrations in enamel from Allia Bay and other East African sites.

Ultimately, studies of post-depositional alteration of paleoecologically relevant elements should be carried out on a site-by-site basis, even when studies of fossil diagenesis are available for other sites in the region. This is underscored by the results from Makapansgat Limeworks, which show that this site, although geologically similar to both Swartkrans and Sterkfontein, differs in the degree to which it imparts Zn to enamel over time. This finding also indirectly demonstrates why analysis of REE and U concentrations is inadequate for gauging the impact of diagenesis on paleoecological information (contra Kolodny et al., 1996; Kohn et al., 1999). Not all trace metals behave similarly in a given site, even if they occupy identical sites within the crystal lattice as a result of the unique taphonomic histories, burial environments, hydrological conditions, and sedimentary matrices of fossil assemblages as well as the

properties of the metals themselves. Thus, while enhanced levels of REEs and U in fossil enamel undoubtedly demonstrate that diagenesis has occurred, one cannot *ipso facto* conclude anything about the suitability of the material for paleoecological applications using, for instance, the alkaline earth elements. In short, diagenesis is only an enemy when it obfuscates the sought after paleoecological signal (e.g., $\delta^{13}\text{C}$ or Ba/Ca browser/grazer patterning).

4.2. A brief look at a potential application

This study suggests that elemental ratio analysis, at certain sites at least, might allow us to address a variety of highly debated paleoecological questions, such as “Did Neanderthals have diets dominated by meat?” (e.g., Stiner, 1994; Richards et al., 2000; Bocherens et al., 2005); “When did early primates first adopt frugivorous, rather than insectivorous, diets?” (Covert, 1986; Strait, 2001); or more immediately relevant to the present study, “What was the diet of the 2.5 Ma hominin *Australopithecus africanus* from Sterkfontein?” In regard to this last question, if we produce a bivariate plot (Ba/Ca and Sr/Ba) of data from this study (Fig. 5), it is evident that *A. africanus* had a different diet than contemporaneous grazers, browsers, and carnivores, which are in turn highly different from each other. Thus, once again, there is very good reason to believe that elemental ratio data are providing valid paleoecological information. Interpretation of these data, however, remains difficult. We can state with confidence that *A. africanus* had a diet fundamentally different than that of browsing and grazing herbivores, but it is much harder to make affirmative statements about its trophic behavior. It is clearly most similar to its carnivorous coevals, so one might suggest that this taxon had begun to increase the amount of animal foods in its diet, which many believe was a key step towards developing the unusually large brains that are the sine qua non of our species (e.g., Aiello and Wheeler, 1995;

Milton, 1999). The enriched $\delta^{13}\text{C}$ of this taxon could also be taken as evidence of this trend, as it necessitates the consumption of C_4 plant foods such as grasses and sedges or animals that ate those foods (Sponheimer and Lee-Thorp, 1999b; van der Merwe et al., 2003; Sponheimer et al., 2005b). Yet, the similarity to carnivores is superficial, as the *Australopithecus* fossils are characterized by high Sr/Ba that is quite distinct from all other fossil specimens we have analyzed, including carnivores. This suggests the possibility that they consumed very different foods than all of these groups—foods with unusually high Sr and relatively low Ba concentrations.

One food that meets this requirement is grass seed, which has Sr/Ba ratios 3–4 times higher than grass straw (data from Smith, 1971). Another potential food is underground storage organs, although the evidence for this is indirect. We analyzed three African mole rats (*Cryptomys hottentotus*) from the KNP, a species which is known to consume underground resources such as roots and bulbs (Kingdon, 1997), and found them to have the highest Sr/Ba of any animal we have studied (Table 2). As a result, the possibility of grass seed and underground storage organ consumption, both of which have been bruited as possible early hominin foods (Jolly, 1970; Wolpoff, 1973; Hatley and Kappelman, 1980; Sillen et al., 1995; O’Connell et al., 1999; Laden and Wrangham, 2005), requires further consideration. Both of these foods are also consistent with the stable isotope evidence showing that *A. africanus* derived considerable dietary carbon from C_4 resources (Lee-Thorp et al., 1994; van der Merwe et al., 2003; Sponheimer et al., 2005b).

5. Conclusion

We have shown that enamel Sr/Ca, Ba/Ca, and Pb/Ca ratios have not been significantly increased during fossilization at three karstic cave sites, aged 1.8–3.0 Ma, in South Africa. Zn/Ca ratios, in contrast, were highly altered at one site, but only moderately at others. It is likely that each site, and in fact each relevant elemental ratio, should be considered *sui generis* where diagenesis is concerned. Nevertheless, we have demonstrated the biogenic ecological patterning has been retained in enamel from Swartkrans and Sterkfontein, which may allow us to test hypotheses about the diets of early hominins as well as other mammalian taxa at these and similar sites. But despite the potential of this technique for improving our understanding of mammalian paleoecology, its proper application requires considerable baseline work in modern ecosystem elemental distributions as well as in diagenesis. The latter requirement has been well-recognized but the first has been all but ignored, in spite of the fact that a sounder understanding of modern elemental distributions is *required* for distinguishing diagenetic from “real” ecological patterns. And while some promising work has been carried out mapping elemental distributions in North America foodwebs (Burton et al., 1999), the same has not occurred for the rest of the world. This problem is especially acute in African

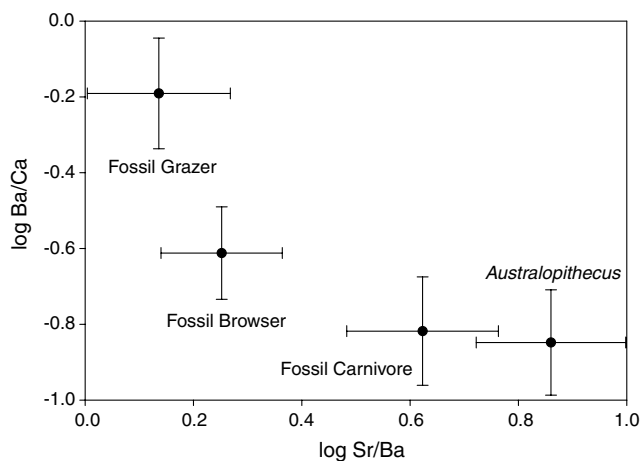


Fig. 5. Bivariate $\log(\text{Ba}/\text{Ca})$ and $\log(\text{Sr}/\text{Ba})$ plot for fossil grazers, browsers, carnivores, and *A. africanus*. The dots are mean values and the whiskers represent standard deviations. The early hominins do not group closely with any of these groups with known diets, and these data suggest a diet high in Sr but with little Ba.

savanna ecosystems, from which we know of no published data on plant elemental compositions. It is only after comprehensive and systematic investigations of plant and mammal elemental abundances have been undertaken in Africa and elsewhere, that this tool can become an important and routine facet of paleoecological studies.

Acknowledgments

We thank Heidi Fourie, Teresa Kearney, Stephany Potze, and Francis Thackeray of the Transvaal Museum, and Lee Berger and Bruce Rubidge of the BPI for facilitating this research. Andreas Spath, Department of Geological Sciences, University of Cape Town, performed the analyses. We thank Darryl De Ruiter, Jacqui Codron, Daryl Codron, and Rina Grant for assistance in the field and in the lab, and Yannicke Dauphin, Miryam Bar-Matthews, Yasmin Rahman, and three anonymous reviewers for comments on the manuscript. This project was funded by the National Science Foundation (USA), the Foundation for Research and Development (RSA) and the University of Cape Town. This is AEON publication #11.

Associate editor: Miryam Bar-Matthews

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2005.12.022](https://doi.org/10.1016/j.gca.2005.12.022).

References

- Aiello, L.C., Wheeler, P., 1995. The expensive tissue hypothesis. *Curr. Anthropol.* **36**, 199–221.
- Andrews, P., 1990. *Owls, Caves, and Fossils*. University of Chicago Press, Chicago.
- Ayliffe, L.K., Chivas, A.R., Leakey, M.G., 1994. The retention of primary oxygen isotope compositions of fossil elephant skeletal phosphate. *Geochim. Cosmochim. Acta* **58**, 5291–5298.
- Balter, V., 2004. Allometric constraints on Sr/Ca and Ba/Ca partitioning in terrestrial mammalian trophic chains. *Oecologia* **139**, 83–88.
- Balter, V., Bocherens, H., Person, A., Labourdette, N., Renard, M., Vandermeersch, B., 2002. Ecological and physiological variability of Sr/Ca and Ba/Ca in mammals of West European mid-Wurmian food webs. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **186**, 127–143.
- Blum, J.D., Taliaferro, H., Weisse, M.T., Holmes, R.T., 2000. Changes in Sr/Ca, Ba/Ca and $87\text{Sr}/86\text{Sr}$ ratios between trophic levels in two forest ecosystems in the northeastern USA. *Biogeochemistry* **49**, 87–101.
- Bocherens, H., Drucker, D.G., Billiou, D., Patou-Mathis, M., Vandermeersch, B., 2005. Isotopic evidence for diet and subsistence pattern of the Saint-Césaire I Neanderthal: review and use of a multi-source mixing model. *J. Hum. Evol.* **49**, 71–87.
- Bocherens, H., Brinkman, D.B., Dauphin, Y., Mariotti, A., 1994. Microstructural and geochemical investigations on Late Cretaceous archosaur teeth from Alberta, Canada. *Can. J. Earth Sci.* **31**, 783–792.
- Brain, C.K., 1981. *The Hunters or the Hunted?* University of Chicago Press, Chicago.
- Brink, A.B.A., Partridge, T.C., 1980. The nature and genesis of solution cavities (Makondos) in Transvaal cave breccias. *Palaeontol. Afr.* **23**, 47–49.
- Brown, A.B., 1974. Bone strontium as a dietary indicator in human skeletal populations. *Contrib. Geol.* **13**, 47–48.
- Budd, P., Montgomery, J., Barreiro, B., Thomas, R.G., 2000. Differential diagenesis of strontium in archaeological human tissues. *Appl. Geochem.* **15**, 687–694.
- Burton, J.H., Price, T.D., Cahue, L., Wright, L., 2003. The use of barium and strontium abundances in human skeletal tissues to determine their geographic origins. *Int. J. Osteoarchaeol.* **13**, 88–95.
- Burton, J.H., Wright, L.E., 1995. Nonlinearity in the relationship between bone Sr/Ca and diet: paleodietary implications. *Am. J. Phys. Anthropol.* **96**, 273–282.
- Burton, J.H., Price, T.D., Middleton, W.D., 1999. Correlation of bone Ba/Ca and Sr/Ca due to biological purification of calcium. *J. Archaeol. Sci.* **26**, 609–616.
- Cerling, T.E., Harris, J.M., Leakey, M.G., 1999. Browsing and grazing in elephants: the isotope record of modern and fossil proboscideans. *Oecologia* **120**, 364–374.
- Comar, C.L., Russell, L., Wasserman, R.H., 1957. Strontium–calcium movement from soil to man. *Science* **126**, 485–496.
- Covert, H.H., 1986. Biology of early Cenozoic Primates. In: Swindler, D.R., Erwin, J. (Eds.), *Comparative Primate Biology, Systematics, Evolution, and Anatomy*. Alan R. Liss, Inc. Press, NY, pp. 335–359.
- Dauphin, Y., 1989. Implications de l'analyse chimique élémentaire de dents de reptiles actuels et fossiles. *C.R. Acad. Sci. Paris, Ser. II* **309**, 927–932.
- Dauphin, Y., Williams, C.T., 2004. Diagenetic trends of dental tissues. *C.R. Paleoevol.* **3**, 583–590.
- Dauphin, Y., Denys, C., 1992. Les mécanismes de formation des gisements de microvertébrés. Composition chimique des tissus minéralisés des rongeurs de Sterkfontein (Afrique du Sud, Plio-Pleistocène). *Mém. Soc. géol. France* **160**, 101–108.
- Denys, C., Williams, C.T., Dauphin, Y., Andrews, P., Yolanda, F.-J., 1996. Diagenetical changes in Pleistocene small mammal bones from Olduvai Bed I. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **126**, 121–134.
- Elias, R.W., Hirao, Y., Patterson, C.C., 1982. The circumvention of the natural biopurification of calcium along nutrient pathways by atmospheric inputs of industrial lead. *Geochim. Cosmochim. Acta* **46**, 2561–2580.
- Elliot, J.C., 1994. *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*. Elsevier, Amsterdam.
- Gilbert, C., Sealy, J., Sillen, A., 1994. An investigation of barium, calcium and strontium as paleodietary indicators in the Southwestern Cape, South Africa. *J. Archaeol. Sci.* **21**, 173–184.
- Grandjean, P., Albarède, F., 1989. Ion probe measurement of rare earth elements in biogenic phosphates. *Geochim. Cosmochim. Acta* **53**, 3179–3183.
- Hatley, T., Kappelman, J., 1980. Bears, pigs, and Plio-Pleistocene hominids: case for exploitation of below-ground food resources. *Hum. Ecol.* **8**, 371–387.
- Hoppe, K.A., Koch, P.L., Carlson, R.W., Webb, S.D., 1999. Tracking mammoths and mastodons; reconstruction of migratory behavior using strontium isotope ratios. *Geology* **27**, 439–442.
- Hoppe, K.A., Koch, P.L., Furutani, T.T., 2003. Assessing the preservation of biogenic strontium in fossil bones and tooth enamel. *Int. J. Osteoarchaeol.* **13**, 20–28.
- Jolly, C.J., 1970. The seed-eaters: a new model of hominid differentiation based on a baboon analogy. *Man* **5**, 5–26.
- Kingdon, J., 1997. *The Kingdon Field Guide to African Mammals*. Academic Press, New York.
- Klepinger, L., 1984. Nutritional assessment from bone. *Annu. Rev. Anthropol.* **14**, 75–96.
- Kobayashi, E., Suzuki, K.T., 1990. Biological discrimination between calcium and strontium in the kidney and bone of calcium deficient growing rats. *J. Trace Elem. Exp. Med.* **3**, 327–336.
- Koch, P.L., Fogel, M.L., Tuross, N., 1994. Tracing the diets of fossil animals using stable isotopes. In: Lajtha, K., Michener, B. (Eds.), *Stable Isotopes in Ecology and Environmental Science*. Blackwell Scientific Publication, Boston, pp. 63–92.

- Kohn, M., Schoeninger, M.J., Barker, W.W., 1999. Altered states: effects of diagenesis on fossil tooth chemistry. *Geochim. Cosmochim. Acta* **63**, 2737–2747.
- Kolodny, Y., Luz, B., Sander, M., Clemens, W.A., 1996. Dinosaur bones: fossils or pseudomorphs. The pitfalls of physiology reconstruction from apatitic fossils. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **126**, 161–171.
- Kostial, K., Gruden, N., Durakovic, A., 1969. Intestinal absorption of calcium-47 and strontium-85 in lactating rats. *Calcium Tissue Res.* **4**, 13–19.
- Laden, G., Wrangham, R., 2005. The rise of the hominids as an adaptive shift in fallback foods: plant underground storage organs (USOs) and Australopithecus origins. *J. Hum. Evol.* **49**, 482–498.
- Lambert, J.B., Simpson, S.V., Szpunar, C.B., Buikstra, J.B., 1984. Ancient human diet from inorganic analysis of bone. *Accounts Chem. Res.* **17**, 298–305.
- Lee-Thorp, J., Sponheimer, M., 2003. Three case studies used to reassess the reliability of fossil bone and enamel isotope signals for paleodietary studies. *J. Anthropol. Archaeol.* **22**, 208–216.
- Lee-Thorp, J.A., van der Merwe, N.J., 1991. Aspects of the chemistry of modern and fossil biological apatites. *J. Archaeol. Sci.* **18**, 343–354.
- Lee-Thorp, J.A., van der Merwe, N.J., 1987. Carbon isotope analysis of fossil bone apatite. *S. Afr. J. Sci.* **83**, 712–715.
- Lee-Thorp, J.A., van der Merwe, N.J., Brain, C.K., 1994. Diet of *Australopithecus robustus* at Swartkrans from stable carbon isotopic analysis. *J. Hum. Evol.* **27**, 361–372.
- LeGeros, R.Z., 1991. *Calcium Phosphates in Oral Biology and Medicine*. Karger, Paris.
- Leggett, R.W., 1992. Fractional absorption of ingested barium in adult humans. *Health Phys.* **62**, 556–561.
- Lengeman, F.W., 1963. Over-all aspects of calcium and strontium absorption. In: Wasserman, R.H. (Ed.), *The Transfer of Calcium and Strontium across Biological Membranes*. Academic Press, New York, pp. 85–96.
- Lough, S.A., Rivera, J., Comar, C.L., 1963. Retention of strontium, calcium and phosphorus in human infants. *Proc. Soc. Exp. Biol. Med.* **112**, 631–636.
- Maguire, J.M., 1998. *Makapansgat: a guide to the palaeontological and archaeological sites of the Makapansgat Valley*. Transvaal Museum, Pretoria.
- McClellan, R.O., 1964. Calcium–strontium discrimination in miniature pigs as related to age. *Nature* **202**, 104–106.
- Michel, V., Ildefonse, P., Morin, G., 1995. Chemical and structural changes in *Cervus elphas* tooth enamels during fossilization (Lazaret Cave): a combined IR and XRD Rietveld analysis. *Appl. Geochem.* **10**, 145–159.
- Michel, V., Ildefonse, P., Morin, G., 1996. Assessment of archaeological bone and dentine preservation from Lazaret Cave (Middle Pleistocene) in France. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **126**, 109–119.
- Milton, K., 1999. A hypothesis to explain the role of meat-eating in human evolution. *Evol. Anthropol.* **8**, 11–21.
- Montgomery, J., Budd, P., Evans, J., 2000. Reconstructing the lifetime movements of ancient people: a Neolithic case study from southern England. *Eur. J. Archaeol.* **3**, 407–422.
- Müller, W., Fricke, H., Halliday, A.N., McCulloch, M.T., Wartho, J.-A., 2003. Origin and migration of the alpine iceman. *Science* **302**, 862–866.
- Nelson, B., DeNiro, M., Schoeninger, M., DePaolo, D., 1986. Effects of diagenesis on strontium, carbon, nitrogen and oxygen concentration and isotopic composition of bone. *Geochim. Cosmochim. Acta* **50**, 1941–1949.
- O’Connell, J.F., Hawkes, K., Blurton Jones, N.G., 1999. Grandmothering and the evolution of *Homo erectus*. *J. Hum. Evol.* **36**, 461–485.
- Palmqvist, P., Gröcke, D.R., Arribas, A., Fariña, R.A., 2003. Paleoeological reconstruction of a lower Pleistocene large mammal community using biogeochemical (d13C, d15N, Sr:Zn) and ecomorphological approaches. *Paleobiology* **29**, 205–229.
- Price, T.D., Blit, J., Burton, J.H., Ezzo, J., 1992. Diagenesis in prehistoric bone: problems and solutions. *J. Archaeol. Sci.* **19**, 513–529.
- Price, T.D., Connor, M., Parsen, J.D., 1985. Bone strontium analysis and the reconstruction of diet: strontium discrimination in white-tailed deer. *J. Archaeol. Sci.* **12**, 419–442.
- Price, T.D., Swick, R.W., Chase, E., 1986. Bone chemistry and prehistoric diet: strontium studies of laboratory rats. *Am. J. Phys. Anthropol.* **70**, 365–375.
- Razic, S., Onjia, A., Potkonjak, B., 2003. Trace elements analysis of *Echinacea purpurea*—a herbal medicinal. *J. Pharmaceut. Biomed.* **33**, 845–850.
- Rey, C., Renugopalakrishnan, V., Shimizu, M., Collins, B., Glimcher, M.J., 1991. A resolution enhanced Fourier transform infrared spectroscopic study of the environment of the CO₃ ion in the mineral phase of enamel during its formation and maturation. *Calcif. Tissue Int.* **49**, 259–268.
- Richards, M.P., Pettitt, P.B., Trinkaus, E., Smith, F.H., Paunovic, M., Karavanic, I., 2000. Neanderthal diet at Vindija and Neanderthal predation: the evidence from stable isotopes. *Proc. Natl. Acad. Sci. USA* **97**, 7663–7666.
- Rivera, J., Harley, J.H., 1965. *The HASL bone program: 1961–1964*, United States Atomic Energy Commission Health and Safety Laboratory Report No. 163.
- Safont, S., Malgosa, A., Subirà, M.E., Gilbert, J., 1998. Can trace elements in fossils provide information about palaeodiet? *Int. J. Osteoarchaeol.* **8**, 23–37.
- Schoeninger, M.J., 1979. *Dietary reconstruction at Chalcatzingo, a Formative Period site in Morelos, Mexico. Technical Report 9*. Ann Arbor, University of Michigan Museum of Anthropology.
- Schoeninger, M.J., Hallin, K., Reeser, H., Valley, J.W., Fournelle, J., 2003. Isotopic alteration of mammalian tooth enamel. *Int. J. Osteoarchaeol.* **13**, 11–19.
- Sealy, J.C., Sillen, A., 1988. Sr and Sr:Ca in marine and terrestrial foodwebs in the Southwestern Cape, South Africa. *J. Archaeol. Sci.* **15**, 425–438.
- Sillen, A., 1986. Biogenic and diagenetic Sr/Ca in Plio-Pleistocene fossils in the Omo Shungura Formation. *Paleobiology* **12**, 311–323.
- Sillen, A., 1989. Diagenesis of the inorganic phase of cortical bone. In: Price, T.D. (Ed.), *The Chemistry of Prehistoric Human Bone*. Cambridge University Press, Cambridge, pp. 211–299.
- Sillen, A., Kavanagh, M., 1982. Strontium and paleodietary research. *Yearb. Phys. Anthropol.* **25**, 67–90.
- Sillen, A., 1981. *Strontium and diet at Hayonim Cave, Israel: an evaluation of the strontium/calcium technique for investigating prehistoric diets*. Ph.D. Dissertation, University of Pennsylvania.
- Sillen, A., 1988. Elemental and isotopic analysis of mammalian fauna from southern Africa and their implications for paleodietary research. *Am. J. Phys. Anthropol.* **76**, 49–60.
- Sillen, A., 1992. Strontium–calcium ratios (Sr/Ca) of *Australopithecus robustus* and associated fauna from Swartkrans. *J. Hum. Evol.* **23**, 495–516.
- Sillen, A., Hall, G., Armstrong, R., 1995. Strontium calcium ratios (Sr/Ca) and strontium isotopic ratios (⁸⁷Sr/⁸⁶Sr) of *Australopithecus robustus* and *Homo* sp. from Swartkrans. *J. Hum. Evol.* **28**, 277–285.
- Sips, A.J.A.M., Barto, R., Netelenbos, J.C., Van der Vijgh, W.J.F., 1997. Preclinical screening of the applicability of strontium as a marker for intestinal calcium absorption. *Am. J. Physiol. Endocrinol. Metab.* **272**, E422–E428.
- Smith, K.A., 1971. The comparative uptake and translocation by plants of calcium, strontium, barium and radium. II. *Triticum vulgare* (Wheat). *Plant Soil* **34**, 643–651.
- Spencer, H., Warren, J.M., Kramer, L., Samachson, J., 1973. Passage of calcium and strontium across the intestine in man. *Clin. Ortho. Rel. Res.* **91**, 225–234.
- Sponheimer, M., Lee-Thorp, J.A., 1999a. The alteration of enamel carbonate environments during fossilisation. *J. Archaeol. Sci.* **26**, 143–150.
- Sponheimer, M., Lee-Thorp, J.A., 1999b. Isotopic evidence for the diet of an early hominid, *Australopithecus africanus*. *Science* **283**, 368–370.

- Sponheimer, M., 1999. *Isotopic Ecology of the Makapansgat Limeworks Fauna*. University Microfilms International, Ann Arbor.
- Sponheimer, M., de Ruiter, D., Lee-Thorp, J., Späth, A., 2005a. Sr/Ca and early hominin diets revisited: new data from modern and fossil tooth enamel. *J. Hum. Evol.* **48**, 147–156.
- Sponheimer, M., Lee-Thorp, J.A., de Ruiter, D., Codron, D., Codron, J., Baugh, A., Thackeray, J.F., 2005b. Hominins, sedges and termites: new carbon isotope data for the Sterkfontein Valley. *J. Hum. Evol. B*, 301–312.
- Sponheimer, M., Reed, K., Lee-Thorp, J.A., 1999. Combining isotopic and ecomorphological data to refine bovid paleodietary reconstruction: a case study from the Makapansgat Limeworks hominin locality. *J. Hum. Evol.* **34**, 277–285.
- Stiner, M.C., 1994. *Honor among Thieves: A Zooarchaeological Study of Neandertal Ecology*. Princeton University Press, Princeton.
- Strait, S.G., 2001. Dietary reconstruction in small bodied omomyoids. *J. Vert. Paleontol.* **21**, 322–334.
- Toots, H., Voorhies, M.R., 1965. Strontium in fossil bones and the reconstruction of food chains. *Science* **149**, 854–855.
- Toyoda, K., Tokonami, M., 1990. Diffusion of rare-earth elements in fish teeth from deep-sea sediments. *Nature* **345**, 607–609.
- Trickett, M.A., Budd, P., Montgomery, J., Evans, J., 2003. An assessment of solubility profiling as a decontamination procedure for the $^{87}\text{Sr}/^{86}\text{Sr}$ analysis of archaeological human skeletal tissue. *Appl. Geochem.* **18**, 653–658.
- Trueman, C.N., Tuross, N., 2002. Trace elements in recent and fossil bone apatite. In: Kohn, M.J., Rakovan, J., Hughes, J.M. (Eds.), *Phosphates—Geochemical, Geobiological, and Materials Importance, Reviews in Mineralogy and Geochemistry*, vol. 48. Mineralogical Society of America, 522, p. 489.
- Tuross, N., Behrensmeier, A.K., Eanes, E.D., 1989. Sr increase and crystallinity changes in taphonomic and archaeological bones. *J. Archaeol. Sci.* **16**, 661–672.
- van der Merwe, N.J., Thackeray, J.F., Lee-Thorp, J.A., Luyt, J., 2003. The carbon isotope ecology and diet of *Australopithecus africanus* at Sterkfontein, South Africa. *J. Hum. Evol.* **44**, 581–597.
- Walser, M., Robinson, B.H.B., 1963. Renal excretion and tubular reabsorption of calcium and strontium. In: Wasserman, R.H. (Ed.), *Transfer of Calcium and Strontium across Biological Membranes*. Academic Press, New York, pp. 305–326.
- Wang, Y., Cerling, T., 1994. A model of fossil tooth and bone diagenesis: implications for paleodiet reconstruction from stable isotopes. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **107**, 281–289.
- Wolpoff, M.H., 1973. Posterior tooth size, body size, and diet in South African gracile australopithecines. *Am. J. Phys. Anthrop.* **39**, 375–394.
- Wyckoff, R.W.G., Doberenz, A.R., 1968. The strontium content of fossil teeth and bones. *Geochim. Cosmochim. Acta* **32**, 109–115.