



## Alteration of Enamel Carbonate Environments during Fossilization

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An understanding of enamel diagenesis is necessary to ensure sound isotopic palaeodietary and palaeoenvironmental reconstructions. Although carbon isotope signals of browsing and grazing herbivores remain distinct in enamel even after millions of years, subtle alteration of isotopic signatures does occur. To better understand this change we analysed modern and fossil enamel from a number of South African sites using Fourier Transform Infra-Red spectroscopy. Our results indicate that while there is little evidence of increased crystallinity in fossil enamel, there is a small but significant change in the proportion of carbonate ions occupying hydroxyl and phosphate sites. This seems to occur early in the process of fossilization, after which there is no noticeable change. It is also important to note that the degree of alteration varies significantly within and between sites. We suggest that this change results from one or some combination of three mechanisms: exogenous carbonate incorporation, endogenous carbonate loss, and endogenous carbonate reorganization. Determining which mechanism(s) contribute to this alteration is important because all three are likely to affect biogenic carbon isotope ratios differently. FTIR spectroscopy promises to increase our knowledge of diagenesis, and in so doing, should improve our palaeodietary and palaeoenvironmental reconstructions.

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### Introduction

Stable carbon isotope analysis of fossil enamel is frequently used for palaeodietary and palaeoenvironmental reconstruction (e.g., Lee-Thorp, van de Merwe & Brain, 1989, 1994; Quade *et al.*, 1992; Cerling, Wang & Quade, 1993; Kingston, Marino & Hill, 1994; Bocherens *et al.*, 1996; Cerling *et al.*, 1997; Sponheimer & Lee-Thorp, 1997). The success of such enterprises requires that the integrity of carbonate in biological apatite is maintained throughout the process of fossilization. Isotopic studies of fossil enamel demonstrate that grazing and browsing taxa from African savanna environments are clearly distinguishable even after millions of years (Lee-Thorp & van der Merwe, 1987; Bocherens *et al.*, 1996; Cerling *et al.*, 1997; Sponheimer & Lee-Thorp, 1997). Subtle, irrevocable alteration of isotopic signatures does occur, however, as manifested by consistently diminished spacing

between fossil grazers and browsers (~11%) compared to their modern counterparts (~14%) (Lee-Thorp, 1989, *in press*; Sponheimer, unpubl. data). To better understand such change we undertook a Fourier Transform Infra-Red (FTIR) spectroscopy study of modern and fossil enamel.

FTIR spectroscopy is performed by irradiating a sample with an infra-red beam. Some of the radiation is absorbed at frequencies determined by the functional groups (e.g.,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ) present and their environments. Moreover, the intensity of absorbance is proportional to the concentration of the absorbing molecule (e.g.,  $\text{CO}_3^{2-}$ ). Thus, FTIR spectroscopy provides information on both the molecular species present and their concentrations in a sample. Furthermore, the sample's overall pattern of absorbance (an infra-red spectrum) provides information not only on its chemical composition, but also on its crystallographic structure. For instance, even though

calcite and aragonite have the same chemical composition ( $\text{CaCO}_3$ ), they have distinct infra-red spectra because they are structurally dissimilar (aragonite is denser because each oxygen atom is bonded to three calcium atoms instead of two as in calcite). Similarly, spectra of phosphate minerals such as enamel, dentine and bone apatite are distinct from each other since they have slightly different compositions and structures. Spectra of biological apatites are also very different from those of carbonate minerals like calcite, making FTIR spectroscopy a useful way to detect diagenetic carbonate minerals within fossils. Even more important for our purposes here, however, is that FTIR spectroscopy can be used to track the structural evolution of biological apatites *in vivo* (Termine & Posner, 1966; Bonar *et al.*, 1991; Rey *et al.*, 1991) and, by extension, after deposition in archaeological or palaeontological contexts.

The use of infra-red spectroscopy for addressing diagenesis is not new. Hassan (1977) first showed that it threw light on crystallographic change in Upper Pleistocene bone. Later, Lee-Thorp & van der Merwe (1991) used it to detect secondary carbonates and structural change in much older fossil bone and enamel. More recently, several researchers documented “crystallinity” increases in fossil bone with infra-red spectroscopy (Weiner & Bar-Yosef, 1990; Michel, Ildefonse & Morin, 1996; Stuart-Williams *et al.*, 1996; Wright & Schwarcz, 1996), which might, under certain circumstances, be used as a form of relative dating within archaeological sites (Sillen & Morris, 1996; Sillen & Parkington, 1996). Michel, Ildefonse & Morin (1995) also observed carbonate alteration in fossil enamel, although their conclusions must be viewed with caution because they compared four fossils to only one modern specimen. Rink & Schwarcz (1996), on the other hand, noted no differences between the spectra of modern and fossil enamel.

This study differs from most previous endeavours for a number of reasons. First, we are concerned only with enamel (like Michel, Ildefonse & Morin, 1995 and Rink & Schwarcz, 1996). As mentioned above, there is abundant evidence that bone is highly altered during fossilization, and there seems little point in revisiting this conclusion here. Secondly, we use a combination of absorption bands that allows us to examine finer structural details of apatites than most previous studies (but see Michel, Ildefonse & Morin, 1995). Furthermore, we analyse modern enamel, as well as fossils from three thousand to three million years old, in order to better understand both the pace and process of enamel fossilization.

Enamel mineral is a carbonate apatite similar to the mineral dahllite, with carbonate ions substituting for trivalent phosphate ions (type B) and, to a much lesser extent, monovalent hydroxyl ions (type A) (Elliot, 1964; LeGeros, 1967, 1991; Vignoles, 1973; Bonar *et al.*, 1991; Rey *et al.*, 1991). Dissolution and exchange studies have also located “labile” carbonate species

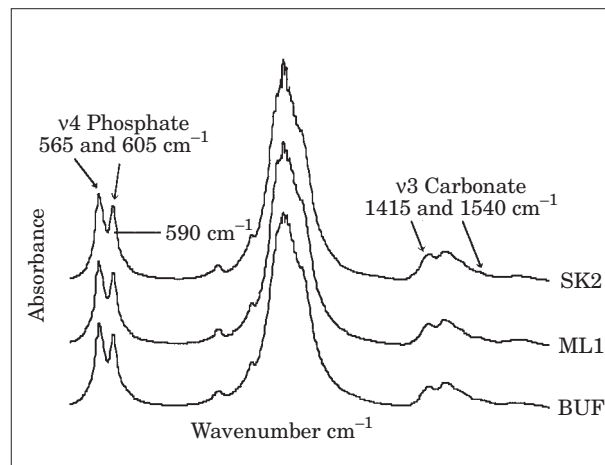


Figure 1. FTIR spectra of one modern (BUF) and two fossil (ML1 and SK2) specimens. Absorption bands used to calculate the various indices used in this study are labelled.

which are likely adsorbed on crystal surfaces or located within poorly-crystalline, high-carbonate domains (Triffitt, Terepka & Neuman, 1968; Poyart, Freminet & Bursaux, 1975; Rey *et al.*, 1989). Rink & Schwarcz (1995) attempted to observe changes in both type A and B carbonate environments of fossil enamel by examining absorption bands at  $1450\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$ , respectively. They were unsuccessful, however, because these bands overlapped on their spectra. We avoid this problem by using bands at  $1540\text{ cm}^{-1}$  and  $1415\text{ cm}^{-1}$  (Figure 1) to represent carbonate ions at A- and B-sites, respectively. Beyond the fact that these bands never overlap, there is another reason that we prefer them: the bands at  $1450\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$  may reflect not only A- and B-site carbonates, but other poorly-understood carbonate environments as well. Elliot (1964) showed that as type A carbonate content increases in apatites, intensity increases more at  $1450\text{ cm}^{-1}$  than  $1540\text{ cm}^{-1}$ . If both bands represent A-site carbonate ions, they should increase by the same amount. Since assignment of the band at  $1540\text{ cm}^{-1}$  to type A carbonate is quite secure, the greater increases at  $1450\text{ cm}^{-1}$  can best be explained by the contribution of an unidentified carbonate environment. There are a number of other reasons to treat the assignments of the bands at  $1450\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$  with scepticism, but further discussion is beyond the scope of this paper. Given these uncertainties, we believe that the relatively well-understood bands at  $1540\text{ cm}^{-1}$  and  $1415\text{ cm}^{-1}$  are preferable for monitoring carbonate diagenesis.

## Materials and Methods

The modern and fossil specimens (permanent molars) analysed for this study are listed in Table 1. It should be noted that all specimens were originally collected for other projects. While it is desirable to analyse the same

Table 1. Index values for modern and fossil enamel

Sample	Species	Site	BAI	BPI	API	PCI	CO <sub>3</sub> <sup>2-</sup> % <sub>wt</sub>
RAP	<i>Raphicerus melanotis</i>	Modern	3.1	0.22	0.071	3.6	2.9
BUF	<i>Syncerus caffer</i>	Modern	2.9	0.27	0.092	3.5	3.4
DOR	<i>Damaliscus dorcas</i>	Modern	2.9	0.35	0.120	3.5	4.2
BAB	<i>Papio cynocephalus</i>	Modern	3.1	0.16	0.050	3.8	2.3
DO2	<i>Damaliscus dorcas</i>	Modern	3.8	0.23	0.061	3.6	3.0
SBK	<i>Raphicerus campestris</i>	Steenbokfontein	4.2	0.19	0.045	3.7	2.6
BC1	<i>Aepyceros melampus</i>	Border Cave	5.6	0.24	0.043	3.7	3.1
BC2	<i>Hippotragus equinus</i>	Border Cave	4.8	0.22	0.046	4.1	2.9
FL1	<i>Tragelaphus oryx</i>	Florisbad	4.0	0.34	0.086	3.4	4.1
FL2	<i>Tragelaphus oryx</i>	Florisbad	3.5	0.25	0.072	3.6	3.2
SK1	<i>Connochaetes taurinus</i>	Swartkrans	3.8	0.34	0.090	3.6	4.1
SK2	<i>Antidorcas bondi</i>	Swartkrans	3.7	0.33	0.090	3.4	4.0
ML1	<i>Giraffa jumae</i>	Makapansgat	4.0	0.26	0.066	3.5	3.3
ML2	<i>Giraffa jumae</i>	Makapansgat	3.3	0.25	0.075	3.7	3.2
ML3	<i>Giraffa jumae</i>	Makapansgat	4.2	0.23	0.055	3.7	3.0

taxa for both modern and fossil samples to control for species-level variability, fossil sites such as Makapan contain few extant taxa (Reed, 1996). As a result, we sampled modern species similar but not identical to those at fossil sites. We included five modern teeth in this study, four of which come from bovids (as they tend to dominate fossil assemblages and are broadly applicable), while the last is a cercopithecoid tooth. All modern specimens were collected in South Africa. Ten fossil teeth were sampled in all: one from Steenbokfontein (3 Ka), two from Swartkrans Member 5 (11 Ka), two from Border Cave (90 Ka), two from Florisbad (200 Ka), and three from Makapansgat Limeworks Member 3 (3 Ma). All fossil specimens are bovids except those from Makapan (giraffids), from which no bovids were available at the time of this study.

Two milligrams of enamel were obtained using a low-speed rotary drill equipped with a 2 mm diamond-tipped bit, which produced virtually no visible damage on specimens. Great care was taken not to induce recrystallization by unduly heating the enamel surface. The powder was lyophilized overnight and 2 mg were ground together with 300 mg of KBr using an agate mortar and pestle. A disc was then created in a vacuum press under 9 tons of pressure for 5 min. Sixty-four scans were taken of each sample on a Perkin-Elmer Paragon 1000 spectrometer at a resolution of 8 cm<sup>-1</sup>. The resulting absorbance spectra were baseline corrected and downloaded to StatView for statistical analysis.

Indices reflecting the amount of type B carbonate to phosphate (BPI), the amount of type A carbonate to phosphate (API), the relative amount of B- to A-site carbonate (BAI), and the "crystallinity" (PCI) of each sample were calculated using the absorption bands labelled in Figure 1. BPI was calculated by dividing the intensity of the band at 1415 cm<sup>-1</sup> by the intensity of the phosphate band at 605 cm<sup>-1</sup>. Although BPI ignores the small contribution of type A carbonate, it closely tracks overall carbonate content (Figure 2)

and has been used for quantitative determination of carbonate content in biological and synthetic apatites (LeGeros, 1991). We used it here to provide an estimate of carbonate content for all specimens analysed. API was obtained by dividing the intensity of the band at 1540 cm<sup>-1</sup> by the intensity of the aforementioned phosphate band at 605 cm<sup>-1</sup>. To get BAI, we divided the intensity of the band at 1415 cm<sup>-1</sup> by the intensity of the band at 1540 cm<sup>-1</sup> (BAI). Lastly, we calculated PCI by adding the intensities of the phosphate bands at 565 cm<sup>-1</sup> and 605 cm<sup>-1</sup> and dividing the sum by the intensity of the trough between them (590 cm<sup>-1</sup>) (Weiner & Bar-Yosef, 1990; Sillen & Morris, 1996; Stuart-Williams *et al.*, 1996; Wright & Schwarcz, 1996). PCI ostensibly reflects crystal size, strain and defects, but in the strictest sense it shows short-range order around phosphate ions by measuring splitting of the ν<sub>4</sub> PO<sub>4</sub> domain. The reproducibilities of these indices (BPI, API, BAI and PCI), as measured in our

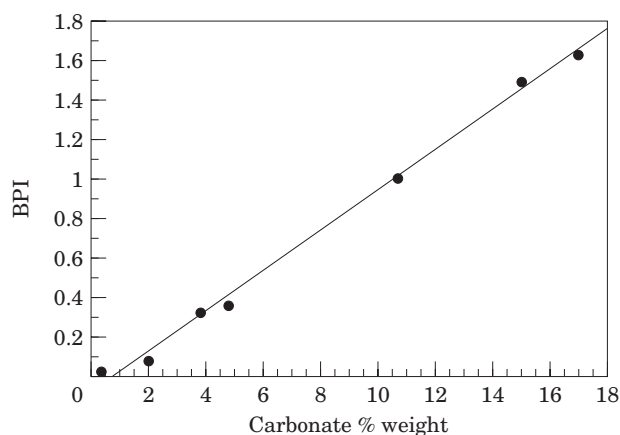


Figure 2. Relationship between BPI and percentage carbonate by weight for synthetic carbonate apatites. Carbonate content was determined by Conway diffusion method. Modified after LeGeros (1991).

lab, are  $\pm 0.01$ ,  $\pm 0.003$ ,  $\pm 0.1$  and  $\pm 0.1$ , respectively. We also monitored for calcite in all samples by checking for a peak at  $711\text{ cm}^{-1}$  which appears in calcite but not modern enamel apatite.

## Results and Discussion

BPI, API, BAI and PCI for all modern and fossil samples are listed in Table 1. There is great variability within and between modern taxa. BPI ranges from 0.16 to 0.35 ( $x=0.24$ ,  $s.d.=0.07$ ,  $N=5$ ). Converted, according to LeGeros (1991), this represents 2.3% to 4.2% carbonate by weight, which falls comfortably within the range published for modern mammalian enamel (e.g., Elliot, 1964; LeGeros, 1967, 1991; Tochon-Danguy, Geoffroy & Baud, 1980; Elliot, Holcomb & Young, 1985; Bonar *et al.*, 1991; Rey *et al.*, 1991; Michel, Ildefonse & Morin, 1995; Rink & Schwarcz, 1996; Koch, Tuross & Fogel, 1997). The one primate (BAB) sampled also has the lowest carbonate content as predicted from the literature. This further supports the contention that BPI is a useful indicator of carbonate content. There is also considerable variation among the bovids. Even within one bovid species, *Damaliscus dorcas*, BPI ranges from 0.23 to 0.35, or 3.0% to 4.2% carbonate by weight. There is similar variability in API, with samples ranging from 0.050 to 0.120 ( $x=0.079$ ,  $s.d.=0.028$ ,  $N=5$ ). The ratio of B to A carbonate species shows much less variation with one exception. Four samples have BAI values between 2.9 and 3.1, with an outlier of 3.7 ( $x=3.1$ ,  $s.d.=0.3$ ,  $N=5$ ). All other indices for this outlier are quite typical; hence, it is unlikely that the anomalous BAI value is an artefact of sample preparation. PCI, indicating local order around phosphate ions, ranges from 3.5 to 3.8 ( $x=3.6$ ,  $s.d.=0.1$ ,  $N=5$ ).

Fossil spectra are virtually indistinguishable from modern spectra to the naked eye (Figure 1). Like their modern counterparts, the calculated indices for fossils show a great deal of variation within and between taxa. BPI ranges from 0.19 to 0.34 ( $x=0.27$ ,  $s.d.=0.05$ ,  $N=10$ ), which translates to 2.6% to 4.1% carbonate by weight and falls entirely within the modern range. Even if the modern cercopithecoid (which has the lowest BPI value and carbonate content) is excluded, only one of 10 fossils falls below the modern range (SBK). Fossil and modern API values also overlap, but the fossil samples seem to have shifted towards slightly lower values: fossil API values run from 0.043 to 0.090 ( $x=0.067$ ,  $s.d.=0.019$ ,  $N=10$ ), with three samples falling below the modern range. None of the fossils approach the upper value for the modern sample (0.12). The fossil PCI range lies between 3.4 and 4.1 ( $x=3.6$ ,  $s.d.=0.2$ ,  $N=10$ ) with three specimens falling outside the modern range. Two of these specimens (FL1 and SK2) have PCI values of 3.4, which falls just below the lowest modern value (3.5). Since PCI reproducibility is  $\pm 0.1$ , their distance from the modern

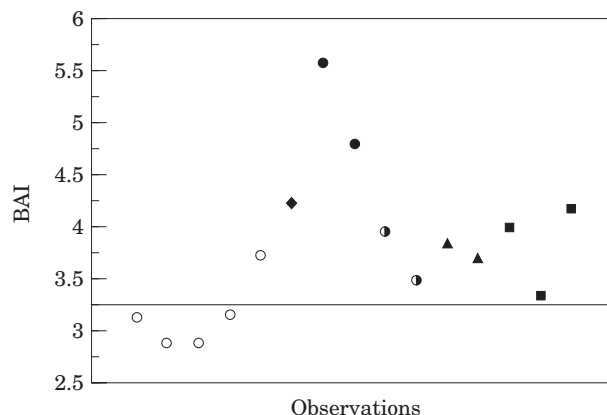


Figure 3. BAI for modern and fossil specimens. Note the great variation within and between fossil sites. ●, Border Cave; ○, Florisbad; ■, Makapansgat M3; ○, Modern; ◆, Steenbokfontein; ▲, Swartkrans M5.

range is not meaningful. BC2, however, has a PCI of 4.1, signifying substantial crystallographic change.

Despite some evidence of change in fossil API and PCI, analyses of variance show that BPI, API and PCI for modern and fossil samples do not differ significantly. The fact that carbonate content (as deduced from BPI) and crystallinity (PCI) do not differ significantly between modern and fossil enamel is not surprising and has been reported previously (Lee-Thorp & van der Merwe, 1991; Wang & Cerling, 1994; Rink & Schwarcz, 1995). The finding that BAI is different for modern and fossil enamel (Figure 3) is less expected (but see Michel, Ildefonse & Morin, 1995). Excluding the modern outlier, all fossil BAI values exceed those of moderns, ranging from 3.3 to 5.6 ( $x=4.1$ ,  $s.d.=0.7$ ,  $N=10$ ). Even with the outlier, modern and fossil samples are significantly different ( $P=0.02$ ).

Interestingly, there is no apparent relationship between sample age and BAI, BPI, API or PCI. Although samples are few, we might deduce that the crystallographic change that takes place occurs quite early during fossilization—certainly within the first 10,000 years. It is also worth noting that the degree of change in carbonate environments varies significantly within and between sites. For instance, BAI values from Makapan range from 3.3 to 4.2 ( $x=3.8$ ,  $s.d.=0.4$ ,  $N=3$ ). This is particularly salient as 3.3 barely exceeds the modern mean (3.1), while 4.2 exceeds most other fossils save those from Border Cave. Could we infer from this that there are “soft” and “hard” alteration zones at Makapan? Might we further surmise that less crystalline materials (bone) would preferentially survive in one or the other leading to taphonomic bias? It is also clear that Border Cave has a special fossilization environment. Analyses of variance show that the high BAI values from Border Cave are strongly different from other fossils ( $P=0.0016$ ) and moderns ( $P=0.0002$ ); furthermore, the only exceptional PCI number (4.1) comes from this site. Could

it be that the process of fossilization is different at this site?

Notwithstanding intra- and inter-site variability, these data allow us to make some general statements about the fossilization process. Calcitic intrusion is excluded for all our samples as no peak is present at  $711\text{ cm}^{-1}$  in any of the fossil spectra. It appears that precipitation of carbonate minerals occurs more frequently within more porous materials such as dentine and bone (Piepenbrink, 1989; Lee-Thorp & van der Merwe, 1991; Michel Ildefonse & Morin, 1996; Sponheimer, unpubl. data). Nonetheless, enamel apatite is altered, albeit subtly, during fossilization as evidenced by increased BAI. Michel, Ildefonse & Morin (1995) reported a similar increase in enamel from Lazaret as did Hassan (1977) in bone from a number of sites. It thus seems reasonable to infer that BAI augmentation (a relative increase in B-site versus A-site carbonate ions) generally characterizes fossilization. Three general mechanisms could induce this change: (1) exogenous carbonate incorporation at B-sites; (2) endogenous carbonate loss at A-sites; and (3) endogenous carbonate reorganization. It is also possible that all of these processes occur to a greater or lesser extent. These possibilities are evaluated individually below.

(1) *Exogenous Carbonate Incorporation*: Incorporation of external carbonate could cause BAI increases in two ways. Either exogenous carbonate ions could replace lattice phosphates, most likely via dissolution and reprecipitation of the original mineral, or new BAI-enriched apatite could be formed. The supplanting of phosphate ions by carbonate ions, the mechanism suggested by Hassan (1977) and Michel, Ildefonse & Morin (1995) for fossil bone and enamel, respectively, should cause increases in BPI and carbonate content. Our data do not support this, as the modern and fossil groups are not significantly different ( $P=0.51$ ) and overlap entirely. The addition of BAI-enriched apatite is more difficult to assess, but given that fossils at sites like Makapan are interred in a carbonate matrix, we might expect newly precipitated apatite to be carbonate-enriched. Once again, there is no evidence for carbonate enrichment at either A- or B-sites.

(2) *Endogenous Carbonate Loss*: As mentioned above, three fossil specimens have API values that fall below the modern range, while their BPI values remain within the modern range. This suggests that, at least in these cases, BAI increases reflect the selective loss of type A carbonate and not the addition of type B carbonate. The remaining fossil API values are within the modern range, though they tend to be lower than API values for modern specimens with similar carbonate content (from BPI). For example, ML3 has a slightly lower API (0.055) than the modern specimen DO2 (0.061), although they both have 3.0% carbonate by weight. It seems that the API range has subtly shifted towards lower values, but not

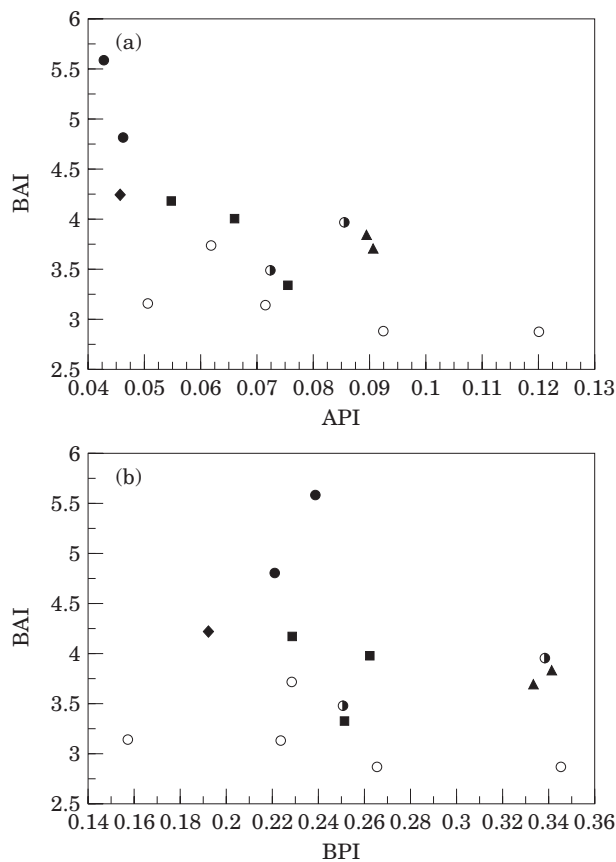


Figure 4. Scattergrams of BAI plotted against (a) API and (b) BPI. Key as for Figure 3.

enough to significantly differentiate the modern and fossil samples ( $P=0.32$ ). BAI and API are also negatively correlated ( $r=-0.65$ ) (Figure 4(a)) while BAI and BPI show no significant relationship ( $r=-0.16$ ) (Figure 4(b)). In tandem, these factors suggest that the selective loss of A-site carbonate ions contributes (at least partially) to the increase in BAI during fossilization.

There are two mechanisms by which this selective loss might take place. The first is the well-known phenomenon of fluorine incorporation during fossilization (Oakley, 1969; Sillen, 1989; Berger & Protsch, 1991). Fluoride ions have a great propensity for A-sites and are known to displace carbonate ions which inhabit them (Trombe, 1972; Grynpas & Rey, 1992). Another possible mechanism is the preferential deletion of type A carbonate ions due to their existence in hyper-soluble domains. Separate carbonate and phosphate domains have been postulated for enamel apatite due to asynchronous crystallinity increases during maturation (Rey *et al.*, 1991), so the possibility of separate type A and type B dominant domains may not be far-fetched. Unfortunately, little is known about how type A carbonate ions affect the solubility of enamel apatite. Presumably, they increase solubility (as do type B carbonates) since they introduce a weaker bond

and decrease crystallinity, but this has never been studied systematically. Could A-site carbonate ions increase solubility even more than those at B-sites? Thermogravimetric analysis suggests the opposite, as type A carbonate is more resistant to thermal decomposition than type B carbonate (LeGeros, 1967, 1991). We leave this as a possibility to be explored.

There is reason to believe that neither of these mechanisms wholly accounts for BAI increases. The incorporation of fluorine should increase crystallinity in apatites (LeGeros, 1967, 1991; Grynypas & Rey, 1992), as should the removal of highly-soluble (poorly-crystalline) material. As mentioned previously, however, there is no statistically significant difference between fossil and modern PCI. It is nevertheless suggestive that the four fossil specimens with the highest BAI values (SBK, BC1, BC2, ML3) have PCI values above the modern mean (3-6).

(3) *Endogenous Carbonate Reorganization*: This is really a special case of type A loss, whereby type A carbonate ions are translocated to B-sites during dissolution and reprecipitation of enamel mineral to a more thermo-dynamically stable form. Carbonate apatites precipitated in basic solutions contain very few carbonate ions at A-sites (Vignoles, Bonel & Holcomb, 1988; Barroug, Rey & Trombe, 1994). It is likely, therefore, that dissolution and reprecipitation of enamel subjected to alkaline groundwater (in limestone caves for instance) would lead to translocation of carbonate ions from A- to B-sites. Labile carbonate species might also be incorporated at B-sites in this manner. This mechanism should cause an increase in B-site carbonate ions in fossil enamel, which is not observed; however, since type B carbonate is about nine times more abundant in the first place, any (small) increases at this position might be very difficult to detect. The great variability of modern BPI also serves to obscure subtle changes in the fossils.

Determining whether exogenous carbonate incorporation, endogenous carbonate loss, or endogenous carbonate reorganization best accounts for BAI increases in fossil enamel is important because they each bear different consequences for the survival of biogenic carbon isotope ratios. Exogenous carbonate incorporation should result in a simple shift towards matrix carbonate values (which are a function of groundwater values). In contrast, endogenous carbonate loss may only affect isotope values if type A and type B carbonates are isotopically distinct. This is a strong possibility, however, since these carbonate species are involved in different bonds and isotopic fractionation is related to differences in bond energy (Koch, Tuross & Fagel, 1997). Endogenous carbonate loss (the loss of type A carbon ions) might then alter fossil signatures by removing an isotopically disparate species. Endogenous carbonate reorganization, on the other hand, may not have any effect on isotopic signatures since carbonate ions are merely being reshuffled from type A and labile environments to B-sites.

## Conclusion

Our results show that FTIR spectroscopy provides a powerful tool for detecting subtle shifts in carbonate environments during fossilization. Given this sensitivity, variation within extant fauna must be fully appreciated when evaluating carbonate diagenesis. Michel, Ildefonse & Morin (1995) published an elegant study of fossil enamel but used only one modern specimen as a basis for comparison with four fossils. Our data reveal that this can lead to misinterpretation. For instance, using one of our modern *Damaliscus* specimens (DOR) as a basis for comparison would lead us to conclude that virtually all fossils have higher BPI values, while using the other (DO2) would suggest that almost all fossils have lower values. Thus, by comparing fossils to individual modern specimens we can come to diametrically opposed conclusions! Clearly a suite of modern samples must be used for comparison to fossil taxa.

Considerable variability also exists in the carbonate environments of fossil specimens, although little crystallographic change seems to accompany fossilization save a subtle change in the ratio of carbonate ions at A- and B-sites. Our limited data suggest that this occurs within a few thousand years, with little alteration occurring thereafter. Moreover, considerable variability exists within and between sites. Exogenous carbonate incorporation, endogenous carbonate loss and endogenous carbonate reorganization are all plausible explanations for the increase in BAI values, but we are unable to choose unequivocally between them as none of the three perfectly fit our data. Indeed, these mechanisms may even work in tandem. Whatever the exact mechanism(s), the sensitivity of FTIR spectroscopy for detecting extremely small changes within carbonate environments promises to provide a valuable, independent tool for assessing diagenesis.

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