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Oxygen isotope analyses of co-existing carbonate and phosphate in biogenic apatite: a way to monitor diagenetic alteration of bone phosphate?

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Abstract

The oxygen isotopic composition of phosphate ($\delta^{18}Op$) and structural carbonate ($\delta^{18}Oc$) of hydroxylapatite was determined in 31 bone and tooth samples of modern mammals from different countries. These two variables are highly correlated ($r^2 = 0.98$) and the calculated best fit of linear regression is very similar to the equation calculated from the phosphate and carbonate palaeotemperature equations [1,2]. According to previous measurements [3–6] on fossils of different ages from different areas it seems quite improbable to find isotopically altered skeletal remains showing a good correlation between $\delta^{18}Op$ and $\delta^{18}Oc$, as is the case with modern samples. It therefore seems possible, at least in some cases, to use these measurements for monitoring fossil bone and tooth diagenetic alteration. When a set of points lie on the equilibrium line or close to it, the $\delta^{18}O$ values could be considered close to the original values. In contrast, when the points lie to the left or to the right of this line this probably means that the values are diagenetically modified, due to interaction with meteoric water or ^{18}O-enriched water, respectively.

Keywords: O-18/O-16; apatite; carbonates; bones; teeth; diagenesis

1. Introduction

For palaeoclimatological studies to be successful fossils that have not preserved their original isotopic signature must be identified and carefully avoided. Some authors are inclined to believe firmly that the phosphate isotopic composition of fossil remains is normally unchanged despite post-depositional processes (e.g. [7–9]). However, carbonate–fluorapatite is the major mineral phase of apatitic fossils and is considered a replacement phase of the original hydroxylapatite via dissolution–reprecipitation processes, which often take place at low temperature. When dissolution takes place under merely inorganic conditions the $\delta^{18}Op$ could be unaltered [10,11]. Evidence for apatite dissolution and re-precipitation processes often enzymatically mediated under natural conditions has been provided by other researchers [12,13]. The $\delta^{18}Op$ would then be re-set during this replacement [14]. Structural carbonate, also present within the apatite lattice, is considered to be less resistant than phosphate to post-depositional alteration [15–17]. However, the isotopic signal of both

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carbonate and phosphate is better preserved by well crystallised tooth enamel than by poorly crystallised dentine or bone phosphate (e.g. [18–23]).

The oxygen isotope composition of phosphate in the structure of biological apatite is directly related to the oxygen isotope composition of body water which, in turn, is related to the $\delta^{18}O$ of ingested water and, hence, to the $\delta^{18}O$ of local precipitation and/or atmospheric relative humidity [24–29]. In the case of fish and other organisms (pelecypods, gastropods, etc.) the $\delta^{18}O$ of body water is close to that of ambient water (fresh or marine water) [3,8,11]. There are few studies of the $\delta^{18}O$ of the structural carbonate of biogenic apatites. However, those that do exist suggest that this variable is also probably related to the oxygen isotope composition of body fluids and should, consequently, be considered as an archive of climatic information. Land et al. [15] showed that the $\delta^{18}O$ of modern bone carbonate was strongly related to latitude and relative atmospheric humidity. More recently, Koch et al. [30] interpreted the $\delta^{18}O$ variations in tusk laminae and molar dentine of mastodonts and mammoths from the late Pleistocene as seasonal changes in the $\delta^{18}O$ of their drinking water.

If the PO_4^{3-} and structural CO_3^{2-} are cogenetic oxygen-bearing phases in isotopic equilibrium with the same oxygen reservoir at the same temperature (for mammals the reservoir is body water and the temperature about 37°C) a linear correlation should exist between $\delta^{18}Op$ and $\delta^{18}Oc$ values. Kolodny and Luz [3] found a poor correlation between these two variables in bone apatite from modern fish whereas these values were linearly correlated in fossil fish. This correlation was explained as the effect of post-depositional interaction with meteoric water, affecting mainly the $\delta^{18}Oc$, the 'end point' of this alteration being a strong correlation between $\delta^{18}Op$ and $\delta^{18}Oc$. In the case of modern fish, the $\delta^{18}Oc$ has apparently no relation with temperature or the isotopic composition of the water in which the fish lived. In this case a good correlation would be synonymous with recrystallization and post-mortem alteration, while a lack of correlation would be synonymous with a good preservation of the pristine isotopic composition.

This paper presents the first set of $\delta^{18}Op$ and $\delta^{18}Oc$ measured on modern mammal tooth and bone, along with similar results obtained by previous authors from fossil fish, mammals and reptiles. The aim of this study was: (1) to check whether or not oxygen of structural apatite carbonate is in equilibrium with body water in modern mammals, as is the case with the phosphate oxygen; (2) if this is the case, to calculate the quantitative relationship between the isotopic composition of oxygen in phosphate and in carbonate of bone and tooth apatite; (3) to check whether it is possible to obtain information about *post-mortem* alteration effects in fossils by means of the coupled isotope measurement of oxygen in carbonate and phosphate.

2. Results

A variety of tooth and bone samples of modern mammals was selected to cover a wide range of $\delta^{18}Op$ and $\delta^{18}Oc$ values. The locations from which the samples come span from the high northern latitude of the Alaska samples to the latitude of about 39°S of the New Zealand sample. The deer samples (*Cervus elaphus*) are the same used by D'Angela and Longinelli [31] to calibrate the $\delta^{18}Op$–water scale. Well established standard procedures were used to prepare the samples ([10,11,32] for phosphate; [33] for carbonate). The standard deviation of our $\delta^{18}Op$ measurements, calculated on a number of samples measured during the last 20 years, is fairly constant, ranging from about ± 0.15 to about $\pm 0.20‰$ (1σ). As regards the reproducibility of our $\delta^{18}Oc$ measurements, the statistical meaning is not so good because we began these measurements only recently. However, the mean standard deviation is quite close to $\pm 0.20‰$ (1σ).

All our samples were run in duplicate and the reported values are the mean of at least two consistent results. The isotopic results are reported in Table 1 and throughout the text vs. V-SMOW isotopic standard.

The $\delta^{18}Oc$ values obtained from modern deer bones were compared with the mean $\delta^{18}O$ values of local meteoric water as reported by D'Angela and Longinelli [31] (Fig. 1). A good positive relationship exists between the two variables, the least-squares fit yielding the following equation:

$$\delta^{18}Oc = 0.998\,\delta^{18}Ow + 33.63 \quad (r^2 = 0.98) \qquad (1)$$

Table 1
Oxygen isotope analyses of phosphate ($\delta^{18}Op$) and carbonate($\delta^{18}Oc$) from teeth and bones of modern mammals from different areas

Species	Locations	No. of specimens	$\delta^{18}Op$ (s.d.)	$\delta^{18}Oc$ (s.d.)	$\delta^{18}Ow$
Cervus elaphus [b]	Bayerische Wald, Germany	3	12.8(±0.27)	22.3(±0.25)	−11.5
Cervus elaphus [b]	Abruzzo Park, Italy	2	14.9	23.9	−9.4
Cervus elaphus [b]	Inland Napier, New Zealand	1	16.4	25.5	−8.2
Cervus elaphus [b]	Bas Rhin, France	4	16.5(±0.75)	25.5(±0.51)	−8.0
Cervus elaphus [b]	Haute Marne, France	3	16.8(±0.26)	26.2(±0.18)	−7.7
Rangifer tarandus [t]	Alaska, USA	1	4.8	13.2	
Ursus americanus [t]	Alaska, USA	1	13.9	22.8	
Canis lupus [t]	Siberia	1	5.3	15.9	
Rangifer tarandus [t]	Norway	1	12.2	19.7	
Bos taurus [t]	Pyrénée, France	1	15.7	24.4	
Ovis aries [b]	Bretagne, France	2	17.5	26.2	
Capra ibex [b]	Montecristo Island, Italy	1	19.4	28.4	
Alcephalus major [t]	Mauritania	1	21.4	30.1	
Camelus dromaderius [t]	Mauritania	5	23.0(±1.4)	33.2(±1.8)	
Syncerus caffer [t]	Ivory Coast	1	22.8	31.4	
Kobus sp. [t]	Ivory Coast	2	23.8	32.7	
Ichneumon albicauda [t]	Cameroon	1	25.4	35.4	

The samples are arranged for decreasing latitudes. In the case of *Cervus elaphus* the mean $\delta^{18}O$ values of local meteoric water according to [31] are also reported. [b] = bone samples; [t] = tooth samples; s.d. = standard deviation. The isotopic results are reported vs. the V-SMOW isotopic standard.

The slope of Eq. (1) agrees remarkably well with the slope of the equation calculated for the $\delta^{18}Op$ and $\delta^{18}Ow$ of the same samples (1.072); the difference between $\delta^{18}Op$ and $\delta^{18}Oc$ values is about 9.2‰. It can be concluded that the isotopic composition of oxygen in bone carbonate is in equilibrium conditions with body fluid, as is the case for the isotopic composition of oxygen in bone phosphate. Assuming the same fractionation effect as for the acid–carbonate reaction, the fractionation factor between phosphate and carbonate ($\alpha CO_3 - PO_4$) is 1.0090 at 37°C. The $\delta^{18}Op$ vs. $\delta^{18}Oc$ values for all the measured modern mammals are plotted in Fig. 2.

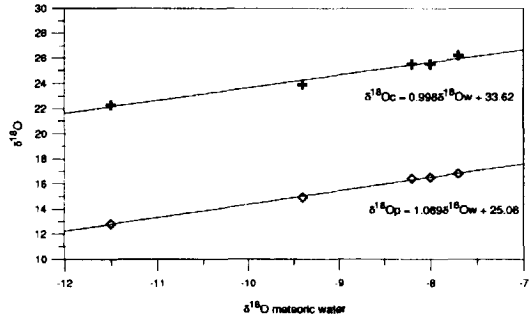

Fig. 1. Oxygen isotope values of tooth and bone phosphate ($\delta^{18}Op$) and carbonate ($\delta^{18}Oc$) of *Cervus elaphus* vs. mean oxygen isotope values of local meteoric water ($\delta^{18}Ow$). The phosphate–water relationship is calculated according to the $\delta^{18}Ow$ values reported in [31].

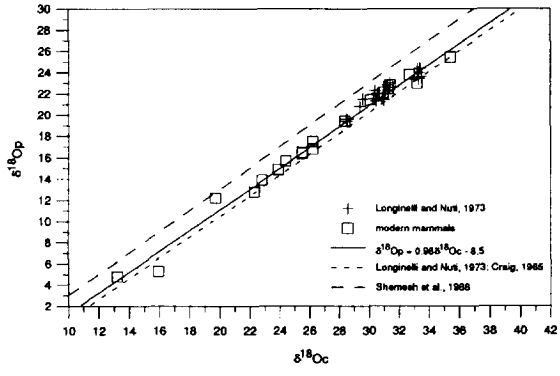

Fig. 2. Relationship between phosphate $\delta^{18}O$ values ($\delta^{18}Op$) and carbonate $\delta^{18}O$ values ($\delta^{18}Oc$) in modern mammals. The calculated best fit is Eq. (2). The $\delta^{18}O$ values of modern carbonate shells (Longinelli and Nuti [1]) are also shown, along with the calculated straight line combining the phosphate and carbonate–water palaeotemperatures scales [1,2] and the straight line calculated for 37°C from the calcite–apatite equation calibrated by Shemesh et al. [34].

Again, the two sets of values are highly correlated ($r^2 = 0.98$) and the calculated best fit is:

$$\delta^{18}Op = 0.98\,\delta^{18}Oc - 8.5 \quad (2)$$

The mean $\delta^{18}Oc - \delta^{18}Op$ difference is 9.1‰. Longinelli and Nuti [1] measured the $\delta^{18}O$ of modern carbonate shells and the phosphate extracted from them and obtained a difference in their $\delta^{18}O$ of about 9.0‰ which is constant in the temperature range considered (0–30°C). As is apparent from Fig. 2, the equation calculated for marine invertebrates combining the phosphate and carbonate–water palaeotemperature scales of Longinelli and Nuti [1] and Craig [2] has the same slope as Eq. (2) calculated for terrestrial mammals. The small difference between the two intercepts seems to be within statistical error. Shemesh et al. [34] derived an empirical calibration for the calcite–apatite system which can be used over a broad temperature range. In Fig. 2 we also report this equation calculated for 37°C but, for this temperature, the differences between $\delta^{18}Oc$ and $\delta^{18}Op$ values are about 7.0‰, a value which is smaller than the previous ones.

3. Discussion

The direct relationship found between the oxygen isotopic composition of phosphate and of structural carbonate of biogenic apatite has interesting implications, suggesting the possibility of using the fossil bone and tooth $\delta^{18}Oc$ of species for which the phosphate palaeotemperature equation is already known, for palaeohydrological and palaeoclimatological studies.

It is important to check the possible use of Eq. (2) and of the simultaneous measurement of $\delta^{18}Op$ and $\delta^{18}Oc$ in fossil apatites to recognise possible effects of *post mortem* alteration related to diagenetic and taphonomic processes on the pristine isotopic values. The $\delta^{18}Op$ and $\delta^{18}Oc$ values obtained by various authors [3–6] from different fossil samples are plotted in Fig. 3. The oxygen isotope composition of human bones from Egypt (7,000–2,000 B.P.) is fairly well related to the straight line of Eq. (2). In this case the samples were buried in the sand in a warm and dry environment and no evidence of bone alteration was detected [5]. The enamel of mammal tooth samples, from the Paglicci cave in southern Italy, 30,000–11,000 B.P. [Iacumin et al., in preparation], does not show clear evidence of alteration and its oxygen isotope values cluster not far from the line. In these two cases the $\delta^{18}Op$ and the $\delta^{18}Oc$ values can be considered close to equilibrium conditions. It should be kept in mind that the difference between $\delta^{18}Op$ and $\delta^{18}Oc$ in apatite does not change considerably with temperature in the range 0–37°C. From a theoretical point of view, post-depositional isotope alteration may re-set the $\delta^{18}O$ of both crystalline sites in a new equilibrium condition. Their position would be definitely shifted away from the equilibrium line in the event of non-equilibrium, partial equilibrium or equilibrium conditions at relatively high temperatures. Three other sets of data from fossil samples in which the phosphate and carbonate oxygen values are not in equilibrium conditions are also plotted in Fig. 3. The samples of group A are bones from one single specimen of *Tyrannosaurus rex* from the Maastrichtian Hell Creek Formation [4] in which the $\delta^{18}Op$ values are relatively constant whereas the $\delta^{18}Oc$ values range from about 21‰ to 29.5‰. This horizontal trend may be interpreted in two different ways: (1) a pristine value of $\delta^{18}Op$ and a large diagenetic effect on $\delta^{18}Oc$ by continuous interaction with isotopically different waters; or (2) the observed trend could result from the effect of

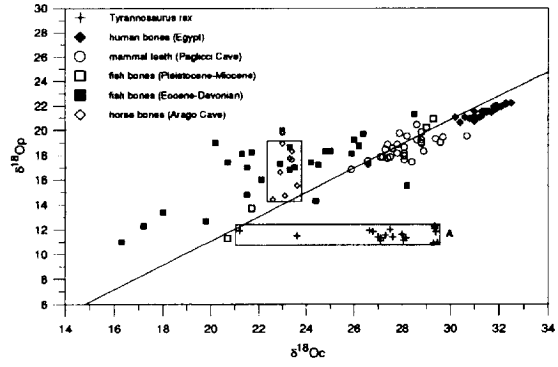

Fig. 3. $\delta^{18}Op$ vs. $\delta^{18}Oc$ of different sets of samples reported in the literature: fish bones [3]; dinosaur (*Tyrannosaurus*) bones [4]; human bones from Egypt [5]; and horse bones [6]. Further information on the fish fossils may be obtained from the original paper by Kolodny and Luz [3]. Detailed data on host sediments are not reported by these authors. The straight line refers to Eq. (2), calculated for modern mammals.

different diagenetic processes, one of which was strong enough to modify completely both the δ^{18}Op and δ^{18}Oc values: subsequent diagenetic processes may have modified δ^{18}Oc values leaving almost unchanged the modified δ^{18}Op. This is possible, particularly in the case of very old samples, since δ^{18}Oc values may be modified more easily than δ^{18}Op values during diagenesis. The samples of group B (bones of *E. caballus* coming from the same stratigraphical level in the Arago Cave, Pyrénées, France, 450,000–480,000 B.P. [6]), have a different behaviour: the δ^{18}Oc values are fairly homogeneous while the δ^{18}Op range from about 14‰ to 20‰. This may be considered as an example of a large isotope exchange which took place between carbonate and meteoric water, leading to mineral–fluid equilibrium. In contrast, the mineral–fluid exchange processes involving phosphate were largely incomplete and far removed from equilibrium conditions. The third set of data refers to fish bones and teeth from museum collections throughout the world, ranging in age from Devonian to Pleistocene [3]. In this case both the δ^{18}Op and δ^{18}Oc values are highly scattered, with the most recent (Pleistocene and Miocene) samples very close to the line of Eq. (2). This was explained by the authors as a shift in the carbonate towards lower δ^{18}O values, related to the fact that the post-depositional interaction of carbonate oxygen with meteoric water is more significant than its phosphate oxygen counterpart.

4. Conclusions

According to the reported data from sets of fossil samples, it would seem to be quite improbable to find isotopically altered assemblages showing a good correlation between δ^{18}Op and δ^{18}Oc, as is the case with modern samples (Eq. (2)). This is obviously related to the extremely different rates of carbonate–water and phosphate–water isotopic exchange, which should prevent re-equilibration of both compounds. One can conclude that, when a set of points lie on the straight line or very close to it, the δ^{18}O values should be considered close to the pristine values. In contrast, when the points do not lie on the straight line the isotopic values are probably modified by diagenetic processes: δ^{18}Op values are also unreliable in the case of a wide scattering of the data.

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References

[1] A. Longinelli and S. Nuti, Revised phosphate–water isotopic temperature scale, Earth Planet. Sci. Lett. 19, 373–376, 1973.

[2] H. Craig, The measurement of oxygen isotope paleotemperatures, in: Stable Isotopes in Oceanographic Studies and Paleotemperatures, E. Tongiorgi, ed., pp. 161–182, CNR, Lab. Geol. Nucl., Pisa, 1965.

[3] Y. Kolodny and B. Luz, Oxygen isotopes in phosphate of fossil fish — Devonian to recent, in: Stable Isotope Geochemistry: A Tribute to Samuel Epstein, H.P. Taylor Jr., J.R. O'Neil and I.R. Kaplan, eds., Vol. 3, pp. 105–119, Geochem. Soc., 1991.

[4] R.E. Barrick and W.J. Showers, Thermophysiology of Tyrannosaurus rex: evidence from oxygen isotopes, Science 265, 222–224, 1994.

[5] P. Iacumin, H. Bocherens, A. Mariotti and A. Longinelli, An isotopic palaeoenvironmental study of human skeletal remains from the Nile Valley, Palaeogeogr. Palaeoclimatol. Palaeoecol., in press.

[6] D. Cominotto, P. Iacumin and A. Longinelli, A stable isotope study of mammal skeletal remains of mid Pleistocene age, Palaeogeogr. Palaeoclimatol. Palaeoecol., in press.

[7] B. Luz, Y. Kolodny and J. Kovach, Oxygen isotope variations in phosphate of biogenic apatites, III. Conodonts, Earth Planet. Sci. Lett. 69, 255–262, 1984.

[8] Y. Kolodny and M. Raab, Oxygen isotopes in phosphatic fish remains from Israel: paleothermometry of tropical Cretaceous and Tertiary shelf waters, Palaeogeogr. Palaeoclimatol. Palaeoecol. 64, 59–67, 1988.

[9] A. Shemesh, Y. Kolodny and B. Luz, Oxygen isotope variations in phosphate of biogenic apatite. II. Phosphorite rocks, Earth Planet. Sci. Lett. 64, 405–416, 1983.

[10] A.P. Tudge, A method of analysis of oxygen isotopes of orthophosphates: its use in the measurement of paleotemperatures, Geochim. Cosmochim. Acta 18, 81–93, 1960.

[11] Y. Kolodny, B. Luz and O. Navon, Oxygen isotope variations in phosphate of biogenic apatite. I: Fish bone apatite, Earth Planet. Sci. Lett. 64, 398–404, 1983.

[12] D. Soundry and Y. Champetier, Microbial processes in the Nagev phosphorites (southern Israel), Sedimentology 30, 411–423, 1983.
[13] J. Lucas and L. Prevot, The synthesis of apatite by bacterial activity: mechanism, Sci. Géol. Mém. 77, 83–92, 1985.
[14] Y. Kolodny and B. Luz, Dinosaur bones: fossil or pseudomorphs? The pitfalls of physiology reconstruction from apatitic fossils, EUG 8, Symp. XV-4, Terra Abstract 238, 1995.
[15] L.S. Land, E.L. Lundelius Jr. and S. Valastro, Isotopic ecology of deer bones, Palaeogeogr. Palaeoclimatol. Palaeoecol. 32, 143–151, 1980.
[16] M.J. Schoeninger and M.J. DeNiro, Carbon isotope ratios of apatite from fossil bone cannot be used to reconstruct diets of animals, Nature 297, 577–578, 1982.
[17] B.K. Nelson, M.J. DeNiro, M.J. Schoeninger and D.J. De Paolo, Effects of diagenesis on strontium, carbon, nitrogen and oxygen concentration and isotopic composition of bone, Geochim. Cosmochim. Acta 50, 1941–1949, 1986.
[18] J.A. Lee-Thorp and N.J. Van der Merwe, Carbon isotope analysis of fossil bone apatite, S. Afr. J. Sci. 83, 712–715, 1987.
[19] J.A. Lee-Thorp and N.J. Van der Merwe, Aspects of the chemistry of modern and fossil biological apatites, J. Archeol. Sci. 18, 343–354, 1991.
[20] L.K. Ayliffe, A.M. Lister and A.R. Chivas, The presevation of glacial–interglacial climatic signature in the oxygen isotopes of elaphant skeletal phosphate, Palaeogeogr. Palaeoclimatol. Palaeoecol. 99, 179–191, 1992.
[21] J. Quade, T.E. Cerling, J.C. Barry, M.E. Morgan, D.R. Pilbeam, A.R. Chivas, J.A. Lee-Thorp and N.J. Van der Merwe, A 16 million year record of paleodiet using carbon and oxygen isotopes in fossil teeth from Pakistan, Chem. Geol. (Isot. Geochem. Sect.) 94, 183–192, 1992.
[22] T.E. Cerling, Y. Wang and J. Quade, Expansion of C4 ecosystems as an indicator of global ecologic change in the late Miocene, Nature 361, 344–345, 1993.
[23] J.D. Bryant, Oxygen isotope systematics in mammalian body water and in modern and fossil equid tooth enamel phosphate, Ph.D. Thesis, Columbia Univ., 1995.
[24] A. Longinelli, Oxygen isotopes in mammal bone phosphate: a new tool for paleohydrological and paleoclimatological research?, Geochim. Cosmochim. Acta 48, 385–390, 1984.
[25] A. Longinelli and A. Peretti-Padalino, Oxygen isotopic composition of water from mammal blood: first results, Mass Spectrom. Biochem. Med. Environ. Res. 1, 135–139, 1980.
[26] B. Luz and Y. Kolodny, Oxygen isotope variations in phosphate of biological apatites. IV. Mammal teeth and bones. Earth Planet. Sci. Lett. 75, 29–36, 1985.
[27] L.K. Ayliffe and A.R. Chivas, Oxygen isotope composition of the bone phosphate of Australian kangaroos: potential as a palaeoenvironmental recorder, Geochim. Cosmochim. Acta 54, 2603–2610, 1990.
[28] B. Luz, A.B. Cormie and H.P. Schwartz, Oxygen isotope variation in phosphate of deer bones, Geochim. Cosmochim. Acta 54, 1723–1728, 1990.
[29] J.D. Bryant, B. Luz and P.N. Froelich, Oxygen isotopic composition of fossil horse tooth phosphate as a record of continental climate, Palaeogeogr. Palaeoclimatol. Palaeoecol. 107, 303–316, 1994.
[30] P.L. Koch, D.C. Fisher and D. Dettman, Oxygen isotope variation in the tusks of extinct proboscideans: a measure of season of death and seasonality, Geology 17, 515–519, 1989.
[31] D. D'Angela and A. Longinelli, Oxygen isotopes in living mammal's bone phosphate: further results, Chem. Geol. 86, 75–82, 1991.
[32] A. Longinelli, Oxygen isotopic composition of orthophosphate from shells of living marine organisms, Nature 207, 716–719, 1965.
[33] H. Bocherens, M. Fizet, A. Mariotti, D. Billiou, G. Bellon, J.P. Borel and S. Simone, Biogéochimie isotopique (13C, 15N, 18O) et paléoécologie des ours Pléistocénes de la grotte d'Aldène, Bull. Mus. Anthropol. Préhist. Monaco 34, 29–49, 1991.
[34] A. Shemesh, Y. Kolodny and B. Luz, Isotope geochemistry of oxygen and carbon in phosphate and carbonate of phosphorite francolite, Geochim. Cosmochim. Acta 52, 2565–2572, 1988.