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Stable isotope composition and rare earth element content of vertebrate remains from the Late Cretaceous of northern Spain (Laño): did the environmental record survive?

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Abstract

Oxygen and carbon isotope measurements have been performed on phosphatic remains from faunal associations (dinosaurs, crocodiles, turtles and fish) of the Late Cretaceous continental and marine sediments from northern Spain (Basque Country). The environmental meaning of the oxygen isotope record in fossil reptiles is discussed on the basis of known paleoecology, modern fauna analogs, and apatite chemistry (rare earth elements (REE), CO_3^{2-} and PO_4^{3-} contents). Fossil remains in sandstones and argillites from two localities (Urria and Cuezva) have low (down to 16‰) and scattered $\delta^{18}O(PO_4,CO_3)$ and $\delta^{13}C$ values with REE patterns characterized by strong middle REE enrichments. These geochemical compositions of the biogenic apatites have most likely been acquired during a multi-stage late diagenesis involving complete recrystallization of the apatite in the presence of aqueous fluids. REE contents of fossils preserved in the clayey sands from the site of Laño suggest that samples have only been affected by early diagenesis. Despite the diversity of analyzed taxa and the close association of marine (sharks and rays) and freshwater species (crocodiles and turtles) evolving in a littoral environment, the narrow range of phosphate $\delta^{18}O$ values is interpreted as reflecting the temperature and isotopic composition of groundwaters that prevailed in the burial environment. The potential information relative to the physiology and thermal regime of the vertebrates has been erased during the process of early diagenesis. If all oxygen in the phosphate has exchanged with groundwaters, the oxygen isotope composition of vertebrate remains suggests that a warm climate ($T = 20–25°C$) prevailed in northern Spain during the Late Cretaceous.

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1. Introduction

During the last decades, stable isotope studies of marine fossils have successfully quantified paleoclimates for the last 150 Ma of the Earth's history (e.g. Shackleton and Opdyke, 1973; Saito and Van Donk, 1974; Savin, 1977; Huber et al., 1995; Price and Sellwood, 1997; Norris and Wilson, 1998). Air temperature, humidity and precipitation sources are important climatic variables that can be inferred from the study of continental fossils. Numerous studies have demonstrated that the oxygen isotope compositions of freshwater aragonite fish otoliths (e.g. Patterson et al., 1993; Thorrold et al., 1997) or apatite from mammalian bones and teeth (e.g. Fricke and O'Neil, 1996; Reinhard et al., 1996; Genoni et al., 1998) are reliable indicators of climatic variations throughout the Quaternary. However, the oxygen isotope compositions of fossils buried in marine and terrestrial environments may be strongly disturbed during diagenetic recrystallization (e.g. Longinelli, 1966; McArthur and Herczeg, 1990; Ayliffe et al., 1994; Longinelli, 1996; Kolodny et al., 1996). It has been shown that the processes of isotopic alteration are not directly linked to the age (Kolodny and Luz, 1991) but more to the conditions of fossilization and the geological history of fossil-bearing formations that are critical for governing the preservation of the pristine isotopic compositions. Moreover, knowledge of the oxygen isotope fractionation between body and ambient waters is necessary to interpret the $\delta^{18}O$ values of mammalian phosphate in terms of physiological or paleoclimatic records (Longinelli, 1984; Luz et al., 1984; Luz and Kolodny, 1985). This can only be performed by studying living species for which the $\delta^{18}O$ values of the drinking water may be measured. Several studies (Longinelli, 1984; Luz and Kolodny, 1985; D'Angela and Longinelli, 1990; Delgado Huertas et al., 1995) have shown that each mammalian species is characterized by a unique oxygen isotope frac-

tionation equation partly depending on diet, body mass, metabolic activity, and the water source. It means that the oxygen isotope fractionation equations cannot be established for extinct mammalian species, hence excluding an accurate determination of the oxygen isotope composition of local fresh waters. Therefore, we examine whether the oxygen isotope compositions of reptiles may be used to study Mesozoic continental paleoenvironments.

Mammalian fossils are rare before the K/T boundary whereas reptilian phosphate remains are abundant in continental sediments since the Permian. By analogy with fish, we can expect that the oxygen isotope fractionation between water and reptile phosphate is likely dependent on both ambient temperature and composition of drinking water. A priority objective is to determine how reptiles fractionate oxygen isotopes relative to co-existing fish and how the isotopic fractionation may also depend on metabolic activity, thermal inertia of the body, mean residence time of body water, and diet. Oxygen isotope compositions of fossil reptile and fish associations will be compared to present-day populations from low-latitude continental environments.

The environmental meaning of the oxygen isotope record in fossil reptiles is tested by analyzing the faunal associations of the Late Cretaceous continental and marine sediments from northern Spain (Basque Country). There is a large abundance of reptilian fossils such as crocodilians and aquatic turtles associated with dinosaur and fish fossils (Astibia et al., 1990). Moreover, the paleogeography is relatively well-known (Lapparent de Broin et al., 1991) and the paleoenvironment of this area has been qualitatively estimated on the basis of sedimentologic criteria, faunal associations, and paleolatitudes inferred from reconstructions of plate motions (Scotese et al., 1988). To evaluate a probable diagenetic alteration of the studied fossils, we measured the CO_3^{2-} weight% substituting in the apatite, the rare earth element
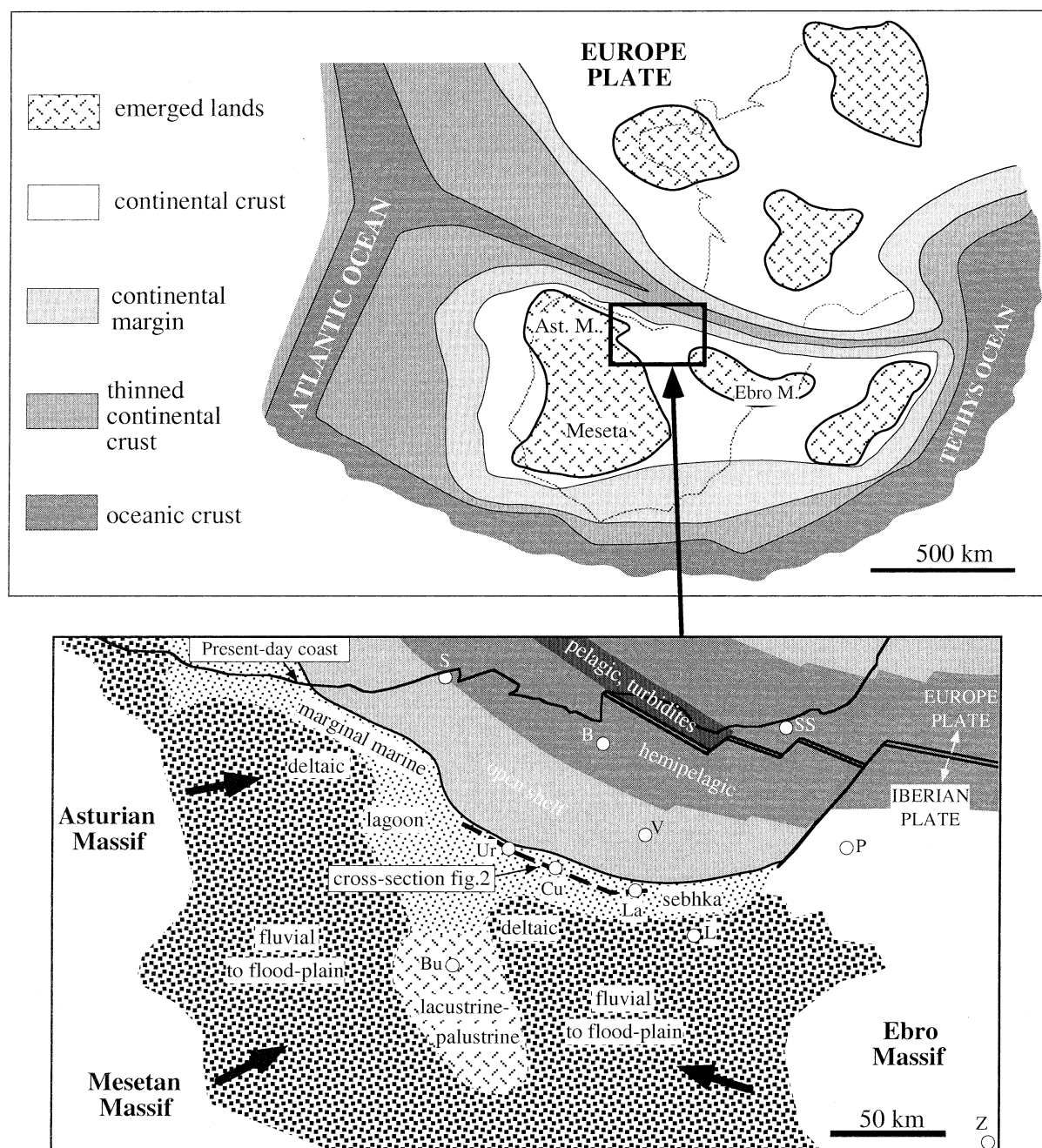
Fig. 1. Paleogeographic location and detailed paleoenvironmental map of northern Spain during the Late Cretaceous. B: Bilbao; Bu: Burgos; L: Logrono; P: Pamplona; V: Vitoria; S: Santander; SS: San Sebastian. Sample sites: Ur: Urria (3°27′40″W, 42°50′45″N); Cu: Cuezva (3°13′50″W, 42°45′45″N), and La: Laño (2°37′30″W, 42°00′45″N). Modified from Floquet (1991).
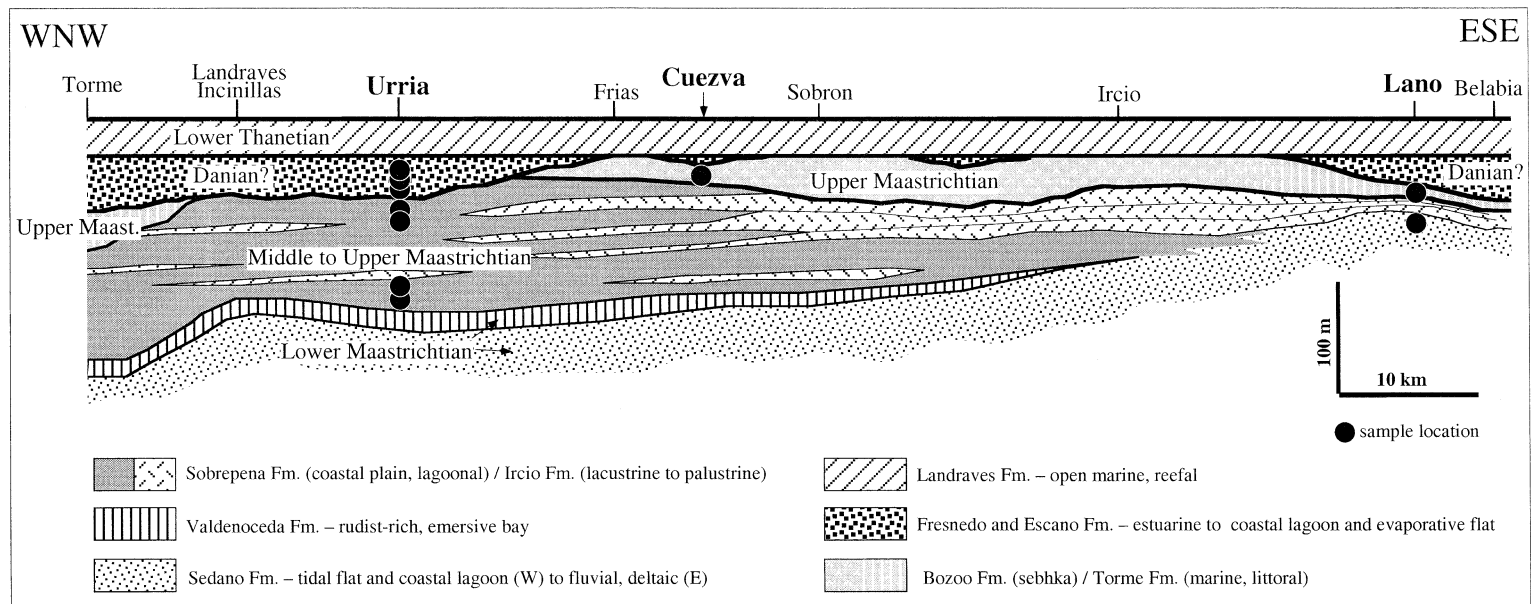
Fig. 2. Stratigraphic correlation and geographic facies variations within the Middle–Upper Maastrichtian formations (Sobrepeña, Ircio, Bozóo and Torme Formations), along a WNW–ESE cross-section passing through the sample localities. The only marine influence occurred during deposition of the Torme (= Nankin) Formation, laterally equivalent to the Bozóo Formation. These formations are erosively overlain by the Fresnedo and Escaño estuarine then lagoonal formations, presumably of Danian age. Finally, the marine Thanetian Landraves Formation is superimposed on a ravinement surface cutting across the whole Maastrichtian–Danian (?) Formations. Note the increasing marine influence eastwards (towards Laño) and to the west in the Maastrichtian (redrawn and modified from Floquet (1991) and Pluchery (1995).

(REE) distributions, and the oxygen isotope fractionation between the CO_3^{2-} and PO_4^{3-} components of the biogenic phosphate. If the above criteria suggest that part of the sample collection preserved the original stable isotope compositions, the deduced environmental information will be compared with climatic models (Bush and Philander, 1997) and paleogeographic reconstructions of the Late Cretaceous of northern Spain.

2. Geological setting

Studied fossil remains come from three outcrop localities of the sedimentary series of northern Spain: Urria, Cuezva, and Laño (Figs. 1 and 2), whose age is considered to be Late Cretaceous (Maastrichtian) and possibly Danian (Pluchery, 1995). According to the plate tectonic reconstructions performed by Scotese et al. (1988), the studied area was at 35°N during the Late Cretaceous. A detailed study of the depositional environments for these three localities was made by Floquet (1991) and Pluchery (1995).

The site of Laño was discovered in 1984 and is one of the most important European sites for its abundance and diversity in continental vertebrate remains such as amphibians, reptiles (aquatic turtles, crocodilians, dinosaurs), fish, and even some rare mammals (Astibia et al., 1987, 1990; Pereda-Superbiola et al., 1995; Lapparent de Broin and Murelaga, 1996; Buscalioni et al., 1997). This site is located on the southern edge of the Miranda–Treviño syncline, in the Basque–Cantabric basin. The sites of Urria and Cuezva also contain vertebrate remains that were sampled for the first time as part of this study. Formations that crop out in these two sites may be correlated to Laño formations (Floquet, 1991; Pluchery, 1995).

Fossils have been sampled from continental to marine formations that are the Sobrepeña and Fresnedo Fm. at Urria, Bozóo Fm. at Cuezva, Sedano and Torme Fm. at Laño. The Sobrepeña (Middle–Upper Maastrichtian) and Bozóo (Upper Maastrichtian) Formations are characterized by predominant green and red lagoonal argillites. The presence of gypsum indicates a temporary marine input and desiccation features reveal frequent exundations. The Bozóo Formation is supposed to be a lateral equivalent of the Torme formation, both erosively superimposed over the Sobrepeña Formation (Pluchery, 1995). It corresponds to a supra-tidal sabhka. In the Laño quarry, channels, inter-channel pools and sandbars testify to the fluvial origin of the S1U3 unit of the Sedano Formation (Astibia et al., 1987). The most important bone accumulation is located in clayey sand between two ferrous hardgrounds. An Early Maastrichtian age has been ascribed to the Laño fauna (Astibia et al., 1987), whereas the whole Sedano Formation is considered to be of Lower Maastrichtian age (Floquet, 1991). Fish teeth from the Torme Formation (S2U1 unit) have been sampled from the white stratified marine limestones that contain Uppermost Maastrichtian foraminifera. These limestones are interpreted as the result of a transgression in the terminal Cretaceous. Their deposition took place in the littoral domain connected to the open sea as attested by the presence of *Nautilus* sp., corals, gastropods, and brachiopods. Crocodile and fish teeth have been sampled in yellow sandstones that were deposited in a transgressive estuarine environment (Pluchery, 1995), corresponding to the sandy and limy Fresnedo Formation in the Urria section that is probably Danian in age (Floquet, 1991; Pluchery, 1995).

3. Analytical methods

3.1. Stable isotopes

Phosphate from biogenic apatites was isolated as Ag_3PO_4 crystals (Crowson et al., 1991; Lécuyer et al., 1993). Most samples of silver phosphate were reduced to carbon dioxide in the presence of graphite at a temperature of 1100°C following the protocol of Lécuyer et al. (1998) adapted from O'Neil et al. (1994). A few others were reacted with BrF_5 at 600°C to release molecular oxygen converted into CO_2 in the presence of hot graphite (Table 1). The CO_2 produced during these reactions was directly trapped in liquid nitrogen then analyzed on a VG Prism™ mass

Table 1
Sample locations, fauna, environment, and stable isotope compositions of phosphate and carbonate from late Cretaceous vertebrate remains of northern Spain

Sample	Location	Formation/level	Fauna remains	Environment	Sedimentary matrix	$\delta^{18}O_{PO_4}$ (‰ SMOW)	$\delta^{18}O_{CO_3}$ (‰ SMOW)	$\delta^{13}C_{CO_3}$ (‰ PDB)	CO_3^{2-} (wt%)	P_2O_5 (wt%)
LL1	Laño	S1U3/L2	turtle plate	fluvial	clayey sand	18.7	27.8	−4.5	4.6	34.1
LL2	Laño	S1U3/L1A	Titanosauridae, dinosaur bone	fluvial	clayey sand	19.2	27.0	−6.8	4.8	27.8
LL3	Laño	S1U3/L1A	crocodilian vertebra	fluvial	clayey sand	18.7	27.1	−7.3	5.1	28.4
Le3	Laño	S1U3/L1A	crocodilian tooth	fluvial	clayey sand	19.1	27.2	−6.0	4.9	31.0
Le4	Laño	S1U3/L1A	crocodilian tooth	fluvial	clayey sand	19.2	25.3	−4.6	4.9	35.2
Le5	Laño	S1U3/L1A	Titanosauridae, dinosaur bone	fluvial	clayey sand	20.3	27.0	−6.8	4.2	32.2
Le6	Laño	S1U3/L1A	*Iguanodon*, dinosaur tooth	fluvial	clayey sand	19.3	26.4	−7.0	4.4	35.6
Le7	Laño	S1U3/L1A	*Ankylosaurus*, dinosaur tooth	fluvial	clayey sand	19.3	n.d.	n.d.	n.d.	38.0
Le8	Laño	S1U3/L1A	fish scale	fluvial	clayey sand	19.7	27.0	−2.9	n.d.	35.2
Le9	Laño	S1U3/L1A	Dortokidae, turtle plate	fluvial	clayey sand	19.5	26.1	−6.2	n.d.	33.2
C1*	Laño	S1U3/L1A	Alligatoridae tooth	fluvial	clayey sand	20.4	–	–	–	
D1*	Laño	S1U3/L1A	Titanosauridae (juvenile), dinosaur tooth	fluvial	clayey sand	19.4	–	–	–	
C2*	Laño	S1U3/L1A	Alligatoridae tooth	fluvial	clayey sand	18.8	–	–	–	
D2*	Laño	S1U3/L1A	ornithopod *Hypsilophodon*, dinosaur tooth	fluvial	clayey sand	18.9	–	–	–	
C3*	Laño	S1U3/L1A	Alligatoridae tooth	fluvial	clayey sand	19.3	–	–	–	
D3*	Laño	S1U3/L1A	Theropoda (juvenile), dinosaur tooth	fluvial	clayey sand	19.1	–	–	–	
LT1	Laño	S2U1	shark tooth	marine–littoral	limestones	19.4	27.1	−1.9	5.5	32.8
LT2	Laño	S2U1	Rhombodontidae, ray tooth	marine–littoral	limestones	18.7	26.4	−3.4	6.6	28.9
LT3	Laño	S2U1	teleostean tooth	marine–littoral	limestones	18.8	25.4	−3.3	7.0	24.9
US1	Urria	Sobrepeña	vertebrate bone	coastal plain	argillites	19.3	29.7	−8.0	6.2	28.2
US2	Urria	Sobrepeña	vertebrate bone	coastal plain	argillites	16.9	28.7	−6.1	6.1	28.2
US3	Urria	Sobrepeña	turtle plate	coastal plain	argillites	17.9	27.1	−7.7	5.2	23.8
US4	Urria	Sobrepeña	fish scale	coastal plain	argillites	17.3	25.4	−7.4	6.4	32.9
UF1	Urria	Fresnedo	crocodilian tooth	lacustrine/estuarine	sandstone	17.9	24.8	−8.6	5.7	36.0
UF2	Urria	Fresnedo	crocodilian tooth	lacustrine/estuarine	sandstone	16.5	25.8	−8.1	3.5	34.6
UF3	Urria	Fresnedo	crocodilian tooth	lacustrine/estuarine	sandstone	17.2	25.4	−5.4	6.1	30.8
UF4	Urria	Fresnedo	fish tooth	lacustrine/estuarine	sandstone	18.3	–	–	–	34.7

Table 1 (*Continued*).

Sample	Location	Formation/ level	Fauna remains	Sedimentary matrix	Environment	$\delta^{18}O_{PO_4}$ (‰ SMOW)	$\delta^{18}O_{CO_3}$ (‰ SMOW)	$\delta^{13}C_{CO_3}$ (‰ PDB)	CO_3^{2-} (wt%)	P_2O_5 (wt%)
CB1	Cuezva	Bozóo	crocodilian osteoderm	argillites	sabhka	19.1	26.6	−9.0	8.3	31.5
CB2	Cuezva	Bozóo	turtle plate	argillites	sabhka	19.4	25.6	−9.0	12.6	21.4
JC1e	Oubangui	–	*Hydrocyon*, fish tooth	modern sample	freshwater ponds	19.2	28.3	−9.2	–	42.1
JC6d	Oubangui	–	*Mormyrus*, fish tooth	modern sample	freshwater ponds	19.5	28.5	−8.9	–	27.0
JC3v	Oubangui	–	*Osteolaemus tetraspis*, crocodile vertebra	modern sample	freshwater ponds	19.3	29.1	−16.8	–	23.3
JC4d	Oubangui	–	*Osteolaemus tetraspis*, crocodile tooth	modern sample	freshwater ponds	20.0	28.8	−16.2	–	28.1
JC4p	Oubangui	–	*Osteolaemus tetraspis*, crocodile osteoderm	modern sample	freshwater ponds	18.9	29.2	−16.5	–	24.8
JC2v	Oubangui	–	*Grayia smithi*, snake vertebra	modern sample	freshwater ponds	18.9	28.7	−15.6	–	24.4

*Samples analyzed with the BrF$_5$ method according to the protocol presented in Lécuyer et al. (1993). CO_3^{2-} wt% of apatite from modern fish and reptile samples are not available because the manometer of the vacuum line was not operating during the CO_2 extraction.

spectrometer at the Ecole Normale Supérieure of Lyon. The isotopic data represent averages of duplicate analyses ($1\sigma \leq 0.2‰$) and are given on the standard mean ocean water (SMOW) scale (Table 1). Silver phosphate precipitated from standard NBS120c (natural Miocene phosphorite from Florida) gave an average $\delta^{18}O$ value of 21.65 ± 0.15 with the fluorination method. This average value is reported along with a mean $\delta^{18}O$ value of $9.55 \pm 0.15‰$ for five analyses of quartz NBS28. Because the oxygen yield when using the graphite method is only 25%, all data obtained with this method have been corrected from a constant offset of $+0.5‰$ that was observed during the inter-calibration of both methods (see Lécuyer et al., 1998).

Carbonate apatite samples were first treated with a 3% sodium hypochlorite solution for 4 h to remove organic matter and rinsed three times with distilled water. Then they were treated with a 1 M acetic acid–acetate buffer for 24 h to remove exogenous carbonates according to the method presented by Bocherens et al. (1996). Oxygen and carbon isotope ratios from the carbonate ion substituting in the apatite were determined using the phosphoric acid method (McCrea, 1950) with a reaction time of 48 h at 30°C. Reproducibility for carbon and oxygen isotope measurements in carbonates is $\pm 0.05‰$ and $\pm 0.1‰$, respectively.

3.2. Rare earth elements

Samples were dissolved in a screw-top Teflon bomb (Savillex™) using 5–10 ml of 6 M HCl and 7 M HNO$_3$ at 120°C. After evaporation to dryness, the residues were taken up with 40 ml of 6 N HCl. Aliquots of these solutions were used for REE abundance determinations at the Institut Dolomieu, Grenoble, by ICP-MS using a Fisons PQ2+ turbo. Results are given in Table 2. The method of sample treatment involves thulium addition and REE separation by ion exchange techniques. REE are separated from Ba and matrix elements (in particular Ca and P) and isobaric interferences are corrected for. Our procedure reduces the BaO interferences considerably, improves instrument stability and detection limits,

Table 2
REE concentrations of Late Cretaceous vertebrate remains from Laño, Urria and Cuezva (northern Spain)

	LL1	LL2	LL3	Le3	Le8	LT1	US1	US2	US3	CB1	CB2
La (ppm)	724	193	197	593	774	527	92.2	119	449	438	296
Ce	1174	285	283	1029	1285	1029	520	550	1185	2446	1928
Pr	126	32.5	27.9	122	183	118	126	122	300	416	416
Nd	484	123	97.8	482	745	500	1048	638	1300	2229	2323
Sm	98.7	24.9	18.0	103	169	105	488	152	272	674	641
Eu	26.8	6.7	5.0	26.0	42.5	26.4	126	34.7	63.9	153	142
Gd	131	27.4	24.3	112	175	130	650	184	330	759	672
Tb	20.6	4.1	4.3	16.5	25.0	18.5	79.0	27.4	44.8	103	93.0
Dy	128	25.2	30.3	92.6	135	105	361	153	222	489	453
Ho	26.4	5.4	6.8	17.7	25.7	20.0	58.5	27.3	35.5	76.8	71.6
Er	69.5	15.4	19.3	45.7	65.4	46.9	119	58.6	69.9	154	145
Yb	47.0	12.8	14.3	33.0	48.5	25.1	51.8	24.8	29.1	65.6	60.2
Lu	6.5	2.0	2.1	4.8	7.1	3.6	6.8	3.0	3.7	8.5	7.7
$(La/Sm)_N$	1.07	1.13	1.59	0.84	0.66	0.73	0.03	0.11	0.24	0.09	0.06
$(La/Yb)_N$	1.14	1.11	1.02	1.33	1.18	1.55	0.13	0.36	1.14	0.49	0.33
$(Gd/Yb)_N$	1.69	1.30	1.03	2.06	2.19	3.12	7.59	4.51	6.87	7.00	6.76
ΣREE	3062.5	757.4	730.1	2677.3	3680.2	2654.5	3726.3	2093.8	4304.9	8011.9	7221.5

but also effectively removes matrix problems. More details on the procedures, the standards used, and comparison with isotope dilution results (ID-TIMS) are given in Barrat et al. (1996). The accuracy is better than 5% for concentrations and 2% for ratios in most cases.

4. Results

4.1. Stable isotopes

Stable isotope compositions of both present-day and Late Cretaceous fish and reptile phosphate remains are presented in Table 1. The small size of fossil teeth did not allow us to analyze enamel separately from the dentine of the bulk tooth. Present-day fish and reptile bones and teeth have been sampled in the stagnant fresh waters of the Gabon equatorial forest (Oubangui river; Table 1). Oxygen isotope data for phosphate range from 18.9 to 20.0‰ for two fish species (*Hydrocion* and *Mormyrus*), one crocodile (*Osteolaemus tetraspis*), and one snake (*Grayia smithi*) from the same aquatic environment from the Oubangui river, Central Africa. It is noteworthy that the 1‰ range in $\delta^{18}O$ values is observed for three different parts of the crocodile specimen; the tooth has a

$\delta^{18}O$ value 1‰ higher than the vertebra and dermic plate samples. The oxygen isotope compositions of the crocodile bones (18.9 and 19.3‰) are, however, similar to that of the snake vertebra (18.9‰) as well as those of teeth (19.2 and 19.5‰) from two different co-living fish species. All these specimens were living in waters with average temperatures of $25 \pm 1°C$ and average $\delta^{18}O$ values of -2 ± 2‰. Both fish and reptile apatite contains CO_3^{2-} with similar $\delta^{18}O$ values (Table 1) but fish have $\delta^{13}C$ values close to -9‰, much higher than those of the reptiles ($\delta^{13}C = -16$‰).

Vertebrate samples from Laño are characterized by a narrow range in oxygen isotope compositions of both phosphate ($\delta^{18}O = 18.7–20.4$‰) and carbonate ($\delta^{18}O = 25.3–27.8$‰) components of their apatite (Fig. 3a). The $\delta^{13}C$ values of structural carbonate range from -7.3 to -2.9‰ for continental faunas whereas three samples of shark and ray teeth from the marine Torme Formation (S2U1) have $\delta^{13}C$ values from -3.4‰ to -1.9‰ (Fig. 3b). The amount of carbonate substituted in the apatite structure of terrestrial Laño samples is rather homogeneous, from 4.2 to 5.1 wt%, and very similar to pristine deer and human tooth enamel (Le Geros and Le Geros, 1984; Michel et al., 1995). Selachian teeth from the Torme For-

mation of Laño contain more CO_3^{2-} (5.5–7.0 wt% of CO_3^{2-}) in the apatite structure compared to those of the terrestrial vertebrates from the same area (Table 1).

In contrast to the Laño samples, those from Urria display highly variable isotopic compositions for both phosphate and carbonate components (Table 1). Oxygen isotope compositions of phosphate range from 16.5 to 19.3‰ and $\delta^{18}O$ values of carbonate range from 25.4 to 29.7‰. The amounts of structural carbonate are also more scattered (3.5–6.4%) and on average higher than those from Laño samples (Fig. 3a). Urria samples have a large range of carbon isotope compositions from −8.6 to −5.4‰, which is lower than the range of values obtained from Laño

fauna (Fig. 3b). The only two available samples from Cuezva, which are a turtle plate and a crocodilian osteoderm, have very low $\delta^{13}C$ values of −9‰, and large amounts of structural carbonate (Table 1). We note that the stable isotope compositions of continental fossil vertebrates do not seem to be related to a specific biological group such as fish, reptiles or dinosaurs (Table 1).

4.2. Rare earth elements

The REE contents of fossil vertebrate remains are presented in Table 2. Two main groups of samples can be distinguished on the basis of REE content and shapes of REE patterns (Fig. 4). The first group is constituted by all the samples from Laño that are characterized by flat (titanosaur LL2) or 'hat-shaped' REE patterns (Fig. 4a) with $(La/Sm)_N$ ratios ranging from 0.66 to 1.59 and $(Gd/Yb)_N$ ratios from 1.03 to 3.12 (Table 2). Middle REE (MREE) content ranges from 5 to 40 times those of PAAS (Post Archean Aus-
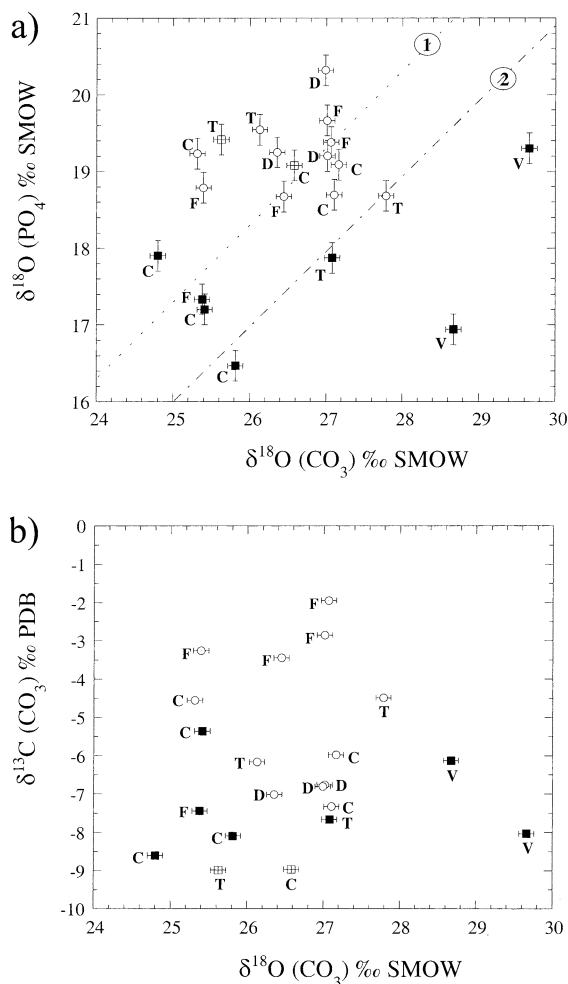

Fig. 3. Oxygen and carbon isotope compositions of apatite from the Cretaceous vertebrate fossils of northern Spain. (a) Variations in the $\delta^{18}O$ values of the structural phosphate and carbonate from the fossil apatite. Symbols are used to identify sampling sites. Open circle: Laño; filled square: Urria; crossed square: Cuezva. Letters are used to identify fauna. T: turtle; D: dinosaur; F: fish; C: crocodile; V: undetermined vertebrate. Two lines have been reported to define an array of 'equilibrium' isotope fractionation values between PO_4^{3-} and CO_3^{2-} molecules. Line 1 has been defined by combining the carbonate–water and phosphate–water fractionation equations determined by O'Neil et al. (1969) and Longinelli and Nuti (1973), respectively. The equation is: $\delta^{18}Op = \delta^{18}Oc − 7.7$. Line 2 describes the oxygen isotope fractionation between structural phosphate and carbonate from modern terrestrial mammals (Iacumin et al., 1996). Note that most samples from Laño are clustered and fall closer to line 1 than line 2 whereas samples from Urria are scattered and are characterized by low $\delta^{18}O$ values for PO_4^{3-}. (b) Variations in the $\delta^{13}C$ values as a function of $\delta^{18}O$ values of structural carbonate from fossil apatite. Fish samples have higher $\delta^{13}C$ values than reptiles from Laño. Note that the fish sample from the fluvial environment of Laño has a $\delta^{13}C$ value comparable to other fishes from the marine–littoral environment of Laño (Torme Formation). Terrestrial samples from Cuezva and Urria have the lowest $\delta^{13}C$ values and are characterized by large variations in the oxygen isotope composition of their structural carbonate.
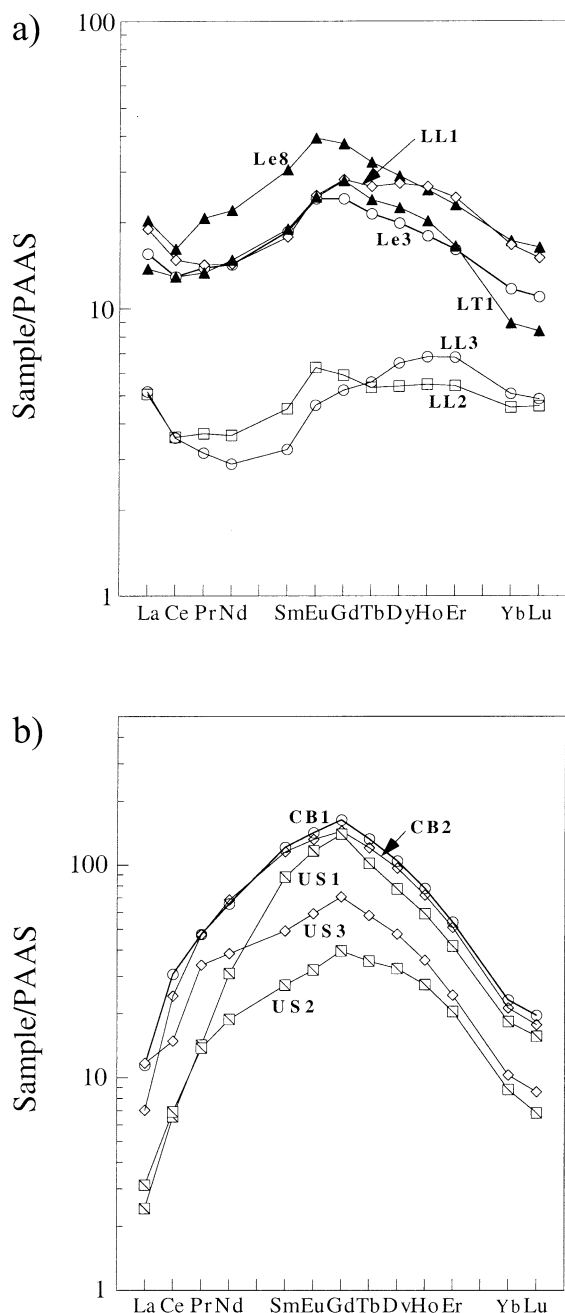
a)

b)

Fig. 4. REE patterns of Late Cretaceous vertebrate remains from (a) Laño and (b) Urria and Cuezva. Urria and Cuezva fossil REE patterns display 'bell-shaped' patterns with strong MREE enrichments when compared to Laño samples. Concentrations are normalized to the Post Archean Australian Shale (PAAS) defined by Mc Lennan (1989). Open squares: dinosaurs; open circles: crocodiles; open diamonds: turtles; filled triangles: fish; crossed squares: other vertebrates.
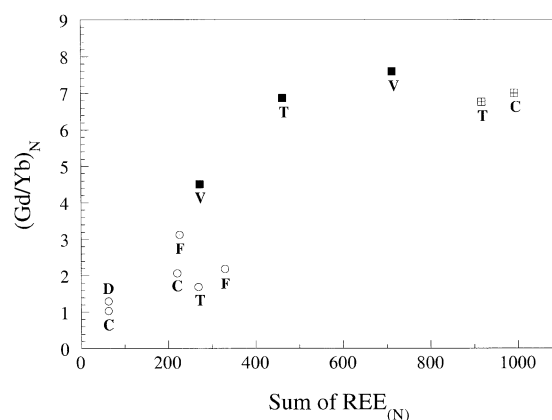

Fig. 5. $(Gd/Yb)_N$ ratios versus the sum of REE concentrations (normalized to the PAAS) of Late Cretaceous vertebrate remains from northern Spain.

tralian Shales, Mc Lennan, 1989). It is interesting to note that the REE pattern of the continental fish scale sample Le8 is similar to the pattern displayed by the marine shark tooth LT1 from the Torme formation.

The second group is constituted by all the samples from Urria and Cuezva sites whose sedimentary matrix is made up of green to red argillites in both cases (Table 1; Fig. 2). Independent of the type of phosphatic remain or the biological affinity of these samples, their REE patterns are highly fractionated (Fig. 4b) with $(La/Sm)_N$ and $(Gd/Yb)_N$ ratios in the ranges 0.03–0.24 and 4.51–7.59, respectively (Table 2). These strong MREE enrichments are correlated with an overall increase in the concentration of all REE (Fig. 5). MREE abundances of the two Cuezva samples are up to four times higher than the most MREE-enriched Laño sample, Le8 (Fig. 4).

5. Discussion

Biogenic phosphatic remains from the localities of Urria and Cuezva provide evidence of extensive recrystallization that can lead to resetting of the original geochemical record. Stable isotope data associated with measurements of CO_3^{2-} content indicate isotopic exchange and the addition of carbonate during transformation of hydroxyapatite into francolite. Carbon isotope compositions

of carbonate (from $-9.0‰$ to $-5.4‰$), enriched in ^{13}C compared to those measured for present-day fauna ($-16 \pm 3‰$) feeding on C3 plants (Emrich et al., 1970; Lee-Thorp et al., 1989), may be explained by an addition of CO_3^{2-} into the apatite structure. It is unlikely that Late Cretaceous C3 plants had much lower $\delta^{13}C$ values than present-day plants (see Bocherens et al., 1993). The additional carbonate may be derived from dissolution of neighboring lacustrine or marine calcium carbonates. All these samples are also characterized by a MREE enrichment positively correlated with an increase in the overall concentration of REE (Figs. 4 and 5). The acquisition of such 'bell-shaped' REE patterns has been recognized by Reynard et al. (1999) as the result of extensive recrystallization of the apatite in the presence of REE-bearing fluids (Fig. 6). Moreover, the great variability of $\Delta(CO_3^{2-}-PO_4^{3-})$ values (from 4.2 to 15.6‰) relative to expected 'equilibrium' values
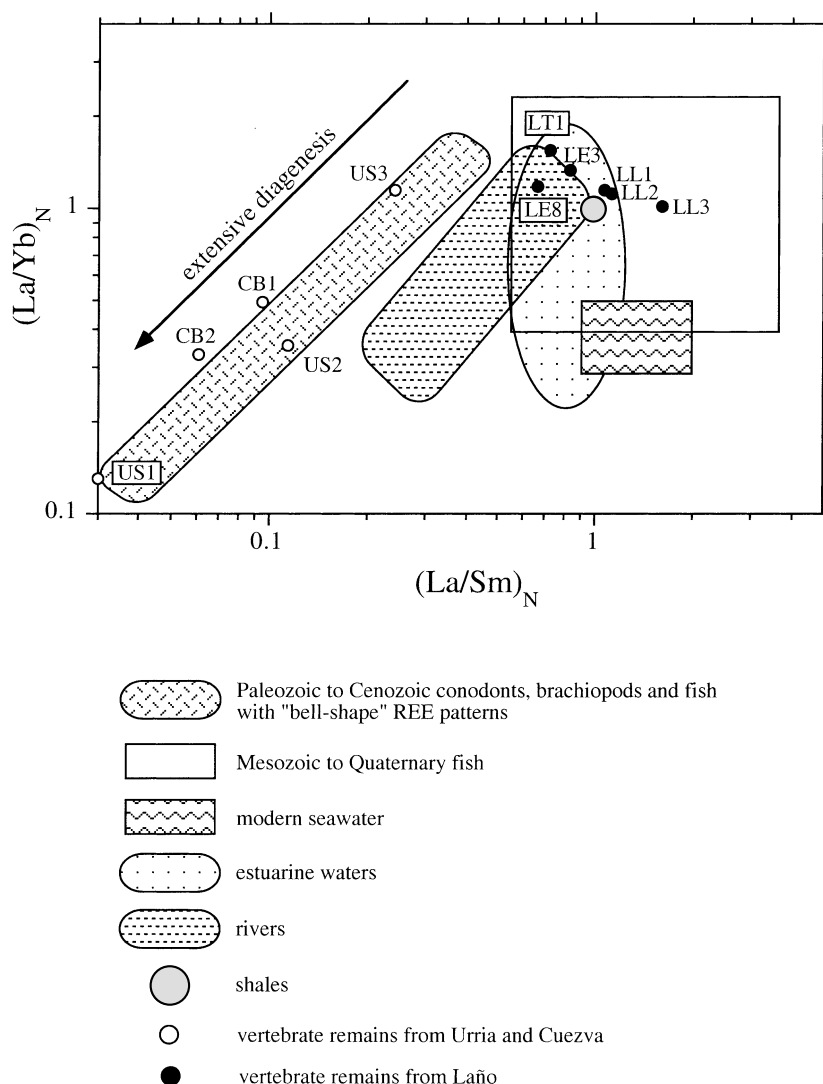

Fig. 6. Normalized La/Yb ratios versus La/Sm ratios of late Cretaceous vertebrate remains reported in the diagram proposed by Reynard et al. (1999). Samples from Cuezva and Urria plot on the field defined by recrystallized Paleozoic and Cenozoic biogenic apatites.

of 9‰ (Iacumin et al., 1996) suggests a multi-phase late diagenesis leading to either ^{18}O enrichment or ^{18}O depletion of the carbonate phase (Fig. 3a). Successive alteration events of unknown age thus changed the pristine geochemical compositions of biogenic phosphates, and interpretations of past environmental or biological conditions of the fauna should be avoided.

In the case of samples from Laño, the interpretation is also complicated, particularly when the δ^{18}O values of PO_4^{3-} that form a cluster in the $PO_4^{3-}-CO_3^{2-}$ space are considered (Fig. 3a). Most samples plot close to the expected equilibrium values without being strongly correlated with values observed for modern samples (Kolodny et al., 1996). Moreover, δ^{18}O values close to 19‰ are similar to those measured for present-day reptiles and fish living in an equatorial climate (Table 1). To a first approximation, these observations could imply that the oxygen isotope composition of PO_4^{3-} was preserved. A few samples, however, have δ^{18}O values of CO_3^{2-} that are anomalously low (Le4 and LT3; Table 1), suggesting possible diagenetic effects. Sample LT3 also provides evidence of CO_3^{2-} addition (7.0 wt%) relative to unaltered biogenic apatite (Le Geros and Le Geros, 1984; Michel et al., 1995). The higher δ^{13}C values (−3.4‰ to −1.9‰) of fish compared to associated reptiles (−7.3‰ to −4.5‰) indicates that all samples are characterized by high δ^{13}C values. These isotopic compositions are incompatible with a source of carbon derived from C3 plants, and C4 plants only appeared during the Cenozoic (e.g. Morgan et al., 1994). Reptile remains from Laño quarry have δ^{13}C values never lower than −7.3‰, whereas that from one present-day crocodile that lived in the Oubangui river has a δ^{13}C value close to −16‰, reflecting the diet of the prey feeding on C3 plants.

REE contents of Laño samples support the absence of any event of late diagenesis involving extensive recrystallization of the apatite (Fig. 4a). REE patterns, either flat or slightly MREE-enriched, are compatible with adsorption mechanisms (Reynard et al., 1999) from sediments deposited in estuarine or littoral environments (Fig. 6). Similar REE patterns have been documented for reptile remains by Elorza et al. (1999).

In contrast to the sites of Urria and Cuezva, vertebrate remains preserved in the Laño quarry have experienced only early diagenetic perturbations. Elorza et al. (1999) studied the petrological and major chemical compositions of several vertebrate remains and concluded that "the diagenetic processes were relatively uniform at the Laño site". The apparent homogeneous oxygen isotope compositions of PO_4, independent of the diversity of taxa, could reflect a homogeneous temperature and isotopic composition of pore waters during the burial of phosphatic remains. This similarity could, however, also be related to the tropical climate where differences in the δ^{18}O values of marine and fresh waters are low and species-specific fractionation effects may serve to reduce the differences. Unfortunately, as already shown by Kolodny et al. (1996), any record of physiological properties such as body thermal regulation has been lost during the early diagenesis of hydroxyapatite into francolite. This can also be demonstrated by applying the available fractionation equations for fish (Kolodny et al., 1983) and turtles (Barrick et al., 1999) to samples LL1, Le8 and Le9 (Table 1). Barrick et al. (1999) have deduced that the skeleton of aquatic turtles is formed at near constant temperature; their oxygen isotope composition, therefore, is directly related to that of water. If the calibration of Barrick et al. (1999) is used, the δ^{18}O value for water is estimated to be −3±0.5, which provides a temperature estimate of 14±2°C on the basis of the δ^{18}O value of the fish sample Le8. We emphasize that the inferred temperature is surely too low to allow the survival of crocodilians that require an annual average temperature of at least 20°C (Markwick, 1998). This result supports the previous interpretation that the vertebrate phosphatic remains from Laño exchanged oxygen isotopes with sedimentary pore waters.

The oxygen isotope composition of Laño samples may indirectly give information about the climate in northern Spain at the end of the Cretaceous. High δ^{18}O values of fossil apatites close to 19‰ are compatible with a warm environment by analogy with the isotopic composition of sedimentary phosphates deposited in tropical or equatorial environments (Kolodny et al., 1983; Lé-

cuyer et al., 1999; Shemesh and Kolodny, 1988; Shemesh et al., 1988; Stoskopf et al., 2001). The occurrence of gypsum and desiccation features in limestones suggest at least an episodically dry environment. This interpretation agrees with general circulation models (e.g. Bush and Philander, 1997) that predict temperatures of about 20°C at low latitudes ($\sim 35°N$) in western Europe at the end of the Cretaceous.

6. Conclusions

The stable isotope compositions of vertebrate remains from Laño provide indirect evidence of a warm climate (subtropical to tropical) during the Maastrichtian in agreement with faunal associations and sedimentary deposits. The common occurrence of evaporites and desiccation features in sediments deposited in a littoral environment suggests that dry conditions prevailed at a paleolatitude of 35°N. High and similar $\delta^{18}O$ values of PO_4 (18.7–20.4‰) from various remains of fish and reptile taxa could be easily misinterpreted as a pristine geochemical record. Following this hypothesis, we could be tempted to believe that most ectotherms including dinosaurs (Titanosauridae, *Iguanodon*, *Ankylosaurus*, *Hypsilophodon*) fractionate oxygen isotopes in a similar way. We propose that the geochemistry of these vertebrate phosphatic remains does not record differences in diet or physiology among the various taxa but reflects the geochemistry of the depositional environment. The REE patterns are interpreted as reflecting an early stage of diagenesis and the narrow range of phosphate $\delta^{18}O$ values is most likely indicative of the temperature and isotopic composition of groundwaters that prevailed in the burial environment.

Acknowledgements

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