

# Thermal excursions in the ocean at the Cretaceous–Tertiary boundary (northern Morocco): $\delta^{18}\text{O}$ record of phosphatic fish debris

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## ABSTRACT

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High precision oxygen isotope analyses were made of phosphate extracted from 17 samples of nektonic and benthic fish debris sampled across the stratigraphic Cretaceous–Tertiary boundary in northern Morocco. A refinement of the silver phosphate method was used to isolate phosphate from biogenic materials. Measured  $\delta^{18}\text{O}$  values of 18.6–20.5‰ are interpreted as reflecting high-resolution thermal variations that affected the ocean water column of the western Tethys. The warm (27°C) water masses that characterized Maastrichtian times underwent rapid cooling and stabilized at an average temperature of 19°C during the Dano-Montian and Thanetian. This period of constant and cool temperature was followed by a relatively rapid but more gradual warming to about 25°C achieved in the Middle Ypresian. Significant small shifts in  $\delta^{18}\text{O}$  values between nektonic and benthic fauna recorded only during the stages of rapid warming or cooling may correspond to averaged thermal differences within the water column that developed in response to global climatic changes. The indicated temperature distribution could have been caused by thermal changes in the atmosphere rather than some signal carried by deep ocean currents. The oxygen isotope data coupled with previous measurements of REE and  $\epsilon_{\text{Nd}(T)}$  on the same samples support the suggestion that paleo-Pacific westward currents progressed as far as the northwestern part of the African platform at the end of the Cretaceous period.

## Introduction

There is increasing interest in the study of global changes and its effect on terrestrial and marine environments. Most paleoclimatic information has been derived from the study of exceptional features that are preserved in the geologic record and exposed in a geographically restricted area. Conclusions concerning climate can be drawn only if the area under examination is free of strong regional control. While the ultimate cause of global change is a matter of great debate, the role and importance of immediate second-order effects like

changes in the temperature of surface or bottom waters of the ocean can be examined in detail and possibly elucidated. The temperature may vary at any location in the ocean as a result of (1) global warming or cooling, (2) changes in ocean circulation patterns as a result of Earth-scale climatic variations, or (3) changes in circulation patterns as a result of regional tectonic events.

One of the most spectacular examples of global change occurred at the Cretaceous–Tertiary boundary, a time characterized by major faunal extinctions and large-scale climatic variations (Alvarez et al., 1980; Shackleton, 1985; Officer

et al., 1987; Keller, 1989). We have made measurements of the oxygen isotope compositions of phosphatic fish remains from the Cretaceous–Tertiary section in northern Morocco in an attempt to understand the causes of oceanic thermal variations that may have occurred around this time period. The usefulness of oxygen isotope compositions of natural phosphates for paleothermometry has been well documented (e.g. Longinelli and Nuti, 1973; Kolodny et al., 1983; Shemesh et al., 1983; Luz et al., 1984; Karhu and Epstein, 1986). Thus if well-preserved marine fish remains (teeth and bones) are available for analysis, it may be possible to determine paleotemperatures of past oceans (Kolodny and Raab, 1988). In addition, REE contents and  $\epsilon_{Nd}$  values of such fish remains provide an effective means of elucidating circulation patterns of ancient ocean water masses (Grandjean et al., 1987; 1988).

Shark and ray teeth from a section in northern Morocco were selected for this study because: (1) Northern Morocco was situated between the Atlantic Ocean and the Tethys Sea in a region where tectonic processes operative in the past are of great geologic interest and are relatively well-understood through the time span under investigation (Scotese et al., 1988; Bardossy and Dercourt, 1990). (2) Splits of the same samples examined for REE contents and Nd isotope ratios by Grandjean et al. (1988) were available for oxygen isotope analysis. (3) The samples provide a very good time resolution from Lower Maastrichtian to Upper Ypresian. (4) The combination of oxygen isotope data with the results of Grandjean et al. (1988) should provide a powerful geochemical tool to gain insight into the direction, amplitude and origin of thermal variations of the oceans during this time interval.

Grandjean et al. (1988) suggested that REE contents and Nd isotope compositions of seawater from continental shelves and platforms result largely from regionally controlled diagenetic fluxes. They proposed, furthermore, that the weak Ce anomalies measured in modern phosphates are a reflection of the isolation of these materials from deep oceanic waters and that the Nd isotope compositions of phosphates are the same as those of average labile sedimentary Nd from the sur-

rounding shelves. Phosphate samples collected in northern Morocco and Israel, however, appear to have recorded deep-water REE characteristics and were not subjected to regional controls. The geochemical data for these materials suggest that deep cold water from the North Atlantic or other water from the eastern Tethys with a strong negative Ce anomaly and a  $\epsilon_{Nd(T)}$  value of  $\approx -5$  flushed out shallow epicontinental seawater as early as the Middle Cretaceous.

In the present study we integrate the REE and Nd isotope database with oxygen isotope analysis of the same phosphates and then address the following questions: (1) can thermal variations in the ancient water column be identified? (2) are such thermal variations caused by introduction of an exotic deep water from the North Atlantic or Tethys or rather by a global thermal change in the atmosphere?, and (3) is there a regional climatic correlation with the Eastern Tethys where samples from Israel and Jordan have previously provided paleotemperatures for Cretaceous to Eocene waters (Kolodny and Raab, 1988).

### Analytical procedures

#### *The $Ag_3PO_4$ method*

Phosphatic oxygen in biogenic materials appears to form in isotopic equilibrium with body fluids and, after the death of the animals, to be relatively resistant to oxygen isotope exchange with environmental fluids, especially during apatite recrystallization at the sediment–water interface (Luz and Kolodny, 1989). The first method of isolating the phosphate radical from fossil phosphatic materials for oxygen isotope analysis was published by Tudge (1960) and modified successively by Longinelli (1965, 1966), Longinelli and Nuti (1973), Longinelli et al. (1976) and Kolodny et al. (1983). This is a laborious method involving the precipitation of a hygroscopic, low-temperature form of  $BiPO_4$  after six days of wet chemistry. The method presented here is a refinement of the  $Ag_3PO_4$  technique developed by Crowson et al. (1992) and was selected because (1) the  $Ag_3PO_4$  procedure is far less time-consuming than the  $BiPO_4$  method, (2) measurements can be per-

formed easily on natural samples as small as 15 mg or less, (3) the  $\text{Ag}_3\text{PO}_4$  crystals are stable and non-hygroscopic, and (4) oxygen can be extracted quantitatively from  $\text{Ag}_3\text{PO}_4$  using  $\text{BrF}_5$  in a conventional silicate extraction line and the isotopic measurements are reproducible with low standard deviations.

After washing in distilled water, the samples are crushed in a stainless steel mortar and ground with an agate mortar and pestle. After dissolution of 15–30 mg of powdered sample in 2M HF at 25°C for 24 hours, the  $\text{CaF}_2$  that precipitates is separated from the phosphate solution by centrifugation. The  $\text{CaF}_2$  precipitate is rinsed three times using double deionized water (DDW) and the rinse water added to the phosphate solution which is finally neutralized with a 2M KOH solution. Before use, the Amberlite™-IRA-400(OH) ion exchange resin is flushed with several liters of DDW to eliminate chloride and avoid precipitation of AgCl. A 2-ml aliquot of cleaned resin is then added along with the neutralized solution to a polypropylene tube. The tubes are placed on a shaker table for 12 hours to promote the ion exchange process. Vanadium molybdate color indicator is used on one test sample to check that all the phosphate ions are adsorbed on the resin. Excess solution is discarded and the resin is washed again three times with DDW to remove the last traces of anion contaminants other than sulfate.

To elute the phosphate ions quantitatively from the resin, 25–30 ml of 0.5M  $\text{NH}_4\text{NO}_3$  are added to bring the pH of the solution close to 7.5–8.5, and the tubes are gently shaken for about 5 hours. The resin and the phosphate are then separated on a 63  $\mu\text{m}$  stainless steel sieve and the resin rinsed with 15 ml of DDW to transfer possible remaining phosphate ions to the solution. Silver phosphate is then precipitated from the solution following the method of Firsching (1961). The solution is placed in a 250 ml Erlenmeyer flask and 1–3 ml of concentrated  $\text{NH}_4\text{OH}$  are added to raise the pH to 9–10; 15 ml of ammoniacal  $\text{AgNO}_3$  solution are then added to the flask. Upon heating this solution to 70°C in a thermostated bath, millimeter-size, brownish crystals of  $\text{Ag}_3\text{PO}_4$  are quantitatively precipitated. The volume of solution is maintained constant during precipitation by

regular addition of a few drops of DDW. The crystals are then collected on a millipore filter, washed three times with DDW and air dried at 60°C. The  $\text{Ag}_3\text{PO}_4$  crystals produced this way are quite pure by the criterion that no contaminants were detected using either SEM or X-ray diffraction analysis.

#### *Fluorination procedure and mass spectrometry*

Aliquots of between 12 and 15 mg of  $\text{Ag}_3\text{PO}_4$  crystals are weighed into nickel reaction vessels and degassed 4 hours at room temperature and an additional 4 hours at 150–200°C. This degassing procedure assures that atmospheric water is efficiently desorbed from the samples. A 5/1 mole excess of  $\text{BrF}_5$  is reacted with the samples at 600°C for 12 hours. Chemical yields of near 100% were obtained routinely at the University of Michigan and replicate analyses at the University of Rennes ( $n = 25$ ) of the NBS 120c Florida phosphate standard were very reproducible at a  $\delta^{18}\text{O}$  value of 21.7‰ ( $1\sigma = 0.16$ ). Samples of NBS 120c were analyzed with each set of natural phosphate samples (Table 1). This method appears very promising for deciphering high-resolution variations in paleotemperature. A few experiments were done under various experimental conditions: (1) degassing up to 400°C for 1 hour, and (2) fluorination at 500, 550, 600 and 650°C for between 10 and 20 hours. No difference in the isotopic analyses were detected through various combination of these conditions. Silicate standards that have been extensively analyzed in several laboratories were used as a supplementary control on the analytical procedure. The  $\delta^{18}\text{O}$ (SMOW) values obtained for these standards are:  $9.5 \pm 0.2$  for NBS 28 quartz,  $16.1 \pm 0.1$  for Snowbird quartz, and  $5.6 \pm 0.1$  for the tholeiitic basaltic glass standard CIRCE93.

#### **Sample collection and geologic setting**

All material analyzed for this study comes from the phosphate deposits of Morocco: the Ouled Abdoun Basin, the Ganntour Basin, and the North Atlas (Imin Tanout) and South Atlas (Oued Erguita) Basins. All the teeth selected for this study are well preserved; they have a pale yellow color

TABLE 1

Location, environment and age of studied phosphatic fish debris with their  $\delta^{18}\text{O}$  values and calculated isotopic temperature of ambient seawater

Sample	Location	Age	Taxonomy	Habitat	$\delta^{18}\text{O}$	$T^\circ\text{C}$	Sedimentary matrix	$\delta^{18}\text{O}^*$
								NBS120c
P1b	Oued Erguita	L. Maastrichtian	<i>Rhombodus meridionalis</i>	benthic	18.66	27	HP	21.59
P2b	Benguerir	L. Maastrichtian	<i>Hypsobatis</i>	benthic	19.81	22	FP	22.00
P3b	Sidi Daoui	U. Maastrichtian	<i>Rhombodus binchorsti</i>	benthic	20.15	21	CP	21.58
P4b	Sidi Daoui	Maastr. term.	' <i>Raja</i> ' <i>mucronata</i>	benthic	20.43	19	FP	21.82
P5b	Sidi Daoui	Dano Montian	<i>Dasyatis hexagonalis</i>	benthic	20.64	19	HP	21.79
P6b	Sud de Delpit	Thanetian	<i>Myliobatis</i> sp.	benthic	20.59	19	CP	21.61
P7b	Sidi Daoui	L. Ypresian	<i>Myliobatis</i> sp.	benthic	20.30	20	FP	21.51
P8b	Mera El Arech	U. Ypresian	<i>Myliobatis</i> sp.	benthic	19.23	25	FP	21.76
P9b	Mera El Arech	U. Ypresian	<i>Myliobatis</i> sp.	benthic	19.32	24	FP	21.82
								22.00
P1a	Oued Erguita	L. Maastrichtian	<i>Cretolamna</i>	nektonic	18.95	26	HP	
P2a	Benguerir	L. Maastrichtian	<i>Squalicorax</i>	nektonic	20.26	20	FP	
P2a-1	Benguerir	L. Maastrichtian	<i>Squalicorax pristodontus</i>	nektonic	20.29	20	FP	
P3a	Sidi Daoui	U. Maastrichtian	<i>Cretolamna biauriculata maroccana</i>	nektonic	19.98	21	CP	
P6a	Sud de Delpit	Thanetian	<i>Striatolamia</i> sp.	nektonic	20.57	19	CP	
P7a	Sidi Daoui	L. Ypresian	<i>Striatolamia</i>	nektonic	19.97	21	FP	
P8a	Mera El Arech	U. Ypresian	<i>Striatolamia</i> sp.	nektonic	19.44	24	FP	
P9a	Mera El Arech	U. Ypresian	<i>Striatolamia</i>	nektonic	19.76	22	FP	

HP = Hard phospharenite.

FP = Friable phospharenite.

CP = Clay phospharenite.

$\delta^{18}\text{O}^*$ : Values of NBS120c standard obtained during sample analysis.

and are free of broken surfaces. The samples were collected by surface picking and by a water-screening technique in localities ranging in age from Lower Maastrichtian to Upper Ypresian (see Table 1). Oued Erguita is located in the Basin of the same name; Sidi Daoui, Sud de Delpit and Mera El Arech are located in the Ouled Abdoun Basin and Benguerir is located in the Ganntour Basin. All the faunas correspond to neritic associations but the occurrence of some bathyal taxa in the Thanetian and Lower Ypresian (Cappetta, 1981) indicates deeper waters during these periods. Water depth probably did not exceed 200 m. The sediment is a phospharenite whose characteristics vary depending on the locality: hard, fine and dark at Oued Erguita; coarse, soft and yellow in Benguerir; clayey at Sidi Daoui and Sud de Delpit (see Table 1).

### Presentation of data

The  $\delta^{18}\text{O}$  values of the shark and ray teeth are reported in Table 1 and presented as a function of geologic time in Fig. 1. The  $\delta^{18}\text{O}$  values as a whole for benthic and nektonic fishes define a regular convex-shaped curve. The Maastrichtian is characterized by a rapid increase from values of 18.6 to about 20‰, followed by a slow increase up to a value around 20.5‰ at the Cretaceous–Tertiary boundary. The  $\delta^{18}\text{O}$  values remain constant through the Thanetian and decrease regularly and rapidly to values of 19.1–19.3‰ in the Ypresian followed by a slight increase to 19.6‰ in the Upper Ypresian.

Our analyses of phosphatic and silicate standards indicate that the maximum analytical error to be applied to our analyses of phosphate in fish

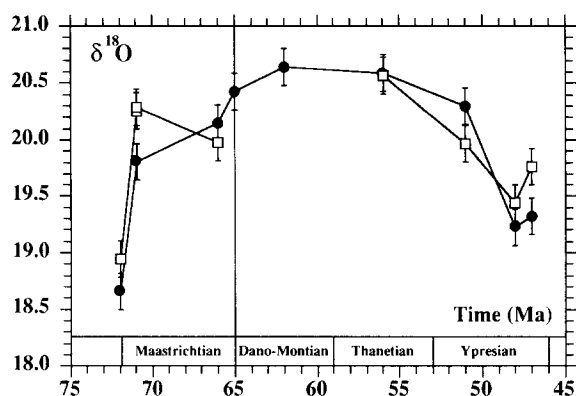


Fig. 1.  $\delta^{18}\text{O}$  (SMOW) variations of phosphate fish debris from Lower Maastrichtian to Upper Ypresian. Open squares = nektonic fauna; filled circles = benthic fauna.  $1\sigma$  deviation =  $0.16\delta$ .

teeth is 0.2‰. Consequently, when examining in detail the different isotopic signals recorded by benthic and nektonic fauna, small shifts in  $\delta^{18}\text{O}$  values of a few tenths per mil are considered significant. In addition, despite the fact that no isotopic data are available for nektonic fauna from Dano-Montian times, the almost identical  $\delta^{18}\text{O}$  values recorded by the two kinds of fauna from the Upper Maastrichtian and Thanetian material suggest that no detectable shift is present when the global isotopic signal remains flat from about 65 to 57 Ma.

## Discussion

Kolodny et al. (1983) showed that temperature and the isotopic composition of ambient water are recorded very sensitively in the isotopic composition of the phosphate of fish bones and teeth. The initial relation between isotopic compositions of phosphate ( $\delta^{18}\text{O}_p$ ), water ( $\delta^{18}\text{O}_w$ ) and temperature ( $T^\circ\text{C}$ ) proposed by Longinelli and Nuti (1973) were confirmed by Kolodny et al. (1983) who provide the following equation:

$$T^\circ\text{C} = 111.4 - 4.3(\delta^{18}\text{O}_p - \delta^{18}\text{O}_w)$$

The power of phosphate oxygen isotope paleothermometry resides in the apparent resistance of most phosphate in nature to oxygen isotope exchange with post-depositional environmental fluids during diagenetic processes. But in any case

the selection of biogenic phosphates must be made very carefully. Indeed, Shemesh et al. (1988) concluded that all pre-Cretaceous phosphorites are isotopically altered due to exchange reactions with surrounding waters at high water/rock ratios while post-Cretaceous phosphorites preserved their primary isotopic compositions. More recently, Shemesh (1990) and Kolodny and Luz (1992) emphasized that the alteration of the oxygen isotope composition of phosphorites is not only age-dependent but more related to the formation environments.

Grandjean et al. (1987) documented the existence of two major groups of phosphatic biogenic remains. The first group has higher REE concentrations, especially for the middle REE, no Ce anomaly, and lower Sr concentrations in the range 500–1500 ppm. This group likely represents samples deposited in near-shore or estuarine environments and were subjected to strong diagenetic fluxes from the continent. The second group is characterized by REE patterns that mimic those of seawater and Sr concentrations in the range 1800–3000 ppm. These samples reflect deposition in the open-sea environment and were not affected by diagenetic processes. Shemesh (pers. comm.) confirmed these results by finding a good correlation between the geochemistry of phosphates (oxygen isotope ratios, REE patterns and Sr concentrations) and the crystallinity index of marine apatites. Only phosphates from the second group preserved low crystallinity indices (lower than 4) typical of “pristine” apatites while those in the first group had high crystallinity indices that suggest possible oxygen isotope exchange between apatite and surrounding waters.

Considering this crucial aspect of diagenetic alteration, all the phosphate teeth analyzed in this study were carefully selected from group 2 on the basis of REE patterns, Sr concentrations and  $\epsilon_{\text{Nd}}$  values of similar samples studied by Grandjean et al. (1987). The sedimentary matrix does not seem to play a role in diagenetic processes. Grandjean et al. (1987) and Grandjean et al. (1988) did not detect any relation between this parameter and the trace element geochemistry of the phosphate samples. In the present study, nearly identical  $\delta^{18}\text{O}$  values (20.64; 20.59; 20.30) were found

for the Dano Montian, Thanetian and Lower Ypresian fauna that have, respectively, a hard, friable and clay phospharenite matrix.

Thus phosphate extracted from this collection of fish teeth can provide a reliable record of aquatic temperatures throughout the K/T boundary. In an attempt to reconstruct changes in seawater temperatures around the Cretaceous–Tertiary boundary, we must choose a  $\delta^{18}\text{O}$  value for seawater. It is generally accepted that before Oligocene time, the world was ice-free (e.g. Vergnaud-Grazzini, 1984). Our samples were selected from open marine environments and are not subject to significant variations in  $\delta^{18}\text{O}$  values of the marine water induced by inputs of continental fresh waters. Moreover, in open marine equatorial regions, high evaporation and precipitation rates have compensatory isotopic effects such that the  $\delta^{18}\text{O}$  value of seawater does not change significantly. The  $\delta^{18}\text{O}$  value of seawater was thus considered close to  $-1\text{‰}$  (SMOW) and constant throughout the span of time studied. This hypothesis was also chosen by Kolodny and Raab (1988) and facilitates comparison of our data with theirs on fish phosphatic remains from Israel.

The isotopic temperatures compiled in Table 1 range between 19 and 27°C. Calculated absolute temperatures like these depend on assumptions employed in the calculation, the accuracy of fractionation factors and the analytical techniques employed and so are not as reliable as relative variations in temperature. We discuss absolute temperatures here only for comparison with those calculated by Kolodny and Raab (1988). The relative variations of seawater temperature recorded by the oxygen isotope compositions of phosphates will be compared to continental climatic changes deduced from floral associations.

The variation in isotopic temperature with time is shown in Fig. 2. Maastrichtian times were affected by a sudden (few million years) and drastic cooling of the water column of about 9°C. It is noteworthy that this dramatic cooling in fact precedes the so-called Cretaceous–Tertiary boundary by about 5 million years, a phenomenon also observed by the gradual radiation of fauna initiated as early as the Campanian (Kauffman, 1984;

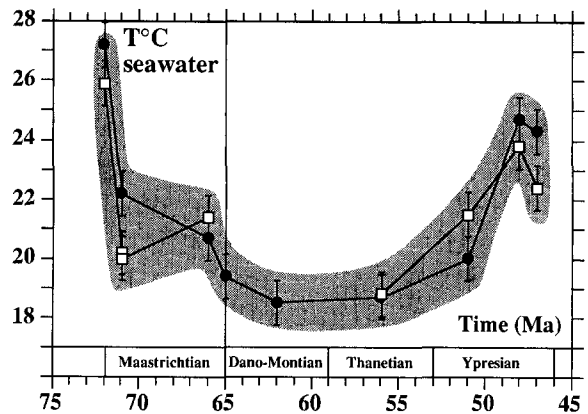


Fig. 2. Calculated temperatures of Tethysian seawater from the Lower Maastrichtian to the Upper Ypresian assuming a  $\delta^{18}\text{O}$  (SMOW) of seawater =  $-1$  (ice-free World).  $2\sigma$  deviation =  $1.5^\circ\text{C}$ . See text for explanations. Same legend as in Fig. 1. Time-scale after Odin (1986) and Odin and Odin (1990).

Self et al., 1984; Officer et al., 1987). The seawater in the western Tethys was cool for at least 10 million years. At the end of the Thanetian, the entire water column warmed slowly up to the Ypresian when the ocean again cooled. Such temperature changes of seawater for this span of time are in agreement with previously published oceanic and continental paleotemperature data (references therein).

On the continents, a major climatic event was identified in the Kef area (Tunisia) on the basis of microflora associations. Méon and Donze (1988) deduced from the spore and pollen flora the existence of a tropical climate at the end of the Cretaceous. The flora indicated that by the beginning of the Danian the climate had cooled. The presence of tropical and sub-tropical floras at European epicontinental margins (Olivier-Pierre et al., 1987) indicates that the Ypresian represents the warmest and dampest period of the Paleogene.

This pattern of cooling from Maastrichtian times to the Thanetian followed by the establishment of a warm climate at the beginning of the Paleocene was also recognized by Kolodny and Raab (1988) who studied similar fish fauna in the eastern Tethys. The same thermal trend was identified previously through isotopic studies of planktic foraminifera (Saito and Van Donk, 1974; Savin, 1982; Douglas and Woodruff, 1981; Hallam, 1985;

Keller, 1989) and on belemnites from sediments in Northern Europe (Savin, 1977). Shackleton (1986) studied Paleogene benthic foraminifera from mid-latitudes of the South Atlantic Ocean and identified a similar positive thermal excursion during the Ypresian. The change of about  $5^{\circ}\text{C}$  he reports for those latitudes are in accord with the  $9^{\circ}\text{C}$  change we are reporting for the deepest and coldest waters, thus suggesting that the proposed thermal excursions reflect a global change in climate. The isotopic record of seawater thermal changes, however, can be the consequence of variations in atmospheric temperature or in seawater circulation patterns.

Grandjean et al. (1988) demonstrated that Cretaceous shelf waters were progressively and continuously replaced by waters more characteristic of deep open waters. They proposed that the source of this water was either cold North Atlantic deep water or the westward progression of the paleo-Pacific equatorial water mass. The former hypothesis was favored by Kolodny and Raab (1988) for the eastern Tethys but a careful inspection of the  $\delta^{18}\text{O}$  data in Fig. 1 provides a new argument against the "North Atlantic current" hypothesis. Small oxygen isotope shifts were recorded during stages of rapid warming or cooling. Vertical oxygen isotope gradients of a few tenths per mil exist in the modern oceans because of deep ocean circulation that involves cold and low salinity polar waters. But such a gradient was probably absent in the KT equatorial marine environments where deep ocean circulation was not yet established. Despite the limited depth of the water column and the possibility that nektonic sharks can swim at varying depths, these shifts could correspond to averaged temperature differences within the water column: a deep water level corresponding to the benthic fauna and a near-surface water level represented by nektonic animals. Surficial water samples recorded lower temperatures than the deep water samples during cooling of the system whereas the inverse pattern was produced during warming. This interpretation is incompatible with thermal effects induced by a cool North Atlantic deep water but is consistent with atmospheric warming.

Global cooling of the surface of the Earth is known to occur after large volcanic eruptions (e.g. Sigurdsson, 1982; Self et al., 1984). Devene et al. (1984) calculated, from an empirical relation between surface cooling and sulphur emissions from large historic eruptions, that a global cooling of several degrees is possible. A similar cause for the global cooling near the Cretaceous-Tertiary boundary is compatible with the intense volcanic activity at that time, for example, the immense eruption of volcanic material at the Deccan traps in India (Courtilot et al., 1986). On the other hand, Alvarez et al. (1980) proposed that the impact on Earth of an approximately 10-km asteroid could have injected considerable amounts of dust into the stratosphere. Such a phenomenon could also reduce solar radiations at the Earth's surface. In the western Tethys, the oxygen isotope data suggest that the atmospheric climatic perturbation was spread over at least 10 Ma. A question thus arises: can a dramatic increase in volcanic activity over a maximum period of 3 Ma (Courtilot et al., 1986) or an extra-terrestrial impact event be responsible for a relatively stable cool stage of 10 Ma duration or longer?

The coupling of oxygen isotope measurements with the previously reported REE and Nd isotope measurements made of phosphatic fish debris from northern Morocco place important constraints on the paleoclimatology and seawater circulation patterns of the Tethys at the time of the Cretaceous-Tertiary boundary. A strong, sharp decrease in temperature of the global water column is more likely to have been the consequence of dramatic climate changes that would have accompanied the progression of the westward-flowing paleo-Pacific equatorial currents as far as the western Tethys in northern Morocco. This hypothesis is compatible with data on the secular evolution of  $\epsilon_{\text{Nd}(T)}$  which requires the input of waters with  $\epsilon_{\text{Nd}(T)} \approx -5$  (Grandjean et al., 1988) as well as with the isotopic characteristics of Pacific waters (Piepgras and Wasserburg, 1980, 1982; Piepgras and Jacobsen, 1988). In addition, this hypothesis supports analogous models (Luyendyk et al., 1972; Gordon, 1973; Roth, 1986) that predict circulation patterns for the Tethys with a dominant westward current component at the end of Cretaceous.

## Conclusions

Variations in  $\delta^{18}\text{O}$  values of shark and ray teeth through the Cretaceous–Tertiary boundary may be recording important features about thermal variations within the water column of the western Tethys. Tropical waters with an average temperature of about 27°C underwent rapid cooling down to about 19°C in the early Maastrichtian, a few million years before the stratigraphic Cretaceous–Tertiary boundary in northern Morocco. A period of consistently low temperatures ensued for about fifteen million years and was followed by a period of gradual warming to a maximum water temperature of about 24–25°C attained in the Ypresian. This temperature is a few degrees lower than that which prevailed initially in the late Cretaceous. The thermal variations recorded by the fauna from northern Morocco have also been recognized from oxygen isotope analyses of the similar kinds of samples from the eastern Tethys and more generally using other kinds of paleothermometers on both oceanic and continental materials from northern Europe. Significant small shifts in  $\delta^{18}\text{O}$  values recorded during stages of rapid warming or cooling could correspond to averaged temperature differences between two different levels in the water column. Surficial water samples recorded lower temperatures than the deep water samples during cooling of the system whereas the inverse pattern was produced during warming. Such a pattern can be explained if the source of thermal changes was located in the atmosphere and not carried by a deep cool ocean current. The global cooling of the Earth's surface initiated at the end of the Cretaceous, a few million years before the K-T limit *sensu stricto*, is in accord with the progressive extinction of shallow marine tropical organisms and also compatible with a long-term atmospheric perturbation whose ultimate cause remains obscure. Nevertheless, a dramatic climatic change through the Cretaceous–Tertiary boundary may be one of the most important long-term environmental factors to account for the faunal extinctions. Rare earth, radiogenic and stable isotope data for materials from the Cretaceous–Tertiary boundary support the concept of paleo-Pacific westward-flowing currents that travelled as far as

the northern Morocco longitude, in agreement with previously proposed computer models. The coupling of REE, neodymium and oxygen isotope analyses of fish debris appears to be successful in identifying the direct causes of thermal variations affecting oceanic masses. The data reported here and elsewhere argue for the use of precise oxygen isotope analyses of phosphates in quantifying thermal excursions in past oceans. Such analyses can provide a reliable database for paleoclimatic models.

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