11. TRACE ELEMENT AND STABLE ISOTOPE GEOCHEMISTRY OF PALEOCENE TO CONIACIAN CARBONATE SAMPLES FROM HOLE 516F, COMPARISON WITH NORTH ATLANTIC AND TETHYS SITES¹

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ABSTRACT

This paper presents data on trace elements (Sr, Mg, Na, K, Mn, Fe, Ni, Cr) and isotopes (¹³C, ¹⁸O) on the carbonate fraction of bulk sediments from the Coniacian to Paleocene samples of Hole 516F. Relationships of trace elements to mineralogy and stratigraphic position are discussed at length, with special emphasis on 1) the differences between Hole 516F and other oceanic sites, and 2) the transitions observed at the Cretaceous/Tertiary boundary. Isotope data are compared to those obtained in other localities of the same age. The sections show the same major ¹³C variations at the Cretaceous/Tertiary boundary, indicating that this event is a planetary phenomenon.

INTRODUCTION

Our previous studies in the North Atlantic (DSDP Legs 44, 47b, 48) have shown that trace element contents and stable isotope variations of bulk pelagic carbonates are, on a large scale, principally controlled by diagenetic phenomena, but many smaller variations seem to be related to oceanic chemistry fluctuations and could be used as stratigraphic and paleoenvironmental indicators. The purpose of this paper is to test this hypothesis by comparison of trace element and stable isotope variation of bulk carbonates from North Atlantic, South Atlantic, and Tethys sites.

Unless otherwise indicated, core numbers in this paper refer to Hole 516F.

METHODS

Abundances of strontium, magnesium, sodium, potassium, manganese, iron, nickel, and chromium relative to the carbonate fraction were measured in samples from Hole 516F. The ages of samples range from Coniacian to Paleocene. After sediments were crushed and washed in distilled water to eliminate contamination by seawater and interstitial waters, they were dissolved in acetic acid. Trace element analysis was carried out by atomic absorption spectrophotometry according to the method described by Renard and Blanc (1971, 1972). X-ray diffraction methods revealed a constant carbonate mineralogy, particularly with respect to low-magnesium calcite. The oxygen and carbon isotope techniques used have been described by Létolle et al. (1965). Results from analysis of Eocene samples are given as preliminary data, and all results are summarized in the appendix at the end of the chapter.

RELATIONSHIP BETWEEN TRACE ELEMENT CONTENTS AND INSOLUBLE RESIDUE

Because the percentage of carbonate is low in the Santonian to Coniacian, early Maestrichtian, and earliest Danian sediments at Hole 516F, great caution was exercised to assure that contamination was not introduced by flushing out the insoluble residue (i.e., interlayer cations in clay minerals).

Strontium

Strontium concentration in Paleocene to early Maestrichtian samples is not correlated with the insoluble residue percentage. A weak correlation appears, however, in Campanian and chiefly Santonian sediments. For samples in which the insoluble proportion is greater than 50%, the carbonate results are unreliable (Fig. 1A).

Magnesium

Magnesium can be flushed out of clay minerals even if the clay mineral content is low. Consequently we shall consider ony magnesium values lower than or equal to 4000 ppm as significant (Fig. 1B).

Sodium

The plot of sodium concentration versus percent carbonate indicates no relationship with the clay mineral content, except for Santonian/Coniacian sediments; the same pattern was shown for strontium (Fig. 1C).

Potassium

There is a very strong positive relationship between potassium and clay mineral content; only Paleocene samples do not fit this pattern (Fig. 1D). It is illusive, however, to insist on using potassium content variations as a paleoenvironment indicator. Only concentrations less than 300 ppm will be used to compare potassium variations with those relative to other elements.

Manganese

There is no relationship between manganese and insoluble contents (Fig. 2A).

¹ Barker, P. F., Carlson, R. L., Johnson, D. A., et al., *Init. Repts. DSDP*, 72: Washington (U.S. Govt. Printing Office).







Figure 2. Relationship between trace element concentration and insoluble residue percentage after acetic acid dissolution. A, manganese; B, iron; C, nickel; D, chromium.

Iron

There is a weak correlation between iron concentration and percent carbonate; the relationship is stronger for Maestrichtian and Santonian samples (Fig. 2B). Iron is in part carried by clay minerals.

Nickel, Chromium

Nickel and chromium are related to the insoluble residue percentage, but it seems that for one clay mineral content, different age samples show different concentrations of these trace elements (Fig. 2C and D).

TRACE ELEMENT DISTRIBUTION IN PALEOCENE-CONIACIAN CORES

Strontium

Strontium decreases with increasing sediment age; high values (\cong 1000 ppm) for Paleocene samples (Cores 83 to 86) change to low values (200-300 ppm) for Santonian-Coniacian samples (Cores 115 to 125) (Fig. 3). This trend has already been observed for DSDP Holes 116, 305, 391, 398D, and 400A, and is related to increasing effects of diagenesis (Renard et al., 1978, 1979a,b). Sample age, residence time in a given diagenesis environment, seems to exert a stronger control on this diagenesis than does depth-in-hole, overloading of sediments (Renard, 1979). In this curve, however, the strontium content fluctuation with depth or with age is not regular, and we think that these irregularities are caused by variations in the oceanic environment (salinity, temperature, strontium/calcium ratio) or in biochemical fractionation.

Sodium

Although the sodium curve variations are less clear, they are similar to those of strontium, with high values (400-500 ppm) for Paleocene samples and low values (200-300 ppm) for Santonian-Coniacian samples (Fig. 4). The sodium content decrease is located approximately at the same sub-bottom depth (Cores 105 to 106). The strontium-sodium correlation graph shows a moderate positive correlation and a good separation of data from different stages (Fig. 5).

Magnesium

The magnesium curve (Fig. 6) does not show clear variations in the Paleocene to Coniacian cores, probably because of the flushing out of magnesium from the argillaceous part of the samples and the presence of some traces of dolomite in Paleocene sediments. New analyses (Renard, unpublished data) show an increase of Mg from top to bottom of the core (Oligocene 1000-1500 ppm, Eocene, 1500-2000 ppm, Paleocene 1500-4000 ppm). The strontium content changes in the opposite way (Oligocene 1600-1200 ppm, Eocene 1300-700 ppm, Paleocene 1000-600 ppm). This reverse behavior of magnesium and strontium, which has already been observed in Sites 116 and 305, and Gubbio outcrops (Italy), seems to be the typical diagenetic chemistry of pelagic carbonates (Renard, 1979). One can compare the trends of strontium and magnesium contents in the sediments

with changes of the interstitial waters (Gieskes et al., this volume). The analysis of relationship between trace element contents of interstitial waters and sediments can be found in Renard (1979) and Baker and others (1982).

Manganese

The manganese curve indicates low values (lower than 1000 ppm) for almost the length of the core; there is a slight rise in upper Campanian and lower Maestrichtian sediments. An increase to values higher than 3000 ppm occurs beneath Core 121 (Fig. 7). These high manganese values are probably the result of the direct influence of basalt or hydrothermal emanations through sediments from the basaltic oceanic floor.

Iron

The iron curve shows a great variability, and it is difficult to see a general trend in sub-bottom depth (Fig. 8). Nevertheless, the highest values occur near the bottom of the core. The behavior of iron seems more random than that of manganese, because of the mixed origin of iron, which is either derived from continental erosion and oceanic hydrothermal activity or contained in clay minerals.

TRACE ELEMENTS AT THE CRETACEOUS/ TERTIARY BOUNDARY

Figures 9 and 10 represent, in a more detailed way, trace element concentrations across the Cretaceous/Tertiary boundary. Whereas the major portion of Paleocene samples are characterized by high and stable carbonate contents (about 90% CaCO₃), the first levels of the Tertiary are very impoverished. Maestrichtian and Campanian samples are moderately carbonate rich (60-70%), but contents always remain lower and, above all, more irregular than during the Tertiary.

The boundary is well indicated for strontium. Most striking is the reduced strontium content within the lower Paleocene (Figs. 3 and 9). Content for the Maestrichtian strontium levels are lower than those of upper Paleocene. A second strontium minimum seems to be located in the middle part of lower Maestrichtian.

For magnesium, the boundary is not particularly obvious, partly because low carbonate content compels us to reject the values corresponding to the lowest Paleocene levels (Figs. 6 and 9). In other sites, such as Gubbio outcrops where carbonate sedimentation is more constant, a magnesium peak related to an early lithification of the first Paleocene abundance marks the Cretaceous/ Tertiary boundary (Renard, 1979). In general, the trends of strontium and magnesium are opposite diagenetic phenomena. In certain restricted parts of the hole, however, strontium and magnesium fluctuate in the same way, and these covariations may be explained in terms of oceanic paleoenvironment variations. The Danian and the middle part of the Maestrichtian are zones with both low strontium and magnesium contents. In the upper Maestrichtian, the same tendency to lower strontium and magnesium contents is apparent.

The sodium curve shows low contents within the uppermost Maestrichtian and lower Paleocene compared to the lower Maestrichtian and upper Paleocene. The



Figure 3. Carbonate strontium content variation in Coniacian-Paleocene cores from Hole 516F.

high value of the first Paleocene level is, doubtless, an artifact caused by a maximum in the clay mineral content (Figs. 4 and 9).

Low potassium content in the Paleocene samples contrasts with the high content in the Cretaceous, but this is a reflection of the difference in the concentration of clay between the Paleocene and the Cretaceous sediments (Fig. 9).

Manganese, iron, nickel, and chromium curves show peak values at the Cretaceous/Tertiary transition zone (Fig. 10). These maxima cannot be explained by clay mineral content variations alone.



Figure 4. Carbonate sodium content variation in Coniacian-Paleocene cores from Hole 516F.

COMPARISON BETWEEN THE STRONTIUM CONTENT OF PALEOCENE-CONIACIAN CARBONATES FROM VARIOUS SITES

A comparison of strontium content and sediment age for North Atlantic Holes 116, 390, 390A, 398D, and 400A (Renard et al., 1978; Renard, 1979; Renard, Létolle, and Richebois, 1979; Renard, Richebois, and Létolle, 1979); the Tethys site represented in the Gubbio outcrop in Italy (Renard, 1979); South Atlantic Hole 516F (this work); and Pacific Sites 305 and 306 (Matter et al., 1975) show the potential use of these element variations as a stratigraphic tool. A number of strontium content variations occur at the same stratigraphic location at these various sites (Fig. 11). For example:

1) Three samples suggest a strontium content increase close to NP10/NP9 zonal boundary in Hole 516F, and two samples from Hole 398D suggest a similar trend



Figure 5. Relationship between strontium and sodium concentrations in Hole 516F.

may occur there. That increase is clearly indicated in the denser sample coverage from Gubbio section.

2) Strontium values are high from the bottom of the NP9 to the NP5 zones in Hole 516F, at Gubbio, and in Hole 398D.

3) Values decrease within Zones NP5 and NP4 in Hole 516F. At Gubbio, this decrease seems to be located at the NP6/NP5 boundary.

4) Strontium content is relatively low within Zones NP3 and NP4 at all four sites.

5) A slight increase of strontium content may be located at the NP3/NP2 zonal boundary in Hole 390 and at Gubbio.

6) Strontium concentrations are relatively low within Zone NP1 in Hole 398D and at Gubbio.

7) Values remain at a relatively high and stable level during Maestrichtian at all four sites and during the Campanian at Gubbio. Maximal values occur during the *Micula mura* and *Nephrolithus frequens* zones at Gubbio, and Holes 390A, 392, and 398D.

8) Strontium content decreases within the Santonian, but it seems that this phenomenon begins earlier in Hole 516F (during *Broinsonia Parca* Zone or even earlier during *Tetralithus trifidus* Zone) than at Gubbio where it starts only in the middle part of *Eiffelithus eximius* Zone.

At the present time, the real meaning of these variations is not very clear; they may be caused by salinity, temperature, or oceanic strontium/calcium ratio variations or by variation of strontium metabolism (biochemical fractionation or discrimination for or against strontium relative to calcium) between various species of calcareous nannoplankton and planktonic foraminifers. Whatever the cause of the strontium variations, the apparent synchronism of strontium variations in numerous oceanic sites indicates that these variations are worldwide oceanic phenomena.

We should mention the difficulties inherent in stratigraphic correlations between the four sections. For example, the zones in the Gubbio sequence were established on the basis of planktonic foraminifers, whereas those in Hole 516F were based on planktonic foraminifers in the Paleocene and calcareous nannoplankton in the Cretaceous. As a result, the relative location of samples from different sites is somewhat arbitrary.

STRONTIUM CONTENT AND PALE-OCEANOGRAPHIC RECONSTRUCTION

Figure 12 shows strontium content variation curves in relation to sediment age from each of the various sites under study. The general trend of curves, high values for recent sediments and low values for ancient sediments, is almost certainly related to increasing diagenesis with age (Renard, 1979). Short-term variations, as described above, reflect periodic fluctuations and crises within the oceanic realm.

Two groups of curves can be distinguished: those for North Atlantic Holes 116, 398, and 400A, and those for Tethys, South Atlantic, and Pacific sites (Gubbio and Holes 516F, 305, and 306). Site 390 is more complicated because the Cretaceous part of the strontium curve is close to values for the North Atlantic group whereas the Paleocene-Eocene part of strontium curve is close to the second group. Strontium contents differ between the two groups by about 200 ppm for Cretaceous carbonates and more for Tertiary carbonates. Originally, we invoked a diagenetic effect to explain this difference between poorly consolidated carbonates of the North Atlantic Ocean and the lithified limestones at Gubbio (Odin et al., 1982). The present work produces proof to the contrary; Gubbio limestones and 516F sediments have the same content of strontium. Latest vadose diagenesis does not play a prominent part in the strontium distribution in pelagic carbonates. Accordingly, the difference between North Atlantic carbonates and the others reflects different oceanic conditions that have prevailed in that basin compared to conditions in the Tethys, South Atlantic, and Pacific. As it will appear later with the isotopic study, it seems that North Atlantic-Tethys communication was very restricted during the Coniacian to Thanetian, whereas circulation between the Tethys and South Atlantic was open. Considering the sites' paleolocations and oceanic paleocirculations (Fig. 13), it is not surprising to find that South Atlantic influences reach Site 390 earlier than the North Atlantic sites.

The strontium content of a precipitated calcite can be described by the expression:

$$[mSr^{++}/mCa^{++}]_{calcite} = K_{Sr}^{C} [mSr^{++}/mCa^{++}]_{seawater}.$$



Figure 6. Distribution curve for magnesium concentration in Coniacian-Paleocene cores from Hole 516F.

The distribution coefficient K_{Sr}^C decreases linearly with increasing temperature from approximately 0.14 at 25°C to about 0.08 at 100°C (Kinsman, 1969), leading to the expression:

$$K_{Sr}^{C}$$
 $\cong~-0.0008 \; Tp$ + 0.16.

Using the oxygen-isotope-derived (see later) temperature

(Tp) difference of 10° between Tethys and North Atlantic seawater, one computes:

$$\Delta K_{Sr}^{C} = 0.008$$
 when ΔTp is 10°.

Strontium determinations in seawater are quite variable, and the result depends heavily on the analytic procedure. At the present time, it is very difficult to get an overall

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Figure 7. Distribution curve for manganese concentration in Coniacian-Paleocene cores from Hole 516F.

idea of strontium concentrations and variations in seawater (Renard, in preparation). However, if one takes the most commonly accepted value of Sr/Ca ratio in seawater ($0.86 \pm 0.04 \times 10^{-2}$; Kinsman, 1969), a Δ Tp of 10° leads to:

$$[\Delta Sr/87.63]/[400,000/40.08] = 0.008 \times 0.86 \times 10^{-2}.$$

From this, one may conclude that a Δ Tp of 10° includes a Δ Sr of about 60 ppm, and a Δ Sr of 200 ppm requires a ΔK_{Sr}^C of 0.0265, which leads to a Δ Tp of about 33°. Thus, the difference of 200 ppm observed between the North Atlantic carbonate strontium content and those of the other oceans cannot be explained by temperature alone. Yet, one must moderate this conclusion because



Figure 8. Distribution curve for iron concentration in Coniacian-Paleocene cores from Hole 516F.

the equation defining K_{Sr}^C was established on inorganic carbonate precipitation data. It is not known if this equation is applicable in the form given above to organic carbonates produced by planktonic foraminifers and by nannoplankton, especially because it is not known if these organisms biochemically fractionate strontium during their skeletogenesis (Lorens, 1978; Renard, 1979). As a result of fractionation, strontium concentration would depend on the different behavior of foraminifers and nannoplankton living in the North Atlantic Ocean compared to those living in the Tethys, South Atlantic, and Pacific. Perhaps, over and above the thermal explanation, there was also a variation of the Sr/Ca ratio between North Atlantic seawater and the seawater of other oceans. Even if local conditions, such as strontium storage by evaporitic deposits in marginal basins, could be found for the South Atlantic Ocean and for the Tethys, it could probably not be extended to the Pacific Ocean.



Figure 9. Calcium carbonate, strontium, magnesium, sodium, and potassium concentration variations during the Cretaceous/Tertiary transition (Hole 516F).

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Figure 10. Manganese, iron, nickel, and chromium variations during the Cretaceous/Tertiary transition (Hole 516F). NRM = natural remanent magnetization.

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Figure 11. Strontium concentration for sites in the North Atlantic (Holes 390A, 392, and 398D), Tethys (Gubbio, Italy), and South Atlantic (Hole 516F). NRM = natural remanent magnetization.



Figure 12. Carbonate strontium concentrations related to sediment ages for North Atlantic (Holes 116, 390, 390A, 392, 398D, and 400A), Tethys (Gubbio, Italy), Pacific (Sites 305-306), and South Atlantic (Hole 516F).

Because the Tethys and South Atlantic were, during the Coniacian-Thanetian, branches of the Pacific Ocean, the strontium variations in carbonates might only reflect chemical differences between Pacific and Atlantic seawater at present.

OXYGEN AND CARBON STABLE ISOTOPES

The potential use of stable isotopic ratios from calcareous nannofossils as paleoceanographic indicators has been shown by Margolis and others (1975). In the pelagic realm, nannofossils are the main producers of carbonate, and it is possible, as a first approximation, to replace isotopic ratios of calcareous nannofossils by isotopic ratios of bulk carbonates, especially when foraminifers cannot be extracted from lithified samples. Cementation and isotopic reequilibration during lithification alter the original oxygen 18 content of samples, but the carbon 13 content seems insensitive to diagenetic phenomena and shows no relationship to increasing lithification (McKenzie et al., 1978; Renard, Létolle, and Richebois, 1979). According to Weissert and others (1979): "The different species of coccoliths living in the surface waters fractionate carbon 13 equally, and subsequently selective dissolution during diagenesis will not alter the carbon 13 content of the nannofossil sediments." The carbon 13 content of bulk carbonates may, therefore, provide relatively good information on variations in carbon 13 content of the surface water. On a large scale, carbon 13 shifts seem to be related to the great transgression/regression cycles, and a striking similarity in the carbon 13 curve and the sea level variation curve has been noted (Cavelier et al., 1981).

Oxygen 18

Oxygen isotopic ratio variation does not show any particularly striking trends (Fig. 14). It should be observed, however, that a trend to the lower values ($\cong -2.5\%$) exists within the lower Maestrichtian (Cores 94, 93, and partly 92), followed by an increase towards values close to -1.75% in the upper Maestrichtian. At the Cretaceous/Tertiary boundary (Cores 89 and 90) values are considerably scattered, but they tend to decrease (about -2.5 to -3%).

Oxygen isotopic ratios become uniform again only within the upper Paleocene. This pattern is similar to that observed by Thierstein and Berger (1978) at Site 356 (Fig. 15). The significance of bulk carbonates δ^{18} O in terms of paleoenvironment is speculative; however, the isotopic curves from Holes 390A, 398D, 356, and 516F and Gubbio outcrops (Fig. 16) show striking similarities (Létolle et al., 1978; Renard, Richebois, and Létolle, 1979).

1) North Atlantic Holes 390 and 398D have, for Maestrichtian to Paleocene sediments, a δ^{18} O average of about -0.5% (Fig. 15). In spite of numerous sedimentary hiatuses, the same phenomenon can be observed at Hole 400A (Renard, Létolle, and Richebois, 1979b).

2) Values from Gubbio outcrops (Tethys) and Holes 356 and 516F (South Atlantic) are between -2.0 and -2.5%.

Neither the disparity between the two groups of data nor the homogeneity of values within a given geographic area can be explained by diagenetic phenomena. A comparison of the depth in the hole and the microfacies of Maestrichtian-Danian sediments (Table 1) to isotopic data shows that there is no relationship between overloading of sediments, microfacies, and lithification on the one hand, and isotopic data on the other hand. We must consider therefore that an important part of the bulk carbonate $\delta^{18}O$ (at least for the Maestrichtian-Danian sediments) is related to paleoenvironment conditions. The difference of 2‰ observed between sediments



Figure 13. Paleolocation of Sites 356, 390, 398, 400, 516, Bidart, and Gubbio at 65 Ma. Paleogeographic reconstitution after Sclater et al. (1977); Tethys-South Atlantic connection after Reyment and Mörner (1977). The dotted area = epicontinental sea/trans-Saharan communication.

from South Atlantic/Tethys areas and those from the North Atlantic suggests a variation of temperature close to 10°C between South Atlantic–Tethys surface waters (warmer) and North Atlantic surface waters (colder). The difference may not fully depend on temperatures; salinity and oxygen isotopic ratios of water may have been relatively different in the two areas. These differences show that communication between the North Atlantic and South Atlantic was still very restricted, at least until the late Paleocene. On the other hand, paleogeographic reconstruction suggests open communication between the Tethys and South Atlantic (Fig. 13). Paleontologic evidence proves that this communication arose either from a trans-Saharan connection established through the Niger Valley between an epicontinental arm of the Tethys and the Gulf of Guinea (Reyment and Mörner, 1977; Blondeau, 1977), or from the Central Atlantic (Moullade and Guerin, 1981).

Carbon 13

Carbon isotope variations are very conclusive (Fig. 14). Above stable values close to +2.0% within the upper Campanian (Cores 100 to 96), the δ^{13} C increases to +2.5% within the lower Maestrichtian (Cores 95 to 94), then level off in the main part of Maestrichtian (Cores 94 to 90). Values begin to decrease at the uppermost Maestrichtian and reach a minimum of +1% in the lowest Paleocene (Core 89). Within the Paleocene and



Figure 14. Oxygen and carbon isotope variations during the Cretaceous/Tertiary transition at Hole 516F. NRM = natural remanent magnetization.

particularly within the Thanetian (Cores 88 to 84), values rise again to +3%. A new negative excursion occurs at the top of Paleocene. These two negative shifts located at Cretaceous/Tertiary and Paleocene/Eocene boundaries are present in many DSDP sites and in continental outcrops (e.g., Kroopnick et al., 1977; Scholle and Arthur, 1980; Létolle and Renard, 1980). Comparison between carbon 13 curves of various sites (Figs. 17, 18) leads to the following conclusions:

1) The δ^{13} C shift at the Cretaceous/Tertiary boundary is more gradual than apparent. The abrupt aspect of the shift is, more often than not, due either to an incomplete sampling or to a pronounced sedimentary hiatus at this boundary. When there is continuous sedimentation (i.e., when G. eugubina Zone is present), the decline of isotopic ratio is gradual. This gradual transition may be in part caused, however, by reworking of Cretaceous thin sediment into the lowermost Paleocene levels; the sediment is a product of mixing of high isotopic ratio carbonate (Cretaceous) and low isotopic ratio carbonate (Paleocene). The lowest values are for samples located in Zones P1C/P1D. Moreover, in detail, two δ^{13} C isotopic minima may exist, the first one at the top of Zone P1A and the second one at the lower part of Zone P1D. The offset between these minima can be seen on the curves for Holes 390 and 516F and Gubbio.

2) The parallelism of isotopic curves achieved at different sites is noteworthy and supports our assertion



Figure 15. Stable isotope curve of the fine fraction carbonate for DSDP Site 356, South Atlantic (modified after Thierstein and Berger, 1978). Triangles indicate δ¹⁸O statistics; circles are δ¹³C statistics.

Table 1. Comparison of lithofacies and depth of the Cretaceous/Tertiary boundary.

Hole	Depth of Cretaceous/ Tertiary boundary (m)	Facies			
390A	150	Ooze			
398D	800	Chalk			
400A	650	Marly nannochalk			
Gubbio	On-shore outcrops	Siliceous limestones			
516F	960	Marly nannochalk			
356	410	Marly nannochalk			

that $\delta^{13}C$ bulk carbonates are a potential stratigraphic tool.

3) Isotopic data of South Atlantic and Tethys sites as well as those of North Atlantic sites are very similar: +2.5‰ in the Maestrichtian, +1.5‰ in the upper Danian, +3.0‰ in the Thanetian, and +1.0‰ at the Paleocene/Eocene boundary. This constancy of δ^{13} C values between very distant localities suggests that, unlike the δ^{18} O fluctuations, the cause of carbon isotopic ratio variations is a worldwide oceanic phenomenon relatively independent of local conditions.²

Only the amplitude of the Cretaceous/Tertiary boundary shift seems variable: 1.25‰, Gubbio (Italy); 1.50‰, Hole 516F; 2.50‰, Holes 398 and 356; and 3.50‰, Bidart (Biscaye, France).

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If, as we think, negative excursions of δ^{13} C curve are, more or less, related to global sea level regressions, it is not surprising that the shallower sites show the greatest amplitude of variations.

An attempt at an explanation of the phenomenon can be taken from Kroopnick (1974, 1977), Weissert and others (1979), Létolle and Renard (1980): the organic material produced in the surface water is depleted in carbon 13, and the decomposition of this material on the bottom of the ocean releases CO₂ to the deep water. The surface waters are, therefore, relatively enriched in carbon 13, whereas deep waters are relatively depleted. Upwelling and mixing return these carbon 13-depleted waters to the surface and prevent an extensive enrichment of carbon 13 in the euphotic zone. Times of high sea level (transgression) appear to correspond to anoxic conditions in the ocean with a very stable salinity stratification and sluggish circulation (Fisher and Arthur, 1977; Scholle and Arthur, 1980). During these periods, the surface of the euphotic zone is very large and, because the oceanic circulation is greatly diminished, there is less mixing of carbon 13-depleted deep waters with surface waters. Nannofossils living during these periods will be relatively enriched in carbon 13. During regressive time (low sea level), the surface of the euphotic zone is reduced, and the restarting of oceanic circulation permits the mixing of carbon 13-depleted deep waters with carbon 13-enriched surface waters. Nannofossils living during these periods will be relatively depleted in carbon 13.

CONCLUSIONS

Geochemical studies of Coniacian-Santonian sediments from Hole 516F indicate:

1) If Site 356 δ^{13} C results are confirmed in their broad outline, the Cretaceous/Tertiary shift is not as sharp as anticipated. The most negative values are located in P1C/P1D planktonic foraminifer zones and not in the *G. eugubina* Zone. Interpretations, extraterrestrial or not, of the Cretaceous/Tertiary crisis must take into consideration the relatively gradual aspect of δ^{13} C variations.

2) At least for the studied part of geologic time scale, the δ^{18} O record in bulk carbonates is not completely destroyed by diagenesis.

3) Variations in strontium and carbon 13 content in carbonates should be considered as potential tools for stratigraphic correlations.

4) For pelagic sediments, strontium and sodium contents of carbonates fluctuate in a parallel fashion, and strontium and magnesium contents vary inversely.

5) Chemical data suggest a very restricted communication between the North and South Atlantic during the Coniacian-Thanetian. On the contrary, Tethys, South Atlantic, and Pacific communication seems to have been very open.

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 $^{^2}$ In some instances, as at Site 356 and at the Bidart outcrops (Figs. 14 and 18), the $\delta^{13}\mathrm{C}$ negative shift of Cretaceous/Tertiary boundary is linked to a $\delta^{18}\mathrm{O}$ negative excursion. At the present time, however, there are not enough available data to know if this is a local or a general phenomenon, or if it is due to early diagenesis or variations in environmental conditions. At Bidart (France), Delacotte (1982) shows that after this $\delta^{18}\mathrm{O}$ sharp negative shift, there is a progressive positive excursion caused by variations in local environmental conditions; the main oceanic influences came from the Tethys (low $\delta^{18}\mathrm{O}$) during the Maestrichtian and from the North Atlantic (high $\delta^{18}\mathrm{O}$) during and after the Paleocene.



Figure 16. Oxygen isotope (bulk carbonates) curve for North Atlantic (Holes 390, 392, and 398D), Tethys (Gubbio, Italy), and South Atlantic (Hole 516F).

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APPENDIX A

Biostratigraphic Ages

Biostratigraphic ages were assigned to samples using various publications:

Gubbio section: Premoli Silva et al. (1976)

Sites 305-306, 356: Perch-Nielsen (1977)

Hole 398D: Iccarino and Premoli Silva (1979), Blechschmidt (1979), Sigal (1979)

Hole 400A: Müller (1979)

Hole 516F: Pujol (this volume)

Bidart section Perch-Nielsen (1979 and personal communication, 1982). Foraminiferal and nannoplankton zone durations and absolute ages of each sample are based on Hardenbol and Berggren (1978) and Odin (1978 and in press) time scales and publications of Premoli Silva and Boersma (1977), Sigal (1977), and Perch-Nielsen (1977).

Core-section (interval in cm)	CaCO3 (%)	Mg	Na	к	Mn	Sr	Ni	Cr	Fe	δ ¹³ C	δ ¹⁸ O
38-1, 98-100	92.07	1.292	424	163	215	1185	- 7	3	1702	+1.99	-0.28
39-1, 42-44	87.34	1319	455	224	214	1266	7	3	1517		0.20
39-2, 37-39	86.31	1073	491	262	210	1347	5	3	1343		
40-1, 95-97	89.03	1274	429	208	188	1305	3	3	1314		
47-1, 18-19	89.67	1765	499	208	202	1160	5	5	1072		7.44
83-1. ?	91.30	1687	523	190	370	652	5	2	1727	+1.14	-2.44
83-3, 10-12	87.45	1252	381	233	655	774	8	3	1204	+1.05	-2.18
83-5, 24-26	89.18	882	556	221	495	977	3	3	1079	+2.65	-2.18
84-3, 80-82	84.80	2294	623	225	688	990	3	2	2806	+ 3.06	-2.13
85-1, 51-53	87.40	770	569	180	790	1033	1	1	1052	+ 2.62	- 2.03
85-5, 100-102	88./3	24/3	389	122	547	1015	4	1	1919	+ 2.54	-2.13
86-6, 26-28	88.61	2695	396	112	545	1029	3	1	1987	+2.50	-2.11
87-3, 105-107	88.78	4316	383	109	636	838	4	î	2233	+ 2.28	-2.41
87-4, 3-5	89.66	3925	523	114	734	739	5	2	2387	+ 2.01	-1.99
87-5, 96-98	86.44	2698	441	140	651	723	3	1	1671	+2.06	-2.05
89-1, 55-57	78.80	1748	419	206	699	653	2	2	1227	+1.55	-2.91
89-3, 08-10	15.23	12,425	626	4152	1122	601	14	8	3020	+0.92	- 3.05
89-6 54-56	82.07	2506	330	198	850	804	1	2	1624	+2.73	-2.19
90-1, 66-68	79.04	1644	310	226	607	948	2	4	1290	+2.55	-2.44
90-2, 52-56	73.64	2354	322	303	679	945	4	4	1800	+2.37	-2.38
90-3, 103-105	60.53	6229	431	559	687	730	8	5	4657	+2.50	-1.95
90-4, 99-100	81.61	2820	365	162	558	731	3	3	2032	+ 2.72	-1.64
90-5, 42-44	81.53	24//	401	1/2	090	724	3	4	1988	+ 2.42	- 2.12
91-1 49-50	76 84	2551	311	209	643	728	1	4	1902	+ 2.43	- 2.07
91-2, 145-147	81.49	2717	376	195	630	796	3	4	2079	+ 2.62	-1.81
91-3, 126-128	78.48	3733	356	238	582	737	3	4	2630	+ 2.58	-1.67
91-4, 51-53	81.42	3942	397	194	510	768	5	4	2822	+2.59	- 1.66
91-5, 106-108	54.01	7094	375	682	743	776	9	7	5804	+2.44	-1.62
91-6, 1-3	72.47	6300	504	285	570	787	8	5	4488	+2.52	-1.65
92-3, 30-3/	20.49	0233	449	097	435	862	8	0	4316	+2.04	-1.62
93-5, 12-14	42.20	2051	549	1197	761	884	7	6	834	+2.03	-2.33
94-2, 126-128	68,72	7754	356	472	1045	609	5	5	5219	+2.58	- 2.31
95-1, 55-57	72.98	6208	376	291	1179	663	5	6	3932	+2.28	-2.61
96-1, 66-68	60.45	9085	450	666	1162	722	7	7	6362	+2.21	-1.80
96-2, 12-13	73.55	8783	541	317	1317	779	7	6	6708	+2.16	-1.62
97-2, 64-65	52.89	3128	473	938	1265	862	12	11	3225	+2.21	-1.92
100-1 27-29	54.15	5419	404	878	1081	809	19	8	5540	+1.72	- 2.13
101-1, 114-116	67.80	6404	433	575	1293	784	5	6	6261	+1.98	-2.35
102-1, 111-113	73.98	6718	351	303	1239	786	4	5	6836	+ 2.05	-2.37
102-2, 96-98	34.19	13,162	790	1645	897	942	26	15	15,280	+1.83	-2.90
102-3, 68-70	49.21	8758	784	915	1258	940	13	9	10,036		
103-2, 98-100	55.29	7235	422	642	876	916	10	9	8045		
104-1, 36-40	68 23	5366	330	230	835	011	10	5	13,003	+ 2 20	- 2.41
104-6, 48-50	61.56	7433	361	339	867	855	10	8	7325	+ 4.69	-2.41
105-1, 42-44	68.54	4426	261	225	855	820	6	6	4086		
105-5, 72-74	57.17	1010	240	322	978	861	4	6	1850		
106-2, 65-67	71.65	766	242	168	855	818	2	4	1219		
106-6, 68-70	67.28	1372	286	260	883	626	4	4	2016	+2.37	-1.86
107-7, 40-43	62.40	6323	312	305	1013	653	12	7	6862		
108-4, 44-45	63.08	2522	295	297	677	719	6	7	3070		
109-3, 75-77	75.22	3679	251	235	636	684	7	6	4730		
109-4, 41-43	71.63	2340	243	281	574	739	6	6	3234		
110-1, 50-52	60.15	3415	258	419	491	738	8	9	4296		
110-3, 144-140	03.90	2000	312	315	526	634	11	10	8002		
113-3 52-54	53.60	4779	456	428	672	567	14	14	5657		
113-6, 40-44	43.04	4618	448	528	725	508	16	13	6405		
114-1, 109-111	82.62	1393	198	97	922	310	4	5	2055		
114-3, 60-62	62.98	6845	425	251	838	467	17	12	8671		
114-6, 116-115	69.78	2908	262	172	773	383	7	8	3400		
115-1, 27-29	49.61	5449	526	459	759	507	18	13	6532		
115-4, 27-29	76 65	2137	324	190	770	314	0	8	2000		
116-3, 31-33	40.83	4602	526	582	614	600	17	21	6268		
116-6, 60-62	77.32	3219	274	161	758	371	8	8	4232		
117-1, ?	79.04	1840	279	164	920	332	4	6	2665		
117-4, 22-24	67.45	2626	359	260	685	466	7	11	3702		
117-6, 16-18	63.01	3199	345	344	640	445	10	10	4678		
118-1, 7	83.28	2893	230	120	694	260	5	6	3696		
119-1. 119-121	79 17	1335	254	165	800	353	3	7	2252		
119-3, 85-87	70.94	3405	321	169	617	355	8	n	5339		
120-1, 36-38	65.29	4084	371	126	773	384	9	18	5922		
120-2, 0-32	54.72	7250	483	100	961	368	10	21	8924		
121-1, 61-63	68.47	2645	305	73	1126	270	4	12	3136		
122-1, 35-37	54.57	24,669	/36	78	1194	288	21	31	30,264		
122-2, 120-122	56.30	1426	311	67	4538	303	4	10	1134		
124-1, 20-22	76.23	4516	401	216	4171	162	2	5	4184		
124-2, 25-27	22.52	9242	663	2864	7302	482	10	5	17,088		
125-1, 24-26	39.96	3893	305	1246	3644	267	1	6	1563		
124-1, 20-22	91.41	3696	3219	677	4172	381	46	13	1051		

APPENDIX B Data Summary of Carbonate Fraction Analysis, Hole 516F

Note: Trace element results are given in ppm; stable isotopes are expressed as deviations per mill from PDB standard. A blank indicates that the analysis was not done; ? indicates that the centimeter range is not available.



Figure 17. Carbon isotope curve for North Atlantic (Holes 390, 392, and 398D), Tethys (Gubbio, Italy), and South Atlantic (Hole 516F).



Figure 18. Stable isotope curves of bulk carbonate for Bidart outcrops (Biscaye, France) after Delacotte and Renard (unpublished data).