Cretaceous-Paleogene transition at the Paraíba Basin, Northeastern, Brazil: Carbon-isotope and mercury subsurface stratigraphies

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ABSTRACT

The Paraíba Basin in northeastern Brazil contains a complete carbonate sequence that recorded the Cretaceous–Paleogene transition, and is composed of the Itamaracá, Gramame and Maria Farinha formations. In this study, the behavior of C and O isotopes, major and trace element chemistry have been examined in core drill carbonate samples from three drill holes (Poty Quarry, Olinda and Itamaracá).

The deposition of carbonates in this basin was initiated during a marine transgression with temperature and bioproductivity increase in the Early Maastrichtian. δ18O values for this interval vary from −3‰ to −5‰ VPDB, and δ13C, from −1.2‰ to 0.1‰, reaching a maximum in the Late Maastrichtian, with values around +2‰. Early Danian carbonates have recorded a small positive δ13C excursion (−2‰), followed by values around +1‰ right after the Cretaceous–Paleogene transition with increase of SiO2 and Al2O3 associated to terrigenous contribution. Upsection, carbonates recorded a period of marine regression, bioproductivity falls as recorded by the δ13C curve (+1‰) and carbonate sediments with higher Mg/Ca ratios were possibly deposited in a shallow-marine environment. Carbon and oxygen isotope pathways in carbonates of the Paraíba Basin from the drill holes at Poty Quarry, Olinda and Itamaracá localities are similar to each other and to that observed in the El Kef type section, Tunisia, and in the Yacoraite Basin, in Argentina. In the Poty drill hole, remarkable negative spikes may have resulted from multiple meteorite impacts that predated the Cretaceous–Paleogene transition. Mercury stratigraphy in the same drill hole displays a prominent positive anomaly in the K-T transition and suggests that important volcanism witnessed the transition scenario.

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1. Introduction

The Late Cretaceous-Paleocene (K-T) transition, a time of very important worldwide massive faunal extinction, has received much attention in the last three decades. Events that characterize this transition, according to Alvarez et al. (1980), include a meteorite impact the consequence of which was the generation of a sun-blocking dust cloud, cessation of photosynthesis, and disruption of the food chain, causing prolonged ecological modification. This impact affected surface-water productivity that, apparently, was less intense at high than at low latitudes, probably as a function of the distance from the impact site. Alternatively, this diverging intensity of perturbation could be related to paleolatitude only (Aberhan et al., 2007).

Although this hypothesis, deemed responsible for the dinosaur extinction, has been largely accepted, other studies have suggested that the Earth faced environmental stress right before the transition. Among alternative hypotheses, volcanism in the last 100,000 years before the Cretaceous-Paleogene transition, multiple meteorite impacts, rapid climatic changes, eustatic variation of the sealevel (Keller et al., 2003, 2004) and more than one meteorite impact appear to be attractive explanations. Those events could have caused environmental stress leading to mass extinction of species (Keller, 2001; Keller et al., 2003; Keller, 2005).

Iridium positive anomalies in the Cretaceous-Paleogene transition, a probable result from a meteorite impact, have been detected in almost one hundred sites and seem to be homogeneously distributed worldwide (Claeys et al., 2002). There is also...
a possibility that higher concentrations of this element derived from non-cosmic sources. According to Sawlowicz (1993), processes leading to iridium enrichment in sedimentary rocks can be extra-terrestrial, volcanic (PGE-enriched condensation), precipitation from seawater (low sedimentation rate, anoxic conditions), microbial (concentration, dissolution, re-precipitation), hydrothermal exhalation, dissolution, transport and precipitation in the KT transition.

The anomalous enrichment of iridium could be an evidence of impact of a bolide with the Earth, once this element is found to be abundant in meteorites. However, volcanic exhalations from the mantle can be also iridium-enriched as observed in volcanic systems such as Piton de La Fournaise, Indic ocean (Toumain and Mayer, 1989) and in Kilauea, Hawai (Zoller et al., 1983). The largest volcanic eruptions in the Late Maastrichtian and Early Danian in Deccan in India could support a hypothesis that volcanism may have played important role in a dramatic change of climatic conditions during the Cretaceous–Paleogene transition (McLean, 1978, 1991; Chatterjee et al., 2003). As already known, the largest Permian–Triassic transition mass extinction coincides with basaltic floods in Siberia (Campbell et al., 1992; Renne et al., 1995; Berner, 2002; Beerling et al., 2007).

According to Palinkás et al. (1996 in Ogorelec et al., 2007), Hg enrichment above the Cretaceous–Paleogene transition in Dolenja Vas too, suggests subaereal volcanic activity (in Ogorelec et al., 2007) and also that Hg concentration in sedimentary rocks that recorded the Cretaceous–Paleogene transition may be a promising tool in tracing the volcanism role in this transition.

According to Claeyss et al. (2002), there are 300–400 localities where the Cretaceous–Paleogene transition has been identified, but only few localities have been studied in South America, Australia, Africa, and in high latitudes. In Brazil, some preliminary studies have been carried out in the Paraiba Basin (Ashrof and Stinnesbeck, 1989; Albertão and Kotsoukos, 1994; Albertão et al., 1994a,b; Ferreira et al., 1996; Menor et al., 1999; Sial et al., 2001; Lima, 2002; Sabino et al., 2005; Barbosa and Neumann, 2005; Koutsoukos, 2006; Barbosa, 2007; Marquillas et al., 2007). This basin is characterized by a complete sequence, recording the Late Cretaceous (Gramame Formation; Maastrichtian) and Early Paleogene (Maria Farinha Formation; Danian; Fig. 2).

In the present study, we examine the behavior of C and O isotopes and bulk chemistry (Si, Al, Mg, Ca, Rb, Sr, and Mn) of core drill carbonate samples of the Paraiba Basin from three drill holes located at the Poty Quarry (52 m), Olinda town (62 m) and Itapessoca Quarry, and compared the O-isotope stratigraphies of carbonate sections at the Poty Quarry in this locality as well as at the Itapessoca Quarry, and compared the characteristics of the Cretaceous–Paleogene transition in the Paraíba Basin with paleoenvironmental registers in other sections that recorded this transition elsewhere.

2. Previous works

Sections where the Cretaceous–Paleogene transition has been well preserved are found in the El Kef type section (Keller and Lindinger, 1989; Adatte et al., 2002), and Ain Settara and Ellès auxiliary sections, Tunisia (Molina et al., 2009), El Mulato (Alegret et al., 2002) and Bochil, Mexico (Molina et al., 2009), Bidart in France (Molina et al., 2009), in the site 25 of the Deep sea Drilling Project (DSDP), in South Atlantic (Li and Keller, 1998; Keller, 2001); Antarctica Peninsula (McArthur et al., 1998; Hathway et al., 1998); Denmark (McArthur et al., 1998) among others.

In South America, sedimentary sequences that contain registers of the Cretaceous–Paleogene transition are found in the Yacoraita and Neuquén basins, Argentina with tsunami deposits (Scasso et al., 2005) and (Sial et al., 2001 and Sial et al., 2003), in the Paraiba coastal Basin, northeastern Brazil, scope of the present study (Ashrof and Stinnesbeck, 1989; Albertão et al., 1994a,b; Ferreira et al., 1996; Menor et al., 1999; Sial et al., 2001; Lima, 2002; Barbosa and Neumann, 2004; Sabino et al., 2005; Barbosa and Neumann, 2005; Koutsoukos, 2006; Barbosa, 2007; Marquillas et al., 2007). Sedimentary sequences that potentially contain registers of the K-T boundary are found in Navidad (Topocalma Point) and Magellan basins (Punta Arenas) in Chile (Sial et al., 2001) (Fig. 1).

An important climatic change in the Paraíba Basin during the Cretaceous–Paleogene transition was recognized by Ashrof and Stinnesbeck (1989) on the basis of fossil record of the Gramame and Maria Farinha formations. The climate during the deposition of the Maastrichtian Gramame Formation limestone according to him was tropical to subtropical and changed into subtropical to temperate during the deposition of the Paleocene Maria Farinha Formation.

Albertão et al. (1994a,b) described a sedimentary section at the Poty Quarry, in this basin, where they found 1 cm thick clay layer between Gramame and Maria Farinha formation limestones that exhibits distinctive features similar to clays observed at the Cretaceous–Paleogene transition globally. They have also pointed to other features such as mass extinction, iridium and total C org anomalies, deviations in the patterns of C and O isotopes, and exotic elements (shocked quartz grains and microspherules) typical of the Cretaceous–Paleogene transition. This is, perhaps, the only locality in Brazil that registered this transition, according to Albertão and Kotsoukos (1994).

Neumann et al. (2009) focused on the Cretaceous–Paleogene transition in the Poty Quarry making a detailed stratigraphic section (about 1 m thick) with description of beds. They assumed that this transition at this quarry is characterized by an erosive contact with pyrite nodules that separates mudstone interbedded with claystone of the Maastrichtian Gramame Formation from a conglomeratic carbonate bed of the Danian Maria Farinha Formation. Ferreira et al. (1996) carried out an isotopic study in this basin and Sabino et al. (2005) have examined the behavior of C and O-isotope stratigraphies of carbonate sections at the Poty Quarry in this basin. In addition, Barbosa and Neumann (2005) and Barbosa (2007) examined the C and O isotope behavior of carbonates at this locality as well as at the Itapessoca Quarry, and compared the characteristics of the Cretaceous–Paleogene transition in the Paraíba Basin with paleoenvironmental registers in other sections that recorded this transition elsewhere.

3. Geological setting

The Paraíba Basin occupies an emergent area of about 7600 km² and its submergent area is of about 31,400 km², extending on the continental shelf down to the bathymetric quota of 3000 m (Fig. 1). This basin was once called Pernambuco-Paraíba Basin, limited by the Pernambuco Shear Zone (PESZ) and the Touros High (TH). Mabesonee and Alheiros (1991, 1993) assumed that this basin encompassed the Olinda, Alhandra and Miriri sub-basins, located between the Pernambuco Shear Zone and the Mamaguape High. Barbosa and Lima Filho, 2006 changed the name Pernambuco-Paraíba Basin to Paraíba Basin, encompassing the three above-mentioned sub-basins (Fig. 1).

The deposition of the Paraíba Basin started with the Beberibe Formation during the Santonian-Campanian (Beurlen, 1967a), followed by the Itamaracá Formation (Kegel, 1955), Gramame Formation (Beurlen, 1967b) and Maria Farinha Formation (Beurlen,
1967a,b) (Fig. 3). These formations were deposited on a carbonate ramp, initially defined as a homoclinal ramp with shallow sedimentary cover (Mabesoone and Alheiros, 1988, 1991, 1993). Barbosa and Lima Filho, 2006 considered, however, this as a distal steepened ramp.

The Paraíba Basin (Fig. 1) is subdivided into three sub-basins: Olinda (southern), Alhandra (mid) and Miriri (northern). The Olinda Sub-basin is bounded in the south by the Pernambuco shear zone, and to the north by the Goiana High. This sub-basin is semicircular in shape and corresponds to the widest area of the Paraíba Basin. It is the only sub-basin where a continuous Maastrichtian-Danian carbonate succession has been preserved.

3.1. Itamaracá Formation (Campanian)

The Itamaracá Formation (Fig. 3) is a transitional unit formed during continental to marine stage, represented by estuarine and coastal lagoon deposits, containing marine and brackish water...
fossils. This formation is composed of calciferous sandstones, shales and limestones with very fossiliferous siliciclastics. Phosphate-rich levels can be found towards the top of the formation and some of these have been studied by Menor et al. (1999) in a geochemical survey of the overlying Maastrichtian Gramame Formation using C and O isotopes. Menor et al. (1999) described a phosphatic layer as part of the Gramame Formation on top of the Beberibe Formation (Santonian-Campanian). However, based on biostratigraphic correlations, Souza (1998, 2006), returned to Kegel’s denomination (1955), with the Itamaracá Formation interlayered between the Beberibe and Gramame formations.

The Itamaracá Formation is characterized by a maximum flood surface that separates a transgressive tract system from a high stand tract (Souza, 1998; Souza, 2006; Barbosa, 2007).

3.2. Gramame formation (Maastrichtian)

The Gramame Formation (Fig. 3) overlies the Itamaracá Formation and, as typical in the Maastrichtian worldwide, it is composed of limestone-marl alternation (rhythmites; Milankovitch-range to millenial scale) deposited on 100–150 m deep carbonate platform that as environmental archives directly reflect high-frequency environmental changes (Westphal, 2006). This formation displays characteristics of a high stand tract and in its upper portion it presents traces of a forced regression, just before the transition to the Paleogene, caused by tectonic uplift (Barbosa et al., 2003; Barbosa, 2007).

3.3. Maria Farinha formation (Danian)

The Maria Farinha Formation (Fig. 3) is composed of limestones, marly limestones and thick levels of marls in its lower portion (Fig. 5), while dolomitic limestones, containing fossil reefs and lagunal reefs characterize its upper portion, according to Beurlen (1967a, 1967b). This formation exhibits regressive characteristics of high- to low-energy oscillations (Mabesoone, 1991).

At the contact between the Gramame and Maria Farinha formations, there is an erosional unconformity characterized by a carbonate sequence with intraclasts, displaying conglomeratic aspect (e.g. Ponta do Funil locality, Fig. 4) associated to the Cretaceous–Paleogene transition (Albertão, 1993; Albertão and Martins, 1996; Stinesbeek et al., 2001; Barbosa and Lima Filho, 2006).

4. Methods and analytical techniques

Only least altered portions of carbonate samples were microdrilled with a 1 mm drill bit. CO₂ was extracted from these samples on a high vacuum line after reaction with phosphoric acid at 25 °C, and cryogenically cleaned, according to the method described by Craig (1957). Released CO₂ gas was analyzed for O and C isotopes in a double inlet, triple collector mass spectrometer (VG Isotech SIRA II), using the BSC reference gas (Bororema skarn calcite) that was calibrated against NBS-18, NBS-19 and NBS-20, and has the δ¹⁸O value of −11.3‰ VPDB and δ¹³C = 8.6‰ VPDB. The external precision based on multiple standard measurements of NBS-19 was better than 0.1‰ for carbon and oxygen. Isotope analyses are expressed in the δ-notation in parts per thousand in relation to the international VPDB standard. Selected samples were also analyzed for major and trace elements at the LABISE, by X-ray fluorescence, using fused beads and an automatic RIX-3000 (RIGAKU) unit. Fused beads were prepared using Li fluoride and Li tetraborate and uncertainties were better than 5% for Sr and Fe and 10% for Mn.

For determination of the Sr isotopic ratios, powdered samples were leached in 0.5 M acetic acid and centrifuged to separate the soluble from the insoluble fractions. Strontium was eluted from solutions by ion exchange chromatography using Sr-Spec resin. ⁸⁷Sr/⁸⁶Sr values were determined in static mode using a Finnigan MAT 262 seven-collector mass spectrometer at the University of Brasília, Brazil. The isotopic ratios were normalized to ⁸⁶Sr/⁸⁶Sr value of 0.1194 and the 2σ uncertainty on Sr-isotope measurements was less than 0.00009. Repeated analyses of NBS 987 standard indicated the value of 0.71024 ± 0.00007 (2σ) for the ⁸⁷Sr/⁸⁶Sr ratio.

For determination of total mercury concentrations, homogenized 0.5–1.0 g samples, dried at 60 °C to constant weight, were digested with an acid mixture (50% aqua regia solution), and heated at 70 °C for 1 h, in a thermal-kinetic reactor “cold finger”. Glass and plastic ware were decontaminated by immersion for 2 days in 10% (v/v) Extraxion solution (MERCK), followed by immersion for 3 days in diluted HNO₃ (10% v/v) and final rinsing with Milli-Q water. All chemical reagents used were of at least analytical grade. Cold Vapor Atomic Absorption Spectro photometry, using a Bacharach Coleman (50D model) equipment, was used for Hg determination, after Hg²⁺ reduction with SnCl₂. All samples were analyzed in duplicates, showing reproducibility within 9.5%. A
certified reference material (NRC PACS-2, Canada) was simultaneously analyzed to evaluate mercury determination accuracy. Such analysis showed a precision of 4%, as indicated by the relative standard deviation of three replicates, and presented a mercury recovery of 103%. The mercury detection limit estimated as 3 times the standard deviation of reagent blanks, was 1.26 ng.g⁻¹. In all cases, blank signals were lower than 0.5% of sample analysis. Concentration values were not corrected for the recoveries found in the certified material.

One hundred sixty five carbonate samples from the drill core at the Poty Quarry collected at centimeter intervals; thirty six samples from the Olinda and thirty three from Itamaracá drill cores, collected respectively at 1.5 and 2.0 m intervals have been analyzed for C and O isotopes.

Twenty five samples from the Poty Quarry drill hole selected from among those analyzed for C and O isotopes; eighteen samples from the Olinda drill hole and eighteen, from the Itamaracá drill hole were analyzed for major and trace chemistry. These analyses were performed on fused disks in a Rigaku RIX 3000 XRF unit, with rhodium tube.

Forty thin sections of carbonate samples have been described under a petrographic microscope and micro-facies have been examined in the light of Folk’s (Folk, 1959) and Dunham’s (1962) classifications. Cathodoluminescence (CL) observations supplemented petrographic observations made with transmitted and/or polarized light. This method is very important for the diagnosis of authigenic material, especially silica and feldspar, is frequently done more easily with CL (Marshall, 1988).

5. Petrography

5.1. Calciferous sandstone, dolostone and dolostone with siliciclastic facies

Sedimentary micro-facies in the Itamaracá Formation are represented by a phosphate horizon deposited over dolostone...
(dolosparites), dolostone with siliciclasts (deep brown quartz from metamorphic country rocks; authigenic, dully to non-luminescent quartz; brilliant, light blue microcline in cathodoluminescence examination, Fig. 6A), calciferous sandstones (Fig. 6B and C). In phosphate-enriched layers, there is a large concentration of phosphatized micro-fossils and bioclasts with dolomite crystals. Calciferous sandstones, deposited below dolostone, are composed of poor-sorted, subangular to subrounded well-packed grains with concave-convex saturated contacts, testimony of dissolution (Fig. 6B and C). The constituent minerals are potassic feldspar, plagioclase and quartz (Fig. 6B). No microfossil has been identified in this facies.

The sedimentary deposition of the Itamaracá Formation happened in a transitional environment where a prevailing continental situation was replaced by a predominantly marine one.

5.2. Wackstone and packstone facies

In the Gramame Formation, micro-facies are represented by biomicrites (wackestone, packstone), containing micro-fossils (ostracodes, foraminifers, calci-spherulides) filled with spatic calcite or pyrite, detrital calcite, algic mats and bioclasts (Fig. 6D and E) disposed in micritic matrix, with little clay minerals (Fig. 6F). Under CL examination, presence of shining blue micro-crystalline K-feldspar, mixed with carbonate matrix, has been registered and according to Marshall (1988) these are detrital feldspars (it is known that non-luminescent feldspars are authigenic according Boggs and Krinsley, 2006). Recrystallization, neomorphism or cement overgrowth as an indication of diageneis have not been observed.

5.3. Wackstone, packstone and mudstones facies

The Maria Farinha Formation is composed of limestones, marly limestones and marls, deposited in a low-stand tract with terrigenous influence (Fig. 6G), as observed in their petrography and geochemistry.

Micro-facies are represented by biomicrites (wackestone, packstone), fossiliferous micrites (mudstone), with micro-fossils (foraminifers, ostracodes, calci-spheres) filled with spatic calcite or pyrite (Fig. 6I and H), bioclasts, intraclasts and micro-crystalline...
Fig. 7. Isotope and chemical stratigraphic profiles at the Olinda drill hole.

Fig. 8. Isotope and chemical stratigraphic profiles for the Poty drill hole.
quartz disposed in a micritic matrix, suggesting a regression with contribution of siliciclastic sediments (Fig. 6G). This larger concentration of siliciclastic material is the main feature in the distinction of this formation from the Gramame Formation. Detrital quartz in the Maria Farinha Formation present bluish-purple color under CL, micro-crystalline K-feldspar are mixed in a micritic matrix. Carbonate samples from this formation in the Poty drill hole display little diagenetic alteration, with minor recrystallized calcite and subordinate dolomitization. In the Olinda and Itamaracá drill holes, carbonate are even more preserved, and very little alteration has been observed.

6. Geochemistry

6.1. C and O isotopes

Carbon and oxygen isotopes stratigraphic profiles from the drill holes at the Poty, Itamaracá and Olinda are shown in Fig. 10. The δ¹⁸O values vary from −0.9 to −1.5‰ VPDB for the Campanian Itamaracá Formation, tending to lower values at the final of this period (−2.7‰ VPDB) leading to assume that, perhaps, a relatively cooler climate prevailed. The Campanian–Maastrichtian transition is marked by a negative excursion which suggests temperature increase, with values of −4 to −4.8‰ VPDB (Fig. 11). δ¹³C values vary from +1 to +1.5‰, suggest good organic productivity. In the Campanian–Maastrichtian transition, values fell down to −1.2‰ (Poty drill hole), but they are about constant at the Olinda drill hole (Fig. 10). During the Maastrichtian, carbonates of the Gramame Formation registered δ¹⁸O values close to −1 and −4‰ VPDB with a positive tendency (values closer to 0‰) and gradual fall of the temperature during this interval. In the Cretaceous–Paleogene transition, δ¹⁸O values fell down to 6.6‰ VPDB suggesting warm up of the climate (Fig. 10), followed by a sudden fall of temperature (values down to 0.1‰ VPDB). Values from +0.14 to −2‰ VPDB follow this transition, with a tendency to values close to 0‰ VPDB. In the beginning of the Maastrichtian, there was an important decrease in δ¹³C values (+0.03 e 0.1‰). During the Maastrichtian, one observes a positive trend (Fig. 8) reaching values up to +2.3‰ that were kept during the Cretaceous-Paleogene transition. There is a perturbation in the δ¹³C values, at the late Maastrichtian, with alternance of values between +0.8 and +2.9‰. These values are associated to an erosional surface represented by a 1-m thick layer within which the Cretaceous-Paleogene transition has been recorded.

The C- and O-isotope stratigraphies, side by side with chemostratigraphic profiles (Mg/Ca, Mn/Sr, Si, Al, Sr, Rb) for the Olinda, Poty and Itamaracá drill holes are shown in Figs. 7–9.

6.2. Strontium isotopes

No absolute age dating is available for sedimentary rocks in the Paraíba Basin. An attempt has been made here to obtain an indirect age estimate through Sr-isotope ratios of pure carbonates, a method suggested by DePaolo and Ingram (1985). This way, based on major and trace chemistry (SiO₂, Al₂O₃, Sr, Rb, Mg/Ca, Mn/Sr) and cathodoluminescence examination, six apparently pure carbonate samples from the Gramame Formation were selected for ⁸⁷Sr/⁸⁶Sr analysis and results were compared to the statistical LOWESS fit to the marine ⁸⁷Sr/⁸⁶Sr record Version 3.
(2001) for age estimate. Five samples yielded values between 0.7080 and 0.7082, slightly above the range for the Late Campanian–Maastrichtian LOWESS curve (0.7076–0.7078). This small $^{87}\text{Sr}/^{86}\text{Sr}$ enrichment is likely due to presence of clay minerals in tiny amounts or, perhaps, to inaccuracy of the LOWESS curve in this age interval.

It seems that the use of the LOWESS curve is limited by the factor that it requires extremely pure carbonates to be analyzed, entirely devoid of late diagenesis, alteration or recrystallization, conditions difficult to control even in a very accurate analysis and well-trained eyes.

6.3. Major and trace chemistry

6.3.1. Silica and alumina

In samples right above the Campanian–Maastrichtian transition, one observes a substantial increase of SiO$_2$ (up to 24.9%) and Al$_2$O$_3$ (up to 9.65%) values (Figs. 7–9; Table 2), related to a maximum flood surface that marks the upper limit of a transgressive system tract (Souza, 2006).

Presence of siliciclasts responsible for the increase of SiO$_2$ and Al$_2$O$_3$ is evident in cathodoluminescence analyses with microcrystalline feldspar grains disposed in a carbonate matrix, composed of rhombohedral crystals of dolomite with high Fe content (Fig. 6A).

In the Maastrichtian Gramame Formation, SiO$_2$ reaches values up to 10% and Al$_2$O$_3$, up to 5%, pointing to a decrease of continental contribution to the basin, with deposition of thick carbonate layers,
and Itamaracá drill holes, these changes were less pronounced. In the Poty and Olinda drill holes (Figs. 7 and 8; Tables 1 and 2), and with averages, respectively, of 0.4 and 0.6 in samples from the Poty and Olinda drill holes (Figs. 7 and 8; Tables 1 and 2).

In the Cretaceous-Paleogene transition, one observes a significant decrease of SiO2 and Al2O3 with values, respectively, up to 0.1% and 0.01% (Table 1). This situation was observed mainly in the drill hole of Olinda, located in the border of the Paraíba Basin. In the Poty and Itamaracá drill holes, these changes were less pronounced.

Above the Cretaceous-Paleogene transition, there was a substantial increase of SiO2 and Al2O3 (respectively 60.5% and 21.43%). This increase corresponds to a low-stand system tract, recorded in the three drillings holes under consideration (Figs. 7–9). In the Maria Farinha Formation, one observes the intercalation of layers composed of carbonates with K-feldspar, micro-crystalline quartz, clay minerals, with layers composed of micritic carbonate with micro-fossils (Fig. 6G–I).

6.3.2. Mg/Ca ratio

Zhuravlev and Wood (2009) associated the deposition of low-Mg calcite with warming cycles, and aragonite with cooling cycles. These authors stated that replacement of low-Mg calcite by aragonite can be episodically reached in mass extinction intervals. The extinction of the Cretaceous-Paleogene transition has selectively and disproportionately withdrawn low-Mg calcite from the biota, favoring aragonite and high-Mg calcite, coinciding with the beginning of the Cenozoic cooling. This way, aragonite + high-Mg calcite produces rocks with Mg/Ca >1, while low-Mg calcite is found in rocks characterized by Mg/Ca <1 (Hardie, 1996; Stanley and Hardie, 1999).

Mg/Ca ratios in Itamaracá Formation carbonates are high (around 0.8) and decrease in the Campanian-Maastrichtian transition with values between 0.02 and 0.09 during the Maastrichtian (Gramame Formation) (Tables 1 and 3). After the Cretaceous-Paleogene transition, in the beginning of the Danian, Mg/Ca ratios increase up to 0.8 in samples from the drill hole of Itamaracá (Fig. 9: Table 3), and with averages, respectively, of 0.4 and 0.6 in samples from the Poty and Olinda drill holes (Figs. 7 and 8; Tables 1 and 2).

In the three studied drill holes, the high-Mg/Ca ratios in samples stratigraphically above the Cretaceous—Paleogene transition (Maria Farinha Formation) correspond to lowering of δ18O values (Figs. 7–9) as expected in the warming—cooling cycles model (Hardie, 1996; Stanley and Hardie, 1999; Zhuravlev and Wood, 2009).

The Mg/Ca ratio also depends upon the presence of either siliciclasts or dolomite or both. In samples from the Itamaracá Formation, there is a larger occurrence of dolomite and a higher Mg/Ca ratio has been observed. In samples from the Gramame Formation, limestones are composed of micritic matrix and fossils filled with spatic calcite with limited dolomitization and low-Mg/Ca ratios.

In the Maria Farinha Formation, there is no dolomite, however there was a significant continental contribution, with siliciclasts,
mainly observed in the Itamaracá drill hole, with Mg/Ca ratios of up to 0.8. In the Olinda and Poty drill holes, there are intercalations of marls and limestone marly layers suggesting deposition in a shallow-marine environment (Fig. 2).

6.3.3. Mn/Sr
According to Jacobsen and Kaufman (1999), carbonate samples with Mn/Sr ratios < 2, with low Rb/Sr ratios (< 5 × 10^{-3}), and high Sr concentrations (150–2500 ppm) likely preserved the original isotopic signal. This way, the Mn/Sr ratio is regarded as a good indicator of degree of diagenetic alteration and often used to discriminate samples with large degree of diagenetic alteration from those whose δ^{13}C composition is from the period of deposition.

In the sixty-one samples from the three drill holes chemically analyzed in this study, Mn/Sr ratios are below 2 at about 94% (Figs. 7–9) and this suggest we are dealing with samples with little to none diagenetic alteration and with near-primary isotopic values.

6.4. Mercury stratigraphy

An alternative hypothesis to the meteorite impact as the main cause of dramatic environmental changes during the Cretaceous-Paleogene transition points to intense volcanism the Earth may have undergone during this time leading to a global cataclysm that marked this transition (Hoffman et al., 2000).

Volcanic eruptions are the main source of mercury injection in the environment, besides mercury of anthropogenic origin (Lacerda and Marins, 2006; Marins et al.; 2004; Kot et al., 1999). Volcanic emissions are important source of mercury to the atmosphere and are able to cause global and regional changes in the cycle of the mercury (Ferrara et al., 2000).

Mercury stratigraphy has been used with success to demonstrate volcanic origin of mercury and of CO₂ of carbonates deposited right after glaciations (cap dolostones) during the Neoproterozoic Snowball Earth events (Sial et al., 2010).

Aiming at the use of mercury as a tracer in the investigation of volcanism concomitant to the Cretaceous-Paleogene transition, twenty two carbonate samples were analyzed. These samples were stratigraphically collected at the Poty drill hole, from the Gramame Formation and the K-T transition. As Campanian to Danian carbonates were collected from drill holes, likely they have not undergone any anthropogenic contamination. In this stratigraphic profile, one observes mercury increase in the K-T transition as well as some Hg spikes in Maastrichtian samples. There is a correspondence between the four negative spikes observed in the δ^{13}C stratigraphy curve (labelled 1 through 4 in Fig. 11) and four small increases in Hg contents (labelled 1 through 4 in the same Figure).

Late Maastrichtian carbonates display mercury contents from 0.12 to 0.17 ng g⁻¹, with peaks around 0.5 ng g⁻¹ associated to changes in the carbon cycle and in the temperature. In the K-T transition, mercury contents reach up to 2.64 ng g⁻¹, where coincidentally one has a temperature rise with δ^{18}O around ~2.9‰ VPDB, followed by values around ~7.5‰ VPDB. This mercury enrichment may have resulted from important volcanism that the K-T transition may have witnessed (e.g. from nearby or even Deccan basaltic volcanism in India).
If meteorite multi-impact that predated the Cretaceous–Paleogene transition was responsible for abrupt changes in the carbon cycle reflected in the $\delta^{13}C$ curve and generating the four above-mentioned negative spikes, then it was also responsible for the observed small modifications in the Hg stratigraphic curve.

Sial and Long (1981) attempted to date Tertiary olivine- to alkaline basalts in the states Rio Grande do Norte and Paraíba, through the K-Ar method, and found ages ranging from 13 to 80 Ma. As this basaltic volcanism was centered in an area geographically close to the Paraíba Basin and active during a time interval which brackets the Cretaceous–Paleogene transition, it may have been the source for the high mercury concentration observed in this transition in this basin. Alternatively, mercury enrichment may have resulted from volcanism within the basin since there is seismic evidence favoring the presence of volcanic rocks offshore within the Paraíba Basin (Almeida et al., 1996).

Mercury as a volatile element, has likely spread into the atmosphere during the intense volcanism of the Deccan in India and was deposited on all over the surface of the Earth, inclusive the Paraíba Basin (Almeida et al., 1996).

7. Discussion

Carbon and oxygen isotopes are important sensors for climatic changes, and investigations using these isotopes can contribute to a better understanding of the Cretaceous–Paleogene transition in the Southern Hemisphere. They can help reconstructing the carbon cycle, by means of variation trends of $\delta^{13}C$ of the seawater (Kaufman and Knoll, 1995; Jacobsen and Kaufman, 1999). Positive oscillations are related to increase of organic carbon in relation to inorganic carbon (e.g. life expulsion and appearance of new species), while negative oscillations are, perhaps, associated to glacial events, as a consequence of substantial mortality increase and dissolution rate of organic carbon. Environmental and climatic changes can be determined at local, regional or global level associating chemical variations in a particular rock with environmental and climatic changes during the time of deposition of this rock.

Negative $\delta^{13}C$ excursions (around $-5\%$) associated to mass extinction events have been observed in the Precambrian-Cambrian, Permian-Triassic and Cretaceous–Paleogene K-T transitions (Margarit, 1989). Abramovich and Keller (2003) have utilized $\delta^{18}O$ values to relate temperature change and decrease in productivity of planktonic foraminifer, in South Atlantic, as well as changes in $\delta^{13}C$ values relate it to photosymbiosis activity. Keller (2001) studied the relationship between oxygen and carbon level changes and marine productivity in the site DSDP 525.

According to Keller (2001) climatic changes have been well documented in Maastrichtian marine sedimentary rocks, where oxygen isotopes show that the climate was relatively cold during all the Late Cretaceous, with a global warming just previous to the Cretaceous–Paleogene transition. Changes in the seawater salinity and strong eustatic level variation, leading to changes in marine bioproductivity, were also observed.

Oxygen isotope studies (Hsu and Wissert, 1980) suggest that during the Late Maastrichtian, temperatures in the South Atlantic Ocean were in the 18–23 °C range, with a cooling immediately before the Cretaceous–Paleogene transition. A gradual temperature decrease to values as low as 10 °C during the Late Maastrichtian was observed by Huber et al. (1995) studying oxygen isotopes in planktonic foraminifera from the Deep Sea Drilling Project in the southern Atlantic Ocean.

The carbon and oxygen isotope patterns in this study are somehow similar to that reported by Keller et al. (1995) in the El Kef section in Tunisia, locality regarded as the stratotype section for the Cretaceous–Paleogene transition (Fig. 12). The carbon-isotope pathway reported by Marquillas et al. (2007) for the Yacoraite Basin at about 70 km southeast of Salta, Argentina keeps some similarity with that obtained for the Itamaracá drill hole, with the best preserved limestones among those studied here.

In a typical $\delta^{13}C$ stratigraphic profile for the Cretaceous–Paleogene transition (El Kef section, Tunisia) one observes a negative excursion from +1 to −2.0 (Keller and Lindinger, 1989, 1995), and from −1 to −2 in the Yacoraite Basin, Argentina; Marquillas et al., (2007) as shown in Fig. 12. At the Paraíba Basin, however, the variation of $\delta^{13}C$ by the Cretaceous–Paleogene transition is less prominent in the three examined drill holes, varying from +2 to +1 and back to values around +2 upsection after this transition.

Above the Cretaceous–Paleogene transition, a small carbon positive excursion with values around +2.9‰, followed by a decrease to values around +1.5‰, suggests some bioproductivity increase. In summary, carbon-isotope stratigraphy reveals cycles of bioproductivity coeval with temperature fluctuation in the Paraíba Basin (Fig. 10).

8. Conclusions

The behavior of oxygen isotopes in the Paraíba Basin shows that the climate was relatively cold in Late Campanian, warming in the beginning of the Maastrichtian and facing gradual decrease during the rest of this stage. Strong fluctuation of $\delta^{18}O$ towards the Late Maastrichtian has been recorded, perhaps associated to climatic instability caused by multiple meteorite impacts that may have preceded the Cretaceous–Paleogene transition.

The behavior of $\delta^{13}C$ reveals that there was a decrease in marine bioproductivity after the Campanian-Maastrichtian transition with gradual increase along this stage with some negative excursions (fall of bioproductivity) coinciding with fluctuations of oxygen isotopes. Oxygen isotope data are compatible with slight increase of temperature during the Cretaceous–Paleogene transition, and a slight temperature decrease right after this transition.

Major and trace chemistry reveals cycles of enrichment and impoverishment in elements (e.g. Si, Al) associated to the contribution of terrigenous sediments. During the Maastrichtian, in high stand, silica and alumina contents remained about constant (10% for $SiO_2$ and 5% for $Al_2O_3$) attesting to a decrease in the terrigenous sediment supply, allowing to the deposition of thick carbonate layers, mainly at Itamaracá (Fig. 9) located in more open-marine environment (more distal area, greater depth). The increase of terrigenous sediment supply corresponds to periods when the basin has been flooded or to regressive periods. The decrease, in turn, was associated to periods of stability of carbonate deposition.

Stratigraphic correlations between these three drill cores show marls-limestone intercalations in the Gramame and Maria Farinha Formations, as well as the influx of terrigenous sediments in the Maria Farinha Formation, in agreement with previous studies in this basin (Fig. 2).

Likewise silica and alumina, fluctuations of the Mg/Ca ratios accompany variations of the continental contribution to the system (Figs. 7–9), the higher the continental contribution, higher the Mg/Ca ratios. High values of the Mg/Ca ratio after the Cretaceous–Paleogene transition correspond to deposition of aragonite – high Mg-calcite and cooling recorded by $\delta^{18}O$ values (Figs. 7–9), as foreseen in a model of warming–cooling cycles (Hardie, 1996; Stanley and Hardie, 1999; Zhuravlev and Wood, 2009).

Cathodoluminescence images further support conclusions drawn from bulk chemistry, showing that higher concentrations of $SiO_2$ and $Al_2O_3$ are associated to beds with concentration of micro-crystalline quartz and K-feldspar (Fig. 6C). Furthermore, the CL examination has failed to spot significant diagenetic process in the studied carbonate sequences, reinforcing the primary nature of the isotope signals.
In the Paraiaba Basin, mercury shows a stratigraphic variation synoptical with δ13C and δ18O stratigraphies around the Cretaceous-Paleogene transition. The subtle increase of mercury content exactly in this transition seems to be compatible with coeval volcanism. This contention seems to support that large concomitant volcanism has been responsible, at least in part, for the drastic climatic environmental changes in the Cretaceous-Paleogene transition, observed worldwide.

Acknowledgments

We would like to thank Gilsa Maria Santana and Vilma Sobral Bezerra for assistance with stable isotope analyses in theLABISE. MVNS is grateful to the National Council for Scientific and Technological Development (CNPq) for a scholarship during graduate studies at the Federal University of Pernambuco. We want to thank two anonymous reviewers whose comments and suggestions helped improving the original manuscript. This study was supported by the Paraiaba Drilling Project/UFPE/CNPq/Princeton University and by grants to ANS (CNPq 470399/2008 and FACEPE APQ 0727/2008). This is the contribution no. 255 of the NEG-LABISE. Drilling was supported by the US National Science Foundation (NSF) and OISE Grant No. EAR-0207407 to Gerta Keller, Princeton University.

References


