Int J Earth Sci (Geol Rundsch) (2005) 94: 475–489
DOI 10.1007/s00531-005-0508-x

ORIGINAL PAPER

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Barium anomaly preceding K/T boundary: possible causes and implications on end Cretaceous events of K/T sections in Cauvery basin (India), Israel, NE-Mexico and Guatemala

Received: 4 October 2004 / Accepted: 2 May 2005 / Published online: 3 June 2005

Abstract Maastrichtian–Danian strata of the Cauvery basin as well as selected sections of NE-Mexico, Guatemala and Israel record Ba anomalies, away from the Cretaceous/Tertiary boundary (KTB) in addition to common occurrences of geochemical and stable isotopic anomalies across the KTB. Ba anomalies were recorded in monotonous shallow marine sandstones of the Cauvery basin (south India) which contain minor amounts of Ba-orthoclase. Barium anomalies were observed also in shallow marine carbonates in sections of Israel, NE-Mexico and Guatemala. Calculation of excess Ba with reference to PAAS (Post-Archaen Average Australian Shale), comparison of coeval geochemical anomalies, depositional pattern and associated petrographic and mineralogical features of the Cauvery basin revealed that while a first Ba peak was related to detrital influx, the second Ba peak was coincident with sea level fall which in turn may have been influenced by emission of volatile hydrocarbons and resultant climatic changes. In view of intrinsic involvement of Ba in various geochemical processes and occurrence of Ba anomalies in K/T sites distributed around the world (NE-Mexico, Guatemala and Israel), it is suggested that probable causes of such widespread Ba-anomalies should be taken into consideration while analyzing end Cretaceous events. These observations support the views espoused by many workers who have stated that the K/T boundary was also accompanied by many non-catastrophic events that might have contributed to environmental stress on marine fauna, as a result of which selective multi-stage extinctions occurred.

Keywords K/T boundary · Ba anomaly · Multi-event scenario · South India · Tethys sea

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Introduction

The close of the Mesozoic era marked the beginning of an eventful phase in geological history in terms of global climatic deterioration that left imprints on faunal and floral distributions and on the sedimentary deposits (Saraswati et al. 1993). An abrupt boundary separates the Cretaceous from the Tertiary virtually everywhere in the global stratigraphic record (Meyers and Simoneit 1989). Consensual explanation for this major perturbation remains elusive, notwithstanding considerable discussions from a large part of the earth science community (e.g. Tschudy et al. 1984; Jiang and Gartner 1986; Sloan et al. 1986; Saito et al. 1986; Hallam 1987; Keller 1988a, b). The nature of climatic changes at the Cretaceous/Tertiary boundary has been the focus of much attention since the formulation of the impact scenario by Alvarez et al. (1980) and the debate still continues (G. Keller et al. submitted; Stüben et al. 2002a, b). According to the models of Broecker (1982) and Hsü et al. (1982), the impact of a large extra-terrestrial body at the end of the Cretaceous might have caused climatic and oceanic changes similar to those expected for a nuclear winter (Ehrlich et al. 1983). In addition to reducing temperature, the partial blackout caused by a global ejecta dust cloud would have caused a reduction of photosynthesis and thus the collapse of the marine trophic structure. Stable isotope patterns in the marine stratigraphic record have been used to document these climatic and biologic effects (Hsü et al. 1982; Hsü 1984; Hsü and McKenzie 1985). On the contrary, an increasing body of evidence points to the presence of abrupt δ^{18}O and δ^{13}C changes associated with the K/T boundary (Romein and Smit 1981; Hsü et al. 1982; Shackleton and Hall 1984; Mount et al. 1986; Zachos and Arthur 1986). But, at a number of localities, δ^{18}O and δ^{13}C changes have been found to precede the K/T boundary (Keller et al. 1998) as defined by the worldwide iridium anomaly (Renard et al. 1984; Williams et al. 1983; Mount et al. 1986; Zachos and Arthur 1986). Similarly, Kramar et al. (2001), Stüben et al. (2002a), G. Keller et al. (submitted) and Adatte et al. (in preparation) recorded anomalies of platinum group elements far below the K/T boundary. Occurrences of pre-K/T boundary anomalies raise questions on the relative timing of biotic and isotopic events near this boundary and their relevance to the impact scenario (Kaminski and Malmgren 1989). This paper documents Ba anomalies far below the K/T boundary in the Cauvery basin of south India, NE-Mexico, Guatemala and Israel discusses the plausible causes.

Geologic setting and depositional history

The Cauvery basin (Fig. 1) is located in the southernmost part of the Indian peninsular shield and is one of the NE–SW trending Late Jurassic–Early Cretaceous rift basins of India (Powell et al. 1988). A more or less complete Upper Cretaceous–Paleocene succession is exposed in the Ariyalur–Pondicherry depression of this basin (Sastry and Rao, 1964). The Maastrichtian–Danian boundary in this basin is represented by an unconformity across which the faunal and lithological characteristics of the strata are very different, making the Cretaceous-Tertiary boundary readily recognized in the field (Sastry and Rao 1964; Sastry et al. 1972; Chandrasekaran and Ramkumar 1995). In this paper, we examine the 236 m thick Maastrichtian–Danian

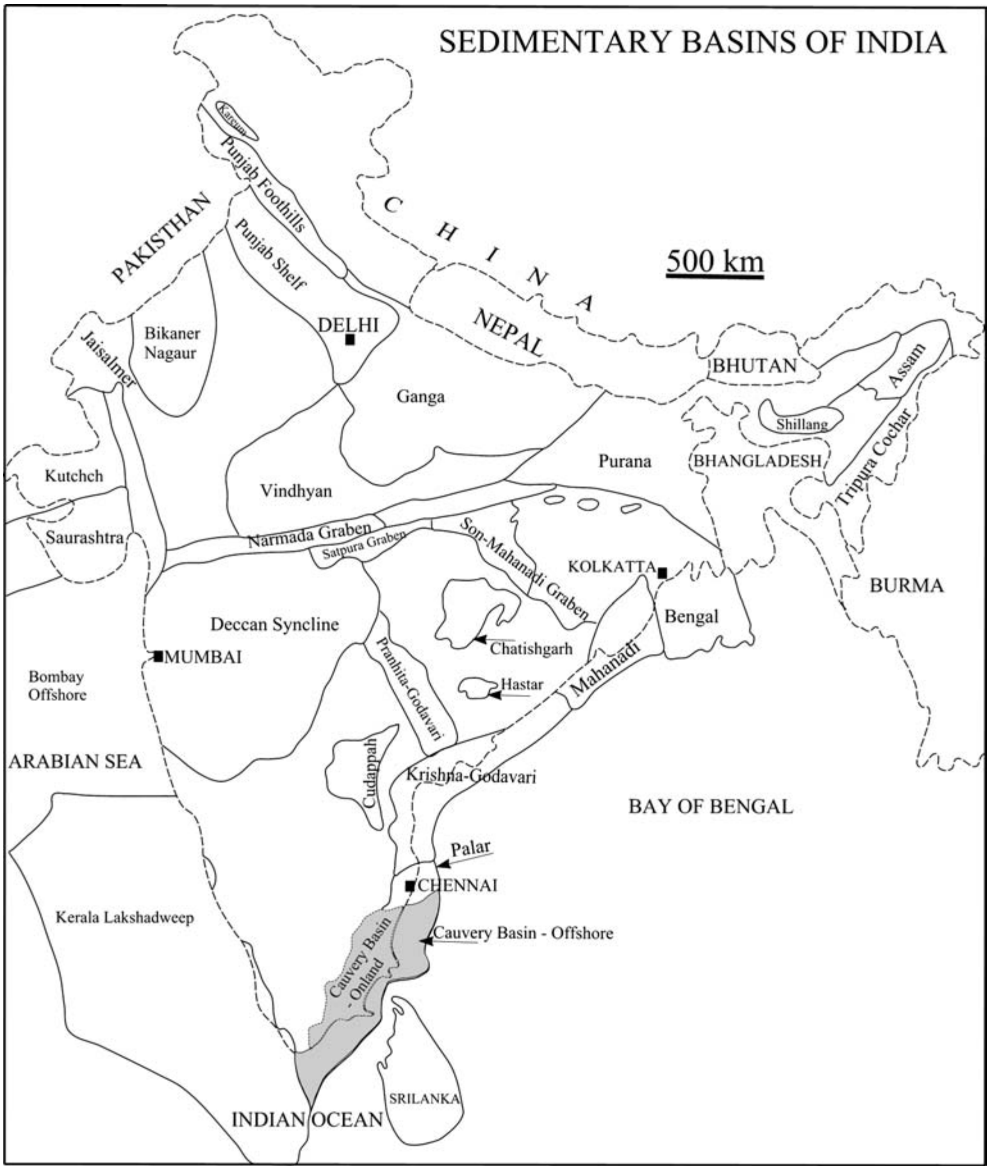
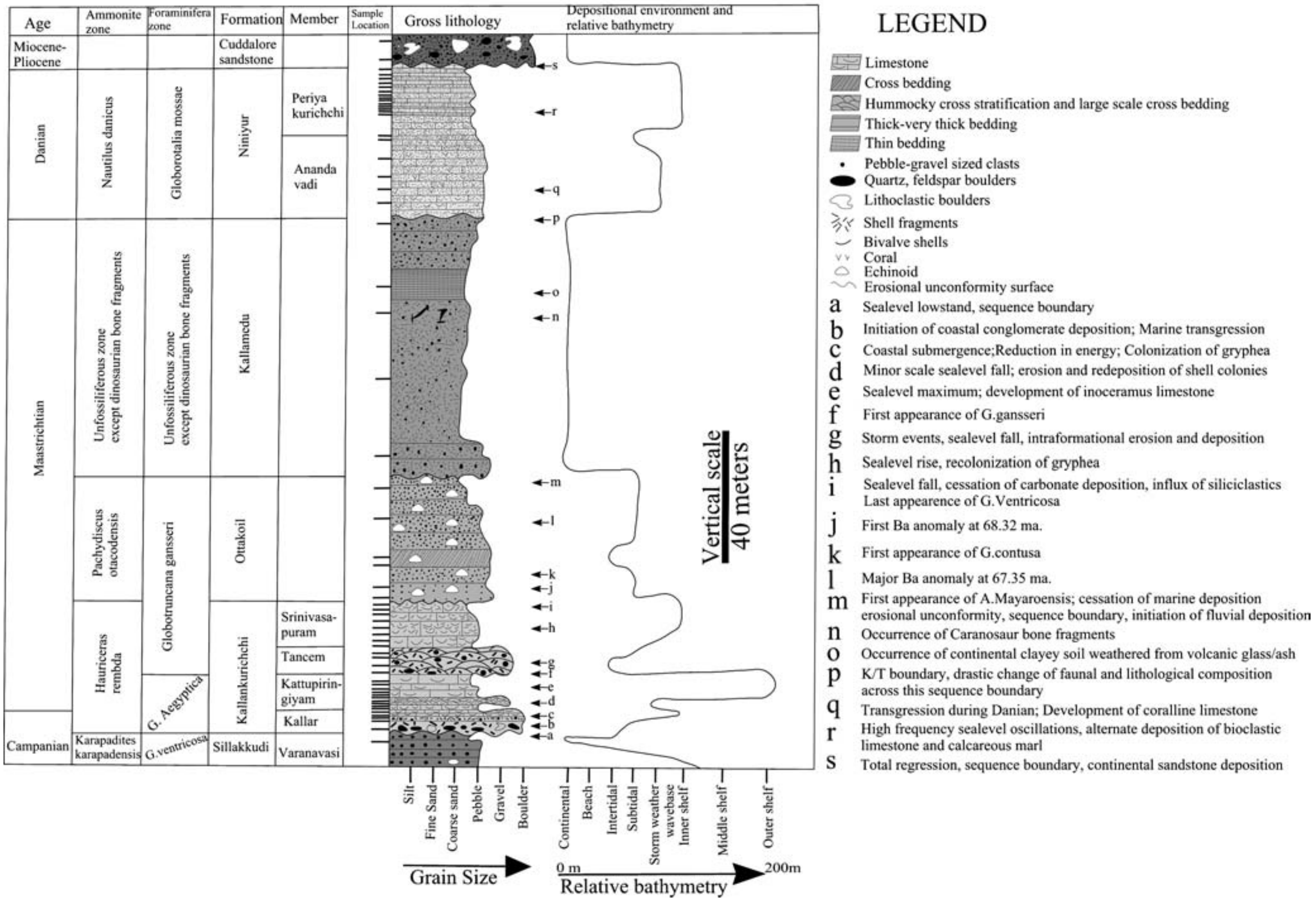


Fig. 1 Sedimentary basins of India. Location map of the Cauvery basin

strata whose lithological characteristics and inferred geological histories are presented in Fig. 2.

Sedimentation of the lowermost deposits of the studied section, the Kallankurichchi Formation, commenced at about 75.5 Ma (Thompson 1994; Raju et al. 1997) with transgression during the latest Campanian–Early Maastrichtian (Hart et al. 2000). As the initial marine flooding started to wane, there was a reduction in the proportion and size of siliciclastic particles that were increasingly replaced by *Gryphean* colonies. In due course, the *Gryphean* banks shifted towards shallower regions, and the locations previously occupied by coastal gravels became middle shelf, where typical *Inoceramus* limestone started developing. Change in depositional conditions of this member to the next member was associated with a regression of sea level that transformed the middle to outer shelf regions into intertidal to fair weather wave-base regions, paving way for deposition of hummocky cross stratified and cross-bedded carbonates. Again, the sea level rose to create a marine flooding surface, as a result of which *Gryphean* shell banks started to develop more widely than before. Raju et al. (1993; 1997) indicated that commencement of this gryphean bank development was coincidental with sea level rise since 70.45 Ma. Towards the top, shell fragments and minor amounts of siliciclastics are observed in these gryphean shell banks indicating onset of regression and higher energy conditions. The occurrence of a non-depositional surface at the top of this formation and deposition of shallow marine siliciclastics (Ottakoil Formation) in a restricted region immediately after carbonate deposition and conformable offlap of much younger fluvial sand deposits (Kallamedu Formation), are all suggestive of gradual regression associated with the establishment of a fluvial system during the end of the Cretaceous. Data after Thompson (1994) and Raju et al. (1997) indicate commencement of deposition of Kallamedu Formation at about 67.1 Ma. Towards the top of the Kallamedu Formation, paleosols are recorded, implying abandoning of the fluvial system and restoration of continental soil formation conditions at the end of the Cretaceous Period. During the Early Danian, a transgression covering the eastern part of the Kallamedu Formation took place. Presence of a unconformable contact between the Anandavadi member and Kallamedu Formation and initiation of carbonate deposition from the beginning of the Danian are indicative of the absence of a fluvial sediment supply and tectonic activity at this time. Another sea level rise during 64.4 Ma (Thompson 1994; Raju and Misra 1996;

Fig. 2 Lithology, stratigraphy, environment and geological events of the Maastrichtian–Danian strata of the Cauvery basin



Raju et al. 1993; 1997) led to the deposition of the Periyakurichchi member under shallow, wide shelf with open circulation conditions. At top, this member has a distinct erosional unconformity, which in turn, when interpreted along with the presence of the huge thickness of continental sandstone (above >4,000-m thick Cuddalore sandstone Formation), indicates restoration of continental conditions in this basin. The absence of any other marine strata above the Cuddalore sandstone Formation (Miocene to Pliocene in age) suggests that the sea which regressed at the end of the Danian never returned thereafter.

Materials and methods

Systematic field mapping of part of the Cauvery basin at the scale of 1:50,000 was conducted to collect data on lithology, sedimentary and tectonic structures and faunal association (mega- and ichno-) from natural exposures, well and mine sections. A composite stratigraphic profile representing a continuous stratigraphic record of Maastrichtian–Danian strata (Fig. 2) was constructed. The global sea level peaks during 73 (±1; Late Campanian), 69.4 (Early to Late Maastrichtian) and 63 Ma (±0.5; Early to Middle Danian) are observed (Raju et al. 1993) to occur in this basin (Fig. 2). Data after Thompson (1994) have provided additional datum-lines of 75.5 Ma, 70.4 Ma, 68.5 Ma, 67.1 Ma, 64.4 Ma, that are traceable in the studied composite stratigraphic section through the documentations of Rao (1956), Sastry and Rao (1964), Chandrasekaran and Ramkumar (1995), Raju and Misra (1996), Raju et al. (1997), Ramkumar (1999), Hart et al. (2000) and Ramkumar et al. (2004a, b).

Construction of composite stratigraphic section representing more or less continuous Maastrichtian–Danian strata of the Cauvery basin had allowed selection of 47 representative whole-rock powder samples for analyzing their trace elemental compositions and bulk mineralogy. Sample selection was such that at first, samples were selected at chrono-, bio- and lithostratigraphic boundaries and also at known datum lines such as sea level lows and highs at which age data of these samples are well constrained. Furthermore, based on characteristics of stratigraphic section such as monotony of lithology, absence of hiatus and thickness of individual beds, samples were collected at equal spacing between known and constrained datum lines as mentioned above. This method of sampling had allowed representation of strata in a continuous profile, linear extrapolation of the age value for samples collected in between known boundaries and datum lines and also avoided encountering stratigraphic breaks except where significant time lapse could have occurred such as lithostratigraphic boundaries (Ramkumar et al. 2004a, b). However, the statements of Rao (1956) that the Maastrichtian–Danian section of the Cauvery basin is one of the continuous stratigraphic records of the world and Chandrasekaran and Ramkumar (1995) and Ramkumar (1999) recorded the absence of significant unconformity surfaces in between studied lithostratigraphic formations/members which in turn suggest the sampling strategy followed could very well represent a continuous geochemical profile of Maastrichtian–Danian section of the Cauvery basin. From these 47 samples, 22 were analyzed for major elements, stable isotopes and clay mineralogy. A few sections from a transect from La Sierrita (~50 km south of Monterey) to Bochil (Yucatan) in the vicinity of the Chicxulub impact crater, one section in Guatemala and another one in Israel were examined and sampled for high resolution geochemical and mineralogical studies. Sample intervals ranged in average around 10 cm. At the K/T boundary layers the sampling intervals were reduced to 1–5 cm. These K/T boundary sections are in proximity of the impact site and represent an excellent study area. Detailed discussions on geologic setting, age, biostratigraphy and environmental interpretations, etc. regarding these sections are presented in many publications (e.g. NE-Mexico sections and Guatemala section—G. Keller et al. (submitted), Keller et al. (2003, 2004); Negev section—Adatte et al. (2004). Trace and major elemental analyses were performed by XRF following the procedures discussed in Kramar (1997) and Stüben et al. (2002a). Stable isotopes were analyzed against laboratory standards, details of which are discussed in Keller et al. (1998) and Stüben et al. (2002b). While this paper discusses in detail only the Ba anomaly of the Cauvery basin, comparison with other sections was made for documentation of similar occurrences elsewhere in the Tethys sea, for which data from G. Keller et al. (submitted) and Adatte et al. (2004) were collected and utilized.

Results and interpretation

Geochemical profiles of selected major and trace elements and stable isotope compositions of Maastrichtian–Danian strata of the Cauvery basin are presented in Figs. 3, 4. They reveal that there are many positive and negative excursions of different elements, but most of those anomalies occur above or below the K/T boundary (65.4 Ma). It is also observed that, Ba shows prominent positive excursions at about 67.4 Ma and 68.3 Ma. Occurrences of positive excursions of Ba profiles and non-occurrences of coeval excursions of any other element itself suggest that the Ba anomaly is a peculiar phenomenon and is not related to syn- or post-depositional chemical mobilization and redistribution. Barium in sediments has been proposed as a proxy for both modern oceanographic processes (Bishop 1988; Dymond et al. 1992) and paleoceanographic conditions (Francois et al. 1995). It is being utilized increasingly as paleoproductivity tracer (Francois et al. 1995; McManus et al. 1998) but there are also disagreements for such usage (e.g. Murray and Leinen 1993). Except these two positive excursions, Ba does not show any significant shifts either from a linear trend (Fig. 3) or mean value of the entire section (497.67 ppm) or Maastrichtian average value (672.89 ppm) or Danian average value (261.78 ppm), which means that the positive excursions of Ba up to 6593 ppm are abnormal from the background values. Computation of excess Ba content in the sediments according to the formula of Murray and Leinen (1993, 1996) with reference to PAAS (Post-Archaen Average Australian Shale—Taylor and McLennan 1985) also indicate high deposition of Ba between 68.3 Ma and 67.4 Ma. These anomalies represent a 4–10 times higher concentration than average shale (~650 ppm—Taylor and McLennan, 1985). Further, the linear trend (Fig. 3) shows general Ba concentration of these rocks more or less equal or fall below the value of average shale.

Positive anomalies of Ba occur in the Ottakoil Formation, represented by shallow marine siliciclastics deposited under slowly waning sea. The first peak (Figs. 2, 3) was found in a cross-bedded, fining-upward sequence while the second and major peak occurs in well-sorted sandstones. The rocks contain abundant and uniform distribution of *Stigmatophygus elatus*, a stenohaline, shallow marine echinoid (Petrovic and Ramamoorthy 1992) and an ichnofauna namely, *Ophiomorpha*, which is also typical of shallow marine regions. McManus et al. (1998) suggested that preservation potential in the near-shore regions is lower than the continental margin and further offshore regions. In this context, occurrence of Ba peaks in shallow marine deposits is itself an intriguing feature.

Based on the exclusive occurrences of Ba peaks in monotonously uniform-featured sandstones, it is inferred that the lithology could not have influenced them. X-ray diffractograms of rock samples of these sandstones show the presence of Ba-orthoclase. If its occurrence is considered to be the reason for Ba anomaly, the Kallar member of Kallankurichchi Formation, wherein large boulders—pebbles of fresh Ba-orthoclase are reported (Photograph 1), should also show a significant Ba anomaly. In addition, the Ba-orthoclase clasts occur in negligible to minor proportions in the Ottakoil Formation. Petrographic observations show stratigraphically uniform distribution of feldspathic grains in the Ottakoil Formation, in which case, had the Ba-orthoclase served as the source of Ba anomaly, the positive excursions of Ba should have had a span covering the entire Ottakoil Formation and also that the background values of Ba of Ottakoil Formation should have been higher than other formation, which in turn is not. Furthermore, Ba has the tendency to adhere onto clay mineral surfaces (Singh 1978) in which case, significant influx of clay and the adherence of Ba onto clay could be inferred. However, clay admixture in these sandstones seldom exceeds 5%

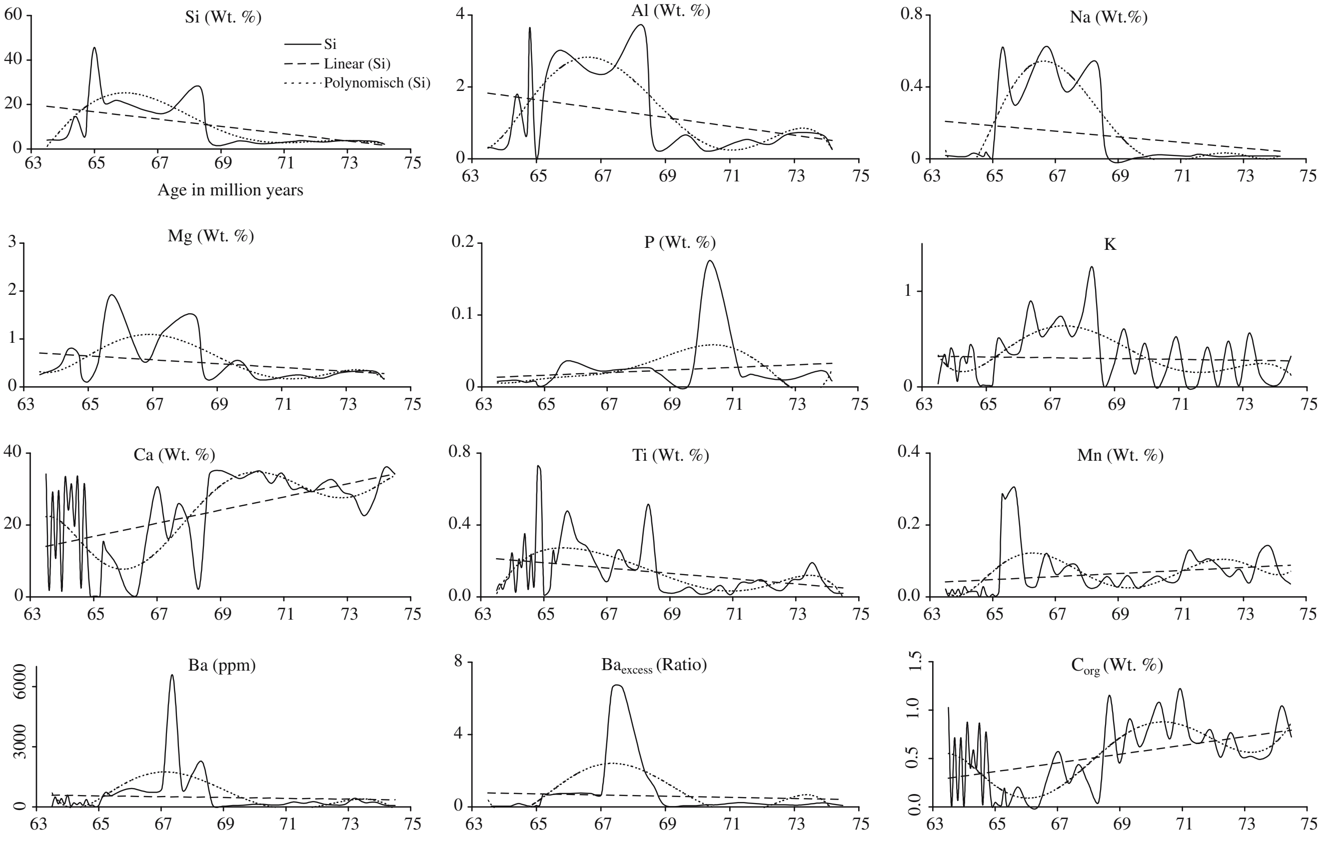


Fig. 3 Geological profiles of selected elements

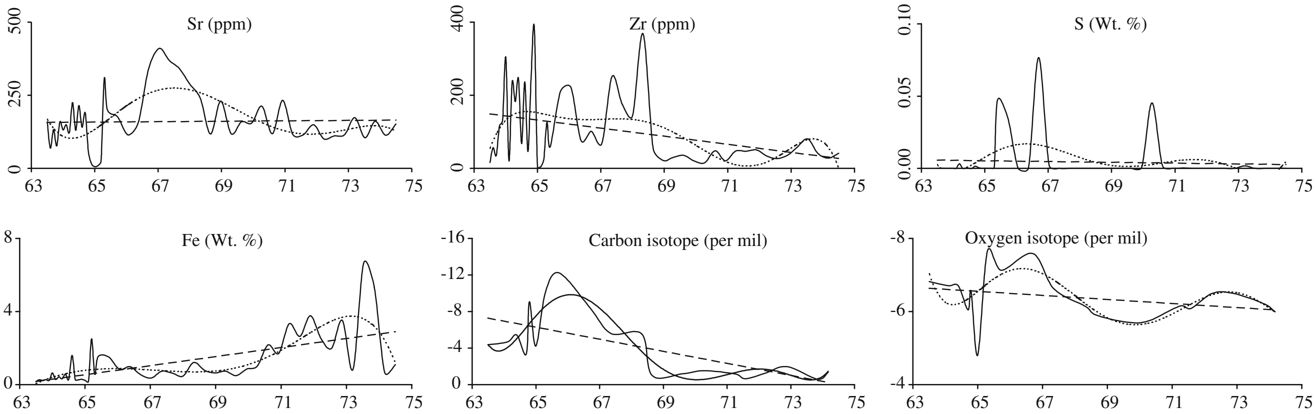


Fig. 4 Geochemical profiles of selected elements and stabile isotopes

and its stratigraphic distribution is more or less uniform. Considering all the clay present in the sandstones to have adhered Ba on their surfaces signifies availability of free Ba during deposition of rocks that show these two peaks. This presumption also calls for weathering of Ba-orthoclase in the continental regions to form clay, transport and deposition of them in the marine basin to cause Ba anomalies. However, occurrence of fresh Ba-orthoclase clasts in Kallar member of Kallankurichchi Formation and feldspathic sandstone in Ottakoil Formation counters but does not excludes such a possibility. Ramkumar et al. (2004a) interpreted that detrital influx in this basin was influenced by sea level lowstands. As the Ottakoil Formation was deposited in a regressive sea, a slow increase in the quantum of detrital influx could be expected. Occurrence of a sudden spurt of Ba concentration does not explain the gradual increase of detrital influx. Ramkumar et al. (2004a, b) and Stüben et al. (2005) argued that the periods of carbonate deposition in this basin occurred during sea level highstands during which, owing to the restricted nature of catchment basin due to basin configuration and hinterland topography, no chemical weathering was prevalent (primarily controlled by reduction in available exposed area of catchment region for weathering), depriving siliciclastics to the basin. They also stated that physical weathering dominated the entire depositional history of the basin owing to the climatological characteristics and basin configuration. These observations also point to the fact that, if Ba was adhered onto clay mineral surfaces (Kumar et al. 1995), its contribution to the Ba anomalies should have been minimal, if not insignificant.

The profiles of Si, Al, Na, Mg and K show distinct peaks at 68.3 Ma indicating significant detrital influx coeval with first Ba peak. They could have been brought to the depocenter together, in the form of Ba-orthoclase and/or albite or clays (weathered from these feldspars). Occurrence of coeval Zr peak confirms significant detrital influx. However, while several coeval peaks for Ba anomalies could be observed, profiles of Si, Al, Na, Mg and K show multiple peaks away from the major (second) Ba peak. If primary source of Ba is considered to be detrital and influx of it in the form of Ba-orthoclase or its weathered derivatives (clay and Ba adsorbed onto such clay), all these elements should show coeval peaks. Absence of such coeval peaks of Ba except at 68.3 Ma indicates either Ba has not been drawn from detrital sources, or Ba had terrestrial sources only during 68.3 Ma and there might have been widespread weathering and transport of terrestrial materials at that time. Neither environmental conditions nor lithological or faunal changes are observed to support this assumption. Furthermore, the magnitudes of peaks of Si, Al, Na, Mg and K are at subdued levels during 67.4 Ma and the peaks of detrital trace elements namely, Zr and Ti are very high during 68.3 Ma and low during 67.4 Ma meaning that, had there been a prime detrital source for Ba, then the major Ba anomaly should have been at 68.4 Ma instead of 67.4 Ma. These observations might be interpreted as evidence for a dual source for Ba (Schroeder et al. 1997). If so, the cause of the major Ba anomaly at 67.4 Ma has to be unraveled and absence of influx of Ba-orthoclase during other periods of detrital influx, as reflected in profiles of Si, Al, Mg, Na and K has to be explained.

Many studies have established a link between relative abundances of Ba and productivity levels (e.g. Lyle et al. 1992; Dymond et al. 1992; Stüben et al. 2002b), but precise mechanisms of Ba precipitation and its resultant incorporation into marine sediments still remain unclear (Schroeder et al. 1997) as it reacts to primary productivity, terrigenous influx and post-depositional preservation processes (Keller et al. 1998; Stüben et al. 2002b). McManus et al. (1998) observed that the Ba maximum in pore waters of sediments in world oceans shows coeval Fe or Mn maxima, reflecting an interaction between Ba and metal oxide cycling. Schroeder et al. (1997) also noted scavenging of Ba by Fe oxides. Torres et al. (1996) recorded high concentrations of microcrystalline barite in sediments of world oceans and concluded that it resulted from the precipitation of Ba sulfate within microenvironments of decaying biological debris in the water column. Absence of barite (as evidenced from X-ray diffractograms) and observation of very low sulphur content (if at all present, they record concentrations below the detection limit of the carbon–sulphur analyzer) in these rocks defies such a possibility for the cause of the Ba anomaly. Furthermore, other proxy of oceanic productivity such as Cd (Oppo and Fairbanks 1989) does not show any coeval peak (measurement of Cd of the rocks had shown concentration of Cd below instrument (XRF) detection limit. Dymond et al (1992) and Schroeder et al. (1997) have established that much of the Ba in marine sediments remains in the form of calcite bound components. If it holds true for the rocks under study, then Ba should show a coeval peak with Ca. On the contrary, the profiles of Ca and Ba show sharp negative correlations. In this basin, sea level highstands have always supported carbonate deposition and the quantum of preserved C_{org} always depended on availability of carbonates (Stüben et al. 2005). As the carbonates of this basin were all generated by shell colonies (e.g. Fig. 2 Photograph 2) or coral reefs, the cause that produced positive anomalies of Ba might also have affected carbonate production. In other words, as accumulation and preservation of C_{org} could occur during sea level highstands and higher primary productivity, reduction of sea level and productivity could be inferred to have occurred to cause the Ba anomaly. Bishop (1988) recorded covariation of Ba with marine organic matter as a result of barite precipitation in microenvironments during decomposition of particulate organic matter. These observations together indicate the possibility of a sudden environmental change that affected the primary productivity and carbonate deposition that might have been the cause of or triggering mechanism for the Ba anomaly. However, cessation of carbonate deposition and occurrence of a Ba anomaly are chronologically wide apart—meaning, lack of correlation between these two.

Discussion

The Cretaceous/Tertiary boundary (KTB) marks a major extinction of both marine and terrestrial species. Explanations for these extinctions typically fall into two main theories, first, the cataclysmic effects of the Chicxulub meteorite impact in the Gulf of Mexico or, second, the fallout from the massive eruptions that created the Deccan flood basalts of India. It is argued that either the Chicxulub impact or the Deccan eruptions could have induced environmental changes serious enough to significantly disturb ecosystems. Typical KTB sediments contain Ir anomalies demonstrating their apparent synchronicity with the Chicxulub meteorite impact. In India, Ir anomalies are linked to the supply by Deccan volcanism (Bhandari et al. 1995) for the recorded occurrence in intertrappean clayey sediments (Anjar region of central India—Khadkikar et al. 1999) or in Kallamedu Formation of the Cauvery basin. The clay layer is considered to have been formed by weathering of volcanic ash and glass (Hansen and Mohabay 2000). These observations signify coeval/more or less contemporaneous meteoritic impact at Gulf of Mexico and Deccan volcanism. However, as the Ir anomalies occur in intertrappean beds, it is inferred that Deccan volcanism predates meteoritic impact (Venkatesan et al. 1993; Bhandari et al. 1993; Khadkikar et al. 1999). In view of the enormity of Deccan volcanism (Glasby and Kunzendorf 1996) and its proximity to the study area, it could be assumed that it would have influenced the sediments of the study area more readily than the meteoritic impact in the Gulf of Mexico region. Furthermore, owing to the sampling interval of this study, lack of Ir data for the analyzed samples, the occurrence of a Ba anomaly far below the perceived K/T boundary and the occurrence of Ir anomaly at the K/T boundary, meteoritic impact and its relevance to Ba anomaly can be excluded from discussion.

Major part of Deccan volcanism occurred between 60 and 65 million years ago, which produced roughly two-thirds of the basalts of the Indian subcontinent (McLean 1985), covering an area of 2.6×10^{6} km^2 in western and central India (Pascoe 1964). Alexander (1981) stated that among major episodes of flood basalt volcanism in earth's history, the Deccan volcanism has by far the greatest in volume over shortest time span. Based on magnetic polarity reversals of Deccan trap rocks, McLean (1985) calculated that this volcanic activity lasted for a time period of between 0.53 million years and 1.36 million years. Although volcanic activity in the Deccan region started during the Early Cretaceous, intensive eruption occurred at about 65 Ma. In the context of the present study, this volcanic activity at this magnitude would have severely affected the equilibrium of carbon between ocean basins and the atmosphere through mantle degassing. Mantle degassing continually liberates CO_2 onto earth's surface via volcanism, fumaroles, hot springs and oceanic ridge systems. Over long time-intervals, general equilibrium exists between mantle CO_2 release and uptake by surficial carbon sinks, contributing to climatic and bioevolutionary stability. However, at times of rapid plate movement, vigorous mantle circulation or continental flood basalt volcanism, the rate of mantle CO_2 release exceeds that of uptake, triggering disequilibrium and perturbation of the carbon cycle. Times of disequilibrium can be times of build up of CO_2 in the atmosphere and the ocean-mixed layer, causing lowering of the mixed layer pH, climatic warming via CO_2-induced greenhouse conditions and bioevolutionary turnover. The magnitude of change is coupled with severity of disequilibrium (McLean, 1985). Coeval with eruption of basaltic lava the Deccan volcanism has also ejected 5×10^{17} mol of CO_2 into atmosphere that amounted to an approx. 25% increase in atmospheric CO_2 concentration (for details Khadkidar et al. 1999 and references therein). Release of this vast amount of mantle material within such a short interval would have perturbed the earth's surficial carbon reservoirs, triggering ecological instability (McLean 1985). Thierstein (1981) noted that prior to the Deccan volcanism, global ecological stability prevailed. Many authors, namely McLean (1985), Bhandari et al. (1993; 1995), Venkatesan et al. (1993) and Glasby and Kunzendorf (1996) have examined the timing of the Deccan volcanism and its effect on global climate. Based on their observations, the following can be inferred with reference to the Ba anomaly.

It seems certain that, although Deccan volcanism commenced during the Early Cretaceous, significant quantities of eruption took place only around 65 Ma while the Ba anomalies preceded this event by about 1.5 million years. Hence, it is safe to interpret that the Deccan volcanic eruption would not have made any direct impact on Ba anomaly. The weathered materials of volcanic ash (presumably spread from Deccan volcanism) form a specific clay layer in the upper portion of Kallamedu Formation (Fig. 2), which is younger than the Ottakoil Formation. Hence, it is inferred that the Deccan volcanism had made its imprints on sedimentary record of the Cauvery basin, but the imprints are younger than the Ba anomaly and thus, influence of Deccan volcanism with reference to the Ba anomaly could be ruled out. As Deccan volcanism impacted the sedimentary record of the Cauvery basin through inducing greenhouse effect, rise in atmospheric temperature and sea level and initiation of carbonate deposition, which are recorded only at or after the end of the Cretaceous (Niniyur Formation), which in turn are much younger than the Ba anomaly. On the contrary, based on the suggestion of Hallam (1987), Glasby and Kunzendorf (1996) noted that extensive Deccan volcanism itself might have caused sea level fall by up to ~100 m and sea level fall may have taken place during latest Maastrichtian. Thus, it is concluded that the impact of Deccan volcanism on sedimentation in the Cauvery basin, if any, postdates the Ba anomaly.

As the major events that have made significant impact on earth’s history have been shown to be not relevant in the context of the Ba anomaly, other causes, namely environmental and climatic factors were examined. It is based on the conclusions of Keller et al. (1998), Pardo et al. (1999) and Stüben et al. (2002b), Stüben et al. (2005) that the end Cretaceous extinctions were multi-level extinctions caused by gradually accumulating environmental stress as a consequence of climatic reversals and sea level fluctuations.

The entire depositional history of the Cauvery basin was essentially controlled by sea level oscillations that occurred at the scales of fourth or still higher orders that stack up to form six third-order cycles, that in turn form part of two second-order cycles. The basin also recorded all seven global sea level peaks of the Barremian–Danian period (Ramkumar et al. 2004a; Stüben et al. 2005), cycles influenced by global scale climate and eustasy. These global scale changes caused lithological alternations of predominant siliciclastics and carbonates in this basin. In this context, occurrences of sharp deteriorations of productivity levels, as reflected in Ca, C_{org} profiles (Murray and Leinen 1993) exactly coincident with positive anomalies of Ba, together with broad scale change of lithology from predominant carbonates (Kallankurichchi Formation) to shallow marine siliciclastics (Ottakoil Formation) were inferred to have been influenced by major climatic and/or environmental perturbation. Existences of conformable contact between Kallankurichchi and Ottakoil Formations and near parallel bedding attitudes of rocks of these formations rules out any major tectonic activity that might have influenced the cessation of carbonate deposition and initiation of siliciclastic deposition.

The sea level curve in Fig. 4 of Maastrichtian–Danian strata (Fig. 4) shows a gradual reduction culminating in total regression during which the Ottakoil Formation was deposited. The fall of sea level from maximum flooding (Srinivasapuram member of Kallankurichchi Formation) to lower levels of the Ottakoil Formation records change in lithology from carbonates to siliciclastics, in line with the general depositional pattern of this basin (Yadagiri and Govindan 2000; Ramkumar et al. 2004a). Sea level rise in this basin was always associated with higher organic carbon accumulation and preservation (Fig. 3) and the fall in sea level resulted in reduction of organic carbon concentration. The carbon budget is of primary importance for understanding climatic change on all timescales. On a glacial–interglacial timescale, terrestrial vegetation, a very reactive carbon reservoir, is destroyed when ice sheets override it. Since the $\delta^{13}C$ of terrestrial biomass is low (Craig, 1953) compared to the mean ocean value (Kroopnick 1985), the $\delta^{13}C$ of mean ocean water is affected by the transfer of carbon between the terrestrial biosphere and the ocean (Shackleton, 1977). Growth and destruction of terrestrial vegetation also occurs on the continental shelf area as sea level falls and rises (Oppo and Fairbanks 1989). Thus, if regional and/or global scale climatic cooling had influenced the sea level falls in this basin, it might also be reflected in the carbon isotopic concentration of the studied samples. The carbon isotopic profile records a broad negative excursion covering the peaks of Ba anomaly and culminates at sharp upturn at the K/T boundary, indicating a major environmental perturbation. It may have been the result of prevalent cooler climates prior to the latter part of the end Cretaceous that peaked during latest Maastrichtian followed by warming at the end of the Maastrichtian. Continuance of such warming and resultant sea level rise is also in conformity with the deposition of carbonates during the Danian, as indicated by the lithological succession (Fig. 2), profiles of Ca, C_{org} (Fig. 3) and carbon isotopes (Fig. 4) as could be observed elsewhere (e.g. Veizer 1985; Carpenter and Lohmann 1997; Wallmann 2001). Although it seems that the oxygen isotopic data of these samples may have undergone diagenetic re-equilibration (as they covary with $\delta^{13}C$ curve—cf. Veizer et al. 1997; Carpenter and Lohmann 1997; Stüben et al. 2002b), general cooling and warming trends and an anomaly at the K/T boundary are evident (Fig. 4). Kaminski and Malmgren (1989), Renard et al. (1984), Williams et al. (1983) and Zachos and Arthur (1986) also observed a negative carbon isotope shift far below K/T boundary and suggested that the shift might be a global phenomenon associated with climatic cooling and fall in productivity. These climatic trends were coupled with a global scale glacial periods, the general association of glaciation with high silicate weathering and terrigenous sedimentation (Wallmann 2001; Stüben et al. 2002b, Stüben et al. 2005) which are in accordance with lithological succession of the study area. Furthermore, periods of sea level lowstands promote carbonate weathering and thus stimulate CO_2 sinks, which in the long-term increase atmospheric temperature and sea level, promoting carbonate deposition. At this juncture, it is also inferred that coeval Deccan volcanism might have compensated for the CO_2 sink if not overridden it as weathering of carbonate rocks is influenced by volcanic CO_2 production, exposure of carbonate rocks and weatherability of silicate rocks (Wallmann 2001).

Change in relative bathymetry of depocenter during Maastrichtian in this basin from outer–inner shelf (150–200 m) to shallow marine intertidal regions (less than 25 m) and subsequently total regression as reflected in lithological and faunal composition of the strata, in addition to the presence of higher quantum of C_{org} in rocks of the Kallankurichchi Formation and sudden change to non-accumulation of C_{org}, indicates environmental change that might have influenced and/or aggravated the environmental conditions prevalent. It may also be due to the release of volatile materials from clathrate hydrates of gas, commonly called gas hydrates. These are crystalline solids composed of gas and water that are stable at high pressure, low temperature and high gas concentration, conditions that are met in the upper few hundred meters of sediment on many continental margins and slopes (Kulm et al. 1986; Kastner et al. 1990; Dickens 2001a). In most cases, the dominant gas in the solid phase is methane, produced through the bacterial decomposition of organic matter. Conductive milieu for entrapment of gas hydrates in continental shelf regions prevail during times of sea level highs. Owing to their unstable nature during sea level fall, they release enormous quantities of methane to the sediment-water interface (Tsunogai et al. 1996) or to the atmosphere. Destabilization of gas hydrates during earth's colder intervals (normally coincident with sea level falls) is an important mechanism at the carbon cycle (Kennedy et al. 2001). Recent studies have indicated that oxidation of sapropel materials promote enrichment of Ba in overlying sediments (van Santvoort et al. 1996, 1997; Passier et al. 1998; Dickens 2001a). Kennedy et al. (2001) and Dickens (2001b, c) suggested that destabilization of gas hydrates and release of methane gas into the atmosphere might have been a widespread phenomenon during earth's history and could be traced by negative excursions of $\delta^{13}C$ in sedimentary records. The $\delta^{13}C$ profile of the study area also shows a consistent featureless nature from 75 Ma to 68.7 Ma and a sudden and progressive negative excursion of carbon isotope between 68.7 Ma and 65 Ma, thus adding support to the presumption of emission of methane gas. Owing to the limitations of the data-set utilized in this paper, this assumption is verified through circumstantial evidence only.

The first line of evidence is the climatic factor that may have caused change in depositional conditions resulting in Ba anomalies. It has been established on several criteria that the warm global climate of the Mesozoic started deteriorating in Late Cretaceous time (Saraswati et al. 1993). It is also established that this climatic change was not gradual but occurred in step-like transitions from one climatic state to the other (Berger et al. 1981). Among these reversals of global climatic records, cooling trends tended to be gradual while warming trends were abrupt (Crowley and North 1988; Koch et al. 1992). In this context, sea level high-stand and enhanced accumulation of C_{org}, (as indicated in the sea level curve and C_{org} profile—Fig. 3), prevalence of high productivity and deposition of carbonates (as indicated by rich faunal assemblage of Kallankurichchi Formation) were followed by climatic cooling, sea level fall and change in deposition from carbonates to siliciclastics. These observations together indicate a general cooling trend followed by sea level fall that promoted siliciclastic deposition with Ba anomalies. Lea and Boyle (1990) have recorded high concentration of Ba in sediments from samples of DSDP sites spread all over the world oceans deposited during last glacial maximum. Kasten et al. (1998) have demonstrated that Ba peaks in the equatorial Atlantic ocean sediments coincide with glacial–interglacial transitions. As the oceanic residence time of Ba is very short (in the order of 10,000 years—Chan et al. 1976), any change in its influx and sink would be immediately recorded in the sedimentary record. Thus, the double peaks might have had immediately preceding causes, presumably climatic changes. The change from carbonate deposition to siliciclastic deposition also brought in non-deposition/accumulation of C_{org} as prime producers of C_{org}, were carbonate secreting sedentary organisms that in turn were unable to survive in highly oxic, shallow marine high energy conditions. Thus, the newer set of environmental conditions might have been the cause for reduction in faunal population from Kallankurichchi to Ottakoil Formation. Such climatic cooling and associated reduction in faunal diversity and population was a widespread phenomenon as reported by Adatte et al. (2000; 2002) based on multi-disciplinary analyses of many K/T boundary sites. As the sea level fall has been considered to be consequence of eustasy influenced by climatic reversal, any catastrophic event to be the cause of biotic turnover across the boundary between Kallankurichchi and Ottakoil Formations could also be ruled out.

A second line of evidence is that the sea level fall may have introduced lesser hydrostatic pressure and increased the prevalent temperature at the sediment-water interface, thus introducing the bottom sediments to

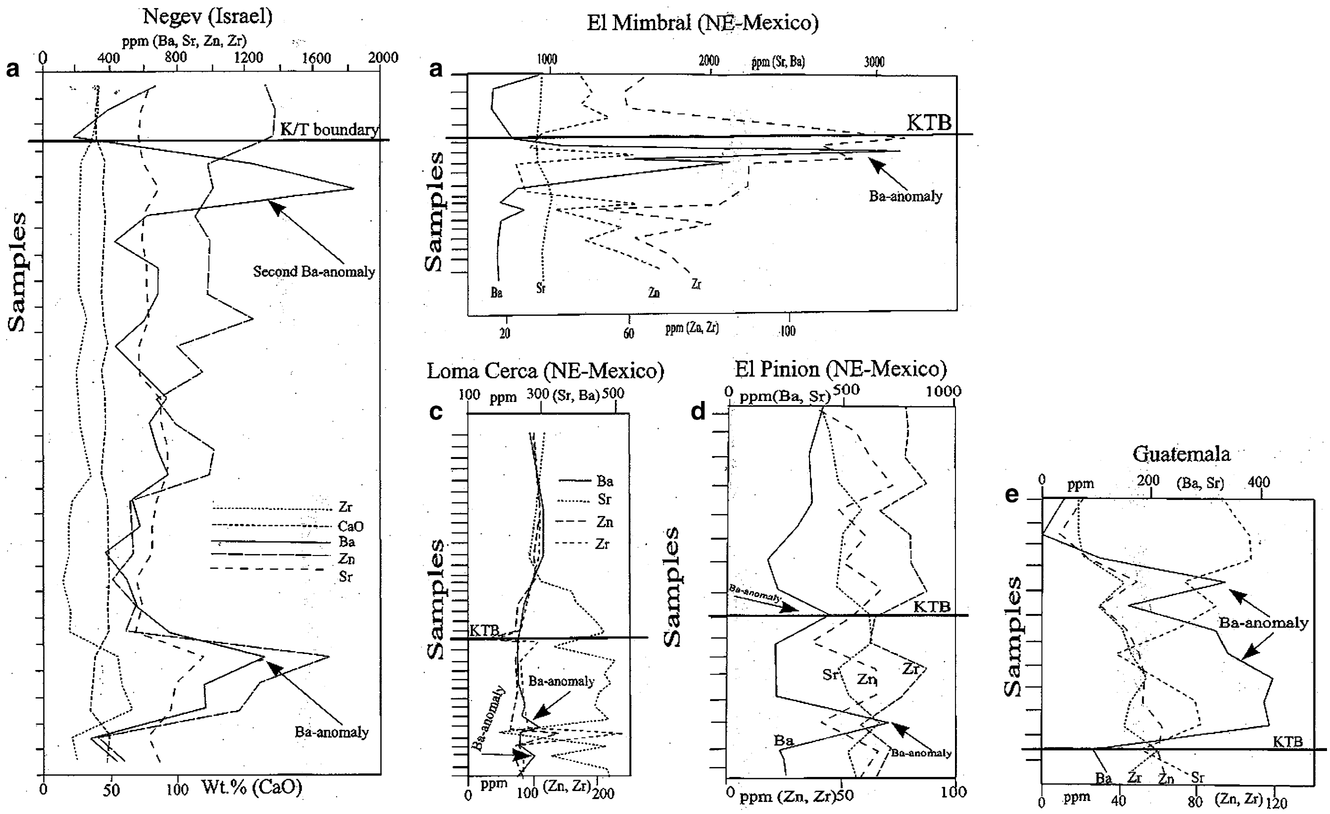


Fig. 5 Elemental profiles of selected Maastrichtian–Danian sections

newer *P*–*T* conditions, conductive for destabilization of gas hydrates (if they were originally accumulated in the former shelf and continental margin regions). Occurrence of viscous, tar-like hydrocarbon residues in fracture planes, micro joints and void spaces (Fig. 6 Photograph 3) of shell cavities and other secondary pores in otherwise dense, well cemented limestone deposits (Fig. 6 Photographs 3 and 4) of the Kallankurichchi Formation was recorded by Ramkumar 2004). Yadagiri and Govindan (2000) examined this hydrocarbon material under flourescense and confirmed the presence of hydrocarbon residues. They found that the residue contains extractable organic carbon of about 7,250 ppm. Analysis of the material under fluorescence confirmed the presence of viscous hydrocarbon residues. They also reported that pyrolysis yields of the residue indicated low maturity ($T_{\max}$ 376°C) and higher Ba values. They concluded that the residues were brought to the subaerial conditions by migration from low in the sedimentary column. Ramkumar (2004), while analyzing the diagenetic features of the Kallankurichchi Formation, noted that, the region in which these hydrocarbon residues occur might have experienced slumping and/or syndepositional instability, owing to which, micro-mesoscale fractures have vented out hydrocarbon materials previously confined within the sedimentary column, releasing volatile contents into the atmosphere, leaving behind the residues.

These observations strongly suggest release of volatile matter from the hydrocarbon (gas hydrates?). While prevalence of volatile hydrocarbons in the rocks of Kallankurichchi Formation is confirmed by the authors cited above, their existence in the form of gas hydrates has not yet been established for want of conclusive evidence. Owing to intense compaction and the resultant fusing of rock components into single crystals, no pseudomorphs of hydrates could be found. However, this does not preclude the possibility of release of volatile hydrocarbons during the end Cretaceous.

In conjunction with the recorded sea level change from highstand to lowstand, the occurrence of a Ba anomaly and global climatic change, supported by lithological change and carbon isotopic excursions lead to the presumption of accumulation of volatile hydrocarbons (gas hydrates?) during the deposition of Kallankurichchi Formation (Kvenvolden 1995; Schmidt et al. 2002). Sea level fall by global climatic reversal and subsequent release of methane gas and associated environmental change could have caused or influenced the Ba anomaly. The sea level fall itself could have been stimulated by Deccan volcanism (Glasby and Kunzendorf 1996). Owing to the cooler climate and falling sea level, no or insignificant continental chemical weathering and persistence of physical weathering would have been introduced, due to which, fresh Ba-orthoclase clasts may have been brought into the ensuing siliciclastic deposits, thereby increasing the background values of Ba concentration, if not influencing the first minor Ba anomaly. However, the relative proportions of influence exerted

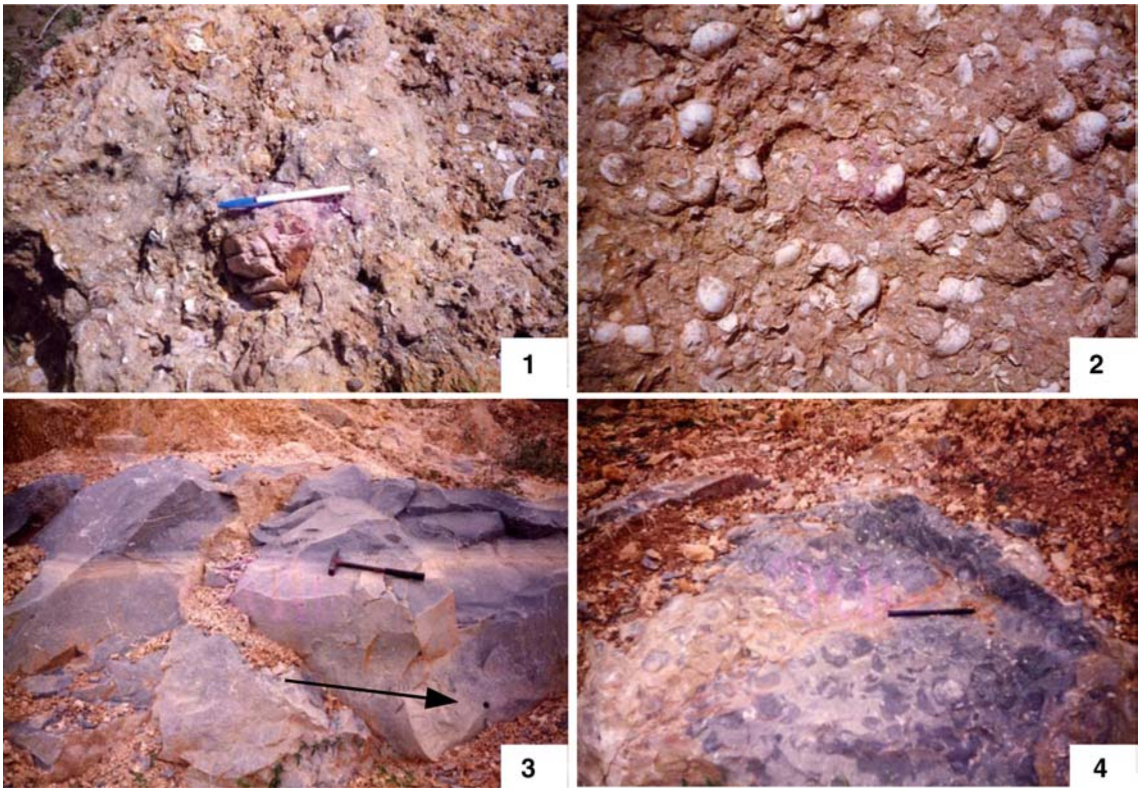


Fig. 6 **1** Fresh Ba-orthoclase clast embedded in the conglomerate beds of Kallar member, Kallankurichchi Formation. Occurrences of such fresh feldspathic clasts do not show any significant Ba anomaly in consecutive geochemical profile and hence influence of Ba-orthoclase over Ba anomaly is ruled out. Furthermore, occurrences of unaltered feldspathic grains signify prevalence of lesser or no chemical weathering in the continental source area. **2** Thick population of the gryphea in the Srinivasapuram limestone member of Kallankurichchi Formation. These grypheans suddenly disappear in the overlying Ottakoil Formation wherein Ba anomaly is reported. Field of photograph covers an area of 2 m x 1.5 m. **3** Dolomitized portion of the limestone beds. Note the hydrocarbon residue in cavity indicated by an arrow. **4** Similar dolomitized shell limestone beds. Compare the photographs 3 and 4 with photograph 2 for the magnitude of alteration

by detrital influx of Ba, climatic reversal, sea level fall and release of volatile materials from hydrocarbon precursors or gas hydrates remain uncertain.

These interpretations pose few implications on the terminal Cretaceous events discussed by the scientific community. According to the decision of the working group on the Cretaceous/Tertiary boundary, the boundary is characterized by the major planktonic foraminiferal extinction event and/or the first appearance datum of Cenozoic species and a major lithologic change, including the presence of a thin red layer at the base of boundary clay marked by various geochemical anomalies (Canudo et al. 1991). This boundary is recognized as marking one of the greatest mass extinctions in earth's history. Mass extinctions of many groups of organisms were accompanied/caused by different abiotic events namely, a large meteorite impact, hot spot volcanism (such as Deccan volcanism), climate warming by 6–10°C, extensive forest fires and sea level regression during latest Maastrichtian (Peryt et al. 1993; Glasby and Kunzendorf 1996). Various workers have presented these competing theories based on evidences drawn from K/T boundary sites. However, there is no consensus as to the nature and geographic extent of these causes. Recent research on the K/T boundary sites, in addition to re-evaluation of previously published data increasingly point to another scenario that of progressive and multi-causal mass extinctions as a result of a combination of environmental and climatic factors during the latest Maastrichtian including rapid climate warming followed by rapid cooling (Keller et al. 2003). This would have led to highly stressful conditions for marine biota vulnerable to environmental changes (Crowley and North 1988; Meyers and Simoneit 1989; Glasby and Kunzendorf 1996; Keller et al. 1998, 2003; Pardo et al. 1999 and references cited therein). Furthermore, many studies have also indicated unequivocally the presence of multiple events predating K/T boundary (e.g. Glasby and Kunzendorf 1996; Keller et al. 1998, 2003; Adatte et al. 2002; Stüben et al. 2002b), supporting the view that the end Cretaceous time was replete with successive occurrences of many events that led gradually to environmental deterioration. Kaiho et al. (1999) also concluded that although significant biotic turnover took place across the K/T boundary, the timing and sequence of key environmental changes caused by catastrophic and non-catastrophic events were not exactly coeval.

The inference of prevalence of multiple, non-catastrophic events is further substantiated by the presence of Ba anomalies in the Maastrichtian–Danian stratigraphic sections of Israel (Fig. 5a), NE-Mexico (Fig. 5b–d) and Guatemala (Fig. 5e). During the Maastrichtian, these sections, which contain siliciclastic and carbonate sediments, were parts of shallow to moderately deep-water shelf-slope regions. They represent an expanded, well-preserved lithological sequence of the terminal Maastrichtian and the K/T boundary, including impact-induced spherule layers as well as Ir-anomalies. Stüben et al. (2002a, b) , Stüben et al. (2005), Keller et al. (2003) and Adatte et al. (2004) have documented detailed biostratigraphic, lithological and geochemical characteristics of these sections. The profiles of NE-Mexico record single or juxtaposed double peaked Ba anomalies preceding the K/T boundary, and the expanded section from Israel records a double peaked Ba anomaly similar to the Cauvery basin section. The Guatemala section also records a Ba anomaly, but during the Danian. The Ba anomalies are not influenced by lithology or any other similar cause. Furthermore, except for the first Ba anomaly in the Israel section, no other coeval trace elemental anomalies could be observed. Together, these observations affirm that, the occurrence of a Ba anomaly is geographically and chronologically widespread, the causes of which may be local or regional. In addition, they also indicate the prevalence of non-catastrophic events, predating the K/T boundary that released Ba into the sedimentary system.

Our data, as enumerated in this paper also recorded a chain of events (not necessarily related to one another) namely, sea level highstand and associated carbon burial → climatic cooling → sea level fall → terrigenous sedimentation, Deccan volcanism, climatic deterioration, destabilization of trapped hydrocarbons or gas hydrates and release of methane gas → Ba anomaly adding yet another event. Although its geographic reach would have been regional, similar regional events may have occurred as the Ba peaks predating the K/T boundary are recorded in other sections located in Israel and NE-Mexico. These may have aggravated the environmental stress already being experienced by the biota (Glasby and Kunzendorf 1996) during the end Cretaceous.

Conclusions

The Ba anomaly in the Cauvery basin was influenced by at least two different causes. The first was detrital influx giving the earliest Ba positive excursion. As the continental source rocks contain Ba-orthoclase, the ensuing sedimentary record shows enhanced background values of Ba. Owing to the absence of chemical weathering in continental regions, enforced by a prevalent cooler climate, the sediments were buried without much chemical alteration. The second cause is presumably related to release of methane gas from unstable hydrocarbons or gas hydrates, generated by prevalent sea level highstand, higher primary productivity bacterial decomposition of organic matter (that in turn would have formed microenvironmental barite—Bishop 1988). Sea level fall, introduced new environmental conditions leading to the venting of trapped gas hydrates, due to which free Ba might have been made available and buried along with the ensuing siliciclastic sediments. Global scale climatic reversals were the causes that triggered the sea level fluctuations that in turn initiated destabilization of hydrocarbons or gas hydrates. The Ba anomalies form part of a major trend of general cooling (as indicated by carbon isotope excursions), sea level fall, subsequent release of methane gas and upsetting of the carbon reservoir equilibrium, followed by increasing paleotemperature may be as the result of a greenhouse effect, triggered by released methane gas. These events were either followed by or in part simultaneous with Deccan volcanism and associated environmental changes. Documentation of the occurrence of Ba anomalies in widely separated Maastrichtian–Danian sections of Tethys located in Israel, NE-Mexico and Guatemala indicates the occurrence of similar events (not necessarily of same type and magnitude) during the end Cretaceous-initial part of Tertiary. It is suggested that the studies that attempt to document end Cretaceous faunal turnover and extinctions should also take into consideration the causes of Ba anomalies.

Acknowledgements MR acknowledges the financial assistance of Alexander von Humboldt Foundation, Germany and Council of Scientific and Industrial Research, New Delhi, India. Special thanks are due to the Institute scientific personnel namely, Dr. Utz Kramar, for major and trace elemental analyses, Dr. E. Karotke and Mrs. B. Oetzel for XRD analyses, Ms. G. Preuss for stable isotopic analyses, Mr. Zrinjscak for carbon and sulphur analyses, Mr. K. Nikoloski for preparation of thin sections for petrographic study and Dr. Ott for computing facilities. Dr. V. Subramanian, Reader, Department of Geology, National College, Tiruchirapalli, India and Dr. Z. Berner, Institute of Mineralogy and Geochemistry, University of Karlsruhe, Germany, are thanked for logistic support. Shri. T. Sreekumar, Department of Geology, National College is thanked for assistance during the field survey.

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