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Anomalous phosphorus episodes during Callovian-Oxfordian times in the Kachchh Basin, western India: Implications for palaeoclimate, productivity, and weathering

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A B S T R A C T

The Upper Callovian-Oxfordian strata of the Kachchh Basin, western India, record three positive excursions of phosphorus. They have been documented in three sections of the Chari Formation from different parts of the basin. Corroboration of field and petrographic data with trends of major and trace elemental data and elemental ratios of the strata revealed that these excursions were coeval with reduced chemical weathering in the source area and significant reduction of siliciclastic influx to the depositional sites. The study also revealed the intrabasinal source of P, and minor sea-level fluctuations and resultant episodic sediment recycling as the causative factors. Considering the geographic locations of the three sections, the phosphorus anomalies seem to be controlled by a regional and/or basin-scale process, if not linked with global signals. Temporal resolution of these anomalies suggests that the processes were episodic and related to short term climate/relative sea-level cycles, the durations of which could be unraveled with high-resolution biostratigraphic data.

1. Introduction

Chemostratigraphy involves the application of elemental and isotopic geochemistry for the characterization of sedimentary successions (Das, 1997). This tool is based on the sedimentary record of changes in certain elements with time. Many studies (e.g., Saraswati and Ramesh, 1992; Pearce et al., 1999; Bekker et al., 2001; Pujol et al., 2006; Ramkumar et al., 2005, 2010a,b, 2011) have utilized this tool for understanding sedimentation events, stratigraphic correlation, fixation of geological boundaries and environmental changes across specific time slices of Earth's history, etc. With the exception of purely bio-produced sediments, marine sediments are largely physical mixtures of a few lithological end-members and these end-members lie within a fairly restricted range of chemical composition (Plank and Langmuir, 1998) that forms the basis of assigning "geochemical signatures" to unique lithological types, sedimentation events, etc. (Ramkumar, 1999). Examination of patterns of stratigraphic variation of sediment geochemistry helps to understand interactions between earth's processes at varying temporal scales. This paper documents anomalous accumulations of phosphorus in Callovian-Oxfordian strata of the Kachchh Basin, western India and discusses the causative factors.

The Jurassic sedimentary strata (Table 1) of the Kachchh Basin (Fig. 1) are known for their rich fauna, ferruginous ooids, condensed sections and hardgrounds (Kulkarni and Borkar, 2000; Singh, 1989; Fürsich and Oschmann, 1993; Fürsich et al., 1991, 1992, 2001, 2004, 2005). Yet, our understanding of the conditions of their origin and of the prevalent climate is not complete. As these deposits are judged to be the result of relative sea level changes (Kulkarni and Borkar, 2000; Fürsich et al., 2001, 2005), have unique depositional features differing from those of the adjacent Jaisalmer Basin (Pandey et al., 2006a,b, 2009, 2010), and have facies characteristics similar to those of Madagascar etc. (Geiger and Schweigert, 2006), understanding their conditions of origin gains further importance. Lack of such information poses constraints on precise correlation of these deposits with coeval strata elsewhere. In the course of an attempt to systematically characterize these strata through an integrated palaeontological, sedimentological, and geochemical analysis, occurrences of positive excursions of P were recognised. This paper documents these anomalies and discusses the conditions of such episodic phosphorus enrichments during the Callovian-Oxfordian time interval in the Kachchh Basin in order to obtain information on palaeoclimate, productivity, and weathering.

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Table 1
Litho- and biostratigraphic framework of the upper Middle and lower Upper Jurassic of Kachchh Mainland (biostratigraphy after Krishna et al. (1996) and Alberti et al. (2011); as well as John H. Callomon, pers. comm (2000).

Lithostratigraphy		Ammonite zones	stages	
Katrol Formation		≥ Divisum	Early	Kimmeridgian
unnamed unit				
Chari Formation	Dhosa Conglomerate Bed	≤ Transversarium	M.	Oxfordian
Chari Formation	Dhosa Oolite mb	Cordatum	Early	Oxfordian
Chari Formation	Dhosa Sandstone mb (west / east)	Mariae	Early	Oxfordian
Chari Formation	Gypsiferous Shale mb	Athleta	Late	Callovian

2. Materials and methods

A systematic field survey was conducted in the mainland part of the Kachchh Basin to log available exposures for lithofacies variation, contact relationships, faunal occurrence and associations, sedimentary structures, etc. and to collect fossil and rock samples. Parts of the Callovian-Kimmeridgian Chari and Katrol formations are exposed on the Kachchh mainland. Good exposures are found in the Jara, Jumara, Keera, Jhura, and Habo domes/areas, located between southeast of Lakhpat and east of Bhuj (Fig. 1). Three well exposed and geographically separated sections, namely Lodai (hereinafter referred as LDS), Fakirwari (FWS) and Jumara (JMS), were selected for detailed study (Fig. 1). LDS is a composite section located northeast of Bhuj in the Habo dome (Fig. 1). The rocks are exposed close to the road 3 km south of Lodai, over a lateral distance of 320 m, showing the occurrences of the Dhosa Sandstone and Dhosa Oolite members of the Chari Formation and part of the Katrol Formation (Fig. 2). The Fakirwari section is located at about 6 km south of Bhuj, along the road to Mundra, exposing the Gypsiferous Shale, Dhosa Sandstone and Dhosa Oolite members of the Chari Formation, and basal part of the Katrol Formation (Fig. 2). The Jumara section is located at about 20 km northeast of Matanomadh close to the Jumara village and exposes Dhosa Oolite member (DOM) and the base of the Katrol Formation (Fig. 2). The basal part of the Katrol Formation differs lithologically from section to section. Typically the beds consist of very coarse sandstones as is the case in LDS. However, the rocks directly overlying the DOM at Fakirwari and Jumara are rather fine-grained and do not resemble typical Katrol Formation. This is the reason they have been included in a yet unnamed unit wedged between DOM below and “true” Katrol Formation above (Fig. 2). A total of 48 rock samples were collected from these three sections and other outcrops (20 from FWS, 17 from LDS and 9 from JMS and 2 from the Jara dome). Fig. 2 shows lithologs of these sections and litho- and biostratigraphic positions of these samples.

These samples were subjected to major and trace elemental analyses following standard laboratory procedures (Kramar, 1997) by XRF and Carbon and Sulphur analyser. Geochemical profiles were constructed and examined for the presence of secular (linear trend) or cyclic trends (polynomial trend) or deviations of absolute concentrations from these trend lines. The observations are corroborated with depositional and diagenetic criteria for understanding the causes involved.

Rock samples from the logged sections were cut in the laboratory and cut surfaces were studied under reflected light macroscopically. Later, large thin-sections (measuring 6 × 10 cm) were prepared from these samples and examined under

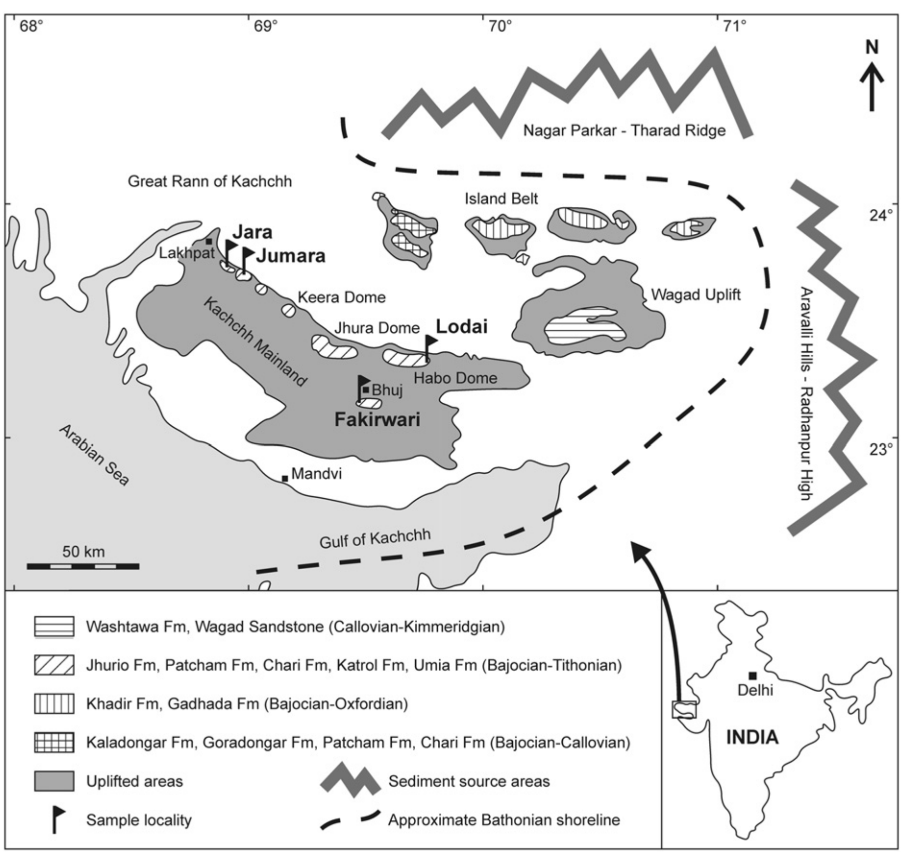

Fig. 1. Location of the study area and studied sections (Fürsich et al., 2004, 2005).

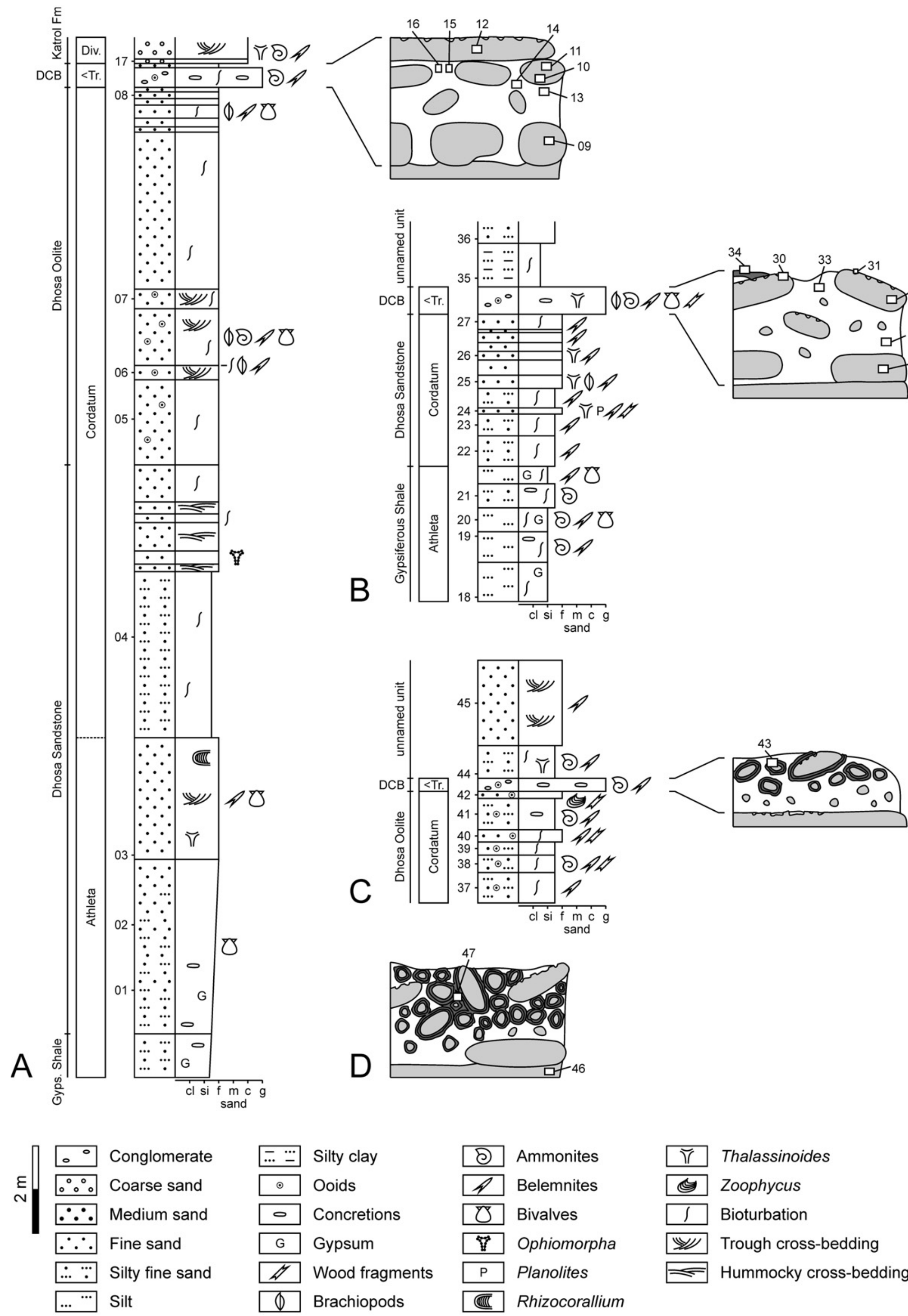

Fig. 2. Lithologs of studied sections and stratigraphic locations of samples. (A) Lodai. (B) Fakirwari. (C) Jumara. (D) Jara (Tr. – Transversarium zone; Div. – Divisum zone).

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polarized light. Data from these observations, along with field criteria and published information, formed the basis of interpretation of depositional and diagenetic environments.

3. Lithology

The top of the oldest stratigraphic unit, the Gypsiferous Shale member is composed of bioclastic calcareous very fine silt with rare intercalations of bioclastic arenaceous packstone and arenaceous peloidal bioclastic packstone. These interlayers are found without any break in sedimentation and resulted from increased influx of bivalve and echinoderm bioclasts. Discontinuous, but bedding-parallel, quartz-rich (<40%) and mud-rich layers also occur. In LDS, this member is represented by very finely laminated, marly/argillaceous very fine silt. The next younger stratigraphic unit, the Dhosa Sandstone member consists of marly/argillaceous coarse silt to fine-grained sandstones and contains varying abundance of bioclasts. The micritic and argillaceous matrix is present only in intergranular porosity and forms about 25% of the rock. The DOM is easily recognizable in the field by its red coloured, well cemented cap rock. Commonly, it is capped by a massive amorphous Fe-rich crust.

In the LDS, the DOM comprises bioclastic wacke-, pack-, floatstones with or without oolites, calcareous siltstones, bioclastic-oolitic siltstones, and stromatolitic oolitic siltstones, distributed almost evenly. Towards top, this member shows a gradual shift from carbonates to arenaceous varieties and finally to oolitic siltstone.

In the FWS, the DOM is predominantly a bioclastic and oolitic wacke-, pack-, and floatstone with varying amounts of quartz silt. Variable siliciclastic admixtures result in arenaceous varieties of these carbonates and bioclastic and oolitic siltstones. Distribution of ooids in these rocks is highly variable resulting in cyclic alternations of bioclastic limestones, arenaceous limestones, and calcareous siltstones in which ooids are abundant, scarce and absent. At top, the bioclastic and oolitic carbonate varieties are capped by stromatolites. Intraclasts of siltstone, packstone, etc. occur commonly in these rocks. The bioclasts and ooids in these intraclasts show features of iron-mineral replacement, probably by siderite, marcasite and ankerite while the bioclasts in the host rock typically show low-magnesian calcitic nature and are texturally mature, indicative of their resedimented nature (Ramkumar et al., submitted for publication).

In JMS, the DOM consists of predominantly oolitic wacke-, packstone, oolitic siltstone and oncoidal oolitic bioclastic wacke-, packstone in order of decreasing abundance. In FWS, the DOM is overlain by the unnamed unit represented by friable, argillaceous/calcareous very fine siltstone. This unit is represented by dusty brown coloured, alternating thin, parallel and even bedded bioclastic and argillaceous siltstones in JMS. Typical Katrol Formation with coarse sand resting directly on the DOM is present only in LDS.

Published information on the lithology, petrography, and faunal characteristics of these rocks along with present observations suggest variable depositional environments ranging from shallow to deep offshore marine regimes. The sedimentary basin was broad and regionally extensive. Deposition principally took place below storm wave-base under low energy conditions, but episodes of high energy spells that reworked the sediments are also recorded (Alberti et al., submitted for publication). Sedimentary features, biostratigraphic evidence, and petrographic characteristics indicate sediment starvation and synsedimentary lithification and phases of shallowing/subaerial exposure. In addition, these features show regional variations across the basin.

4. Phosphorus anomalies

Phosphorus shows three distinct positive excursions (Fig. 3a) in the upper part of the Chari Formation, the magnitudes of which diminish from the oldest to the youngest lithostratigraphic unit, i.e., the Gypsiferous Shale member (first and largest anomaly), Dhosa Sandstone member (second and moderate anomaly), and Dhosa Oolite member (third and smallest anomaly). Regardless of the magnitudes of these excursions, the anomalies significantly differ from background values. These anomalies are typically recorded in the FWS. The LDS, where the Dhosa Sandstone member, Dhosa Oolite member, and the basal Katrol Formation are exposed, shows the development of second and third anomalies. In the JMS, where the DOM and the unnamed unit are exposed, only the third anomaly is recorded. Magnitude and pattern of these anomalies in LDS and JMS are not as typical as in FWS. Absence of distinct secular or cyclic trends in the linear and polynomial trendlines respectively indicates that the observed anomalies are distinct from the background values. Hence, it is considered to be the result of immediate causes for those anomalous excursions.

5. Plausible causes of P anomalies

Phosphorus is an essential ingredient for primary production in the life cycle (Tappan, 1967; Munnecke et al., 2010) and is directly connected with oceanic productivity at a global scale (Ruttenberg, 1993), on time scales longer than several multiples of its residence time in seawater (Froelich, 1988). As primary productivity affects the global carbon cycle, changes in fluxes and reservoirs of P may play a critical role in long-term global climatic and thus, relative sea-level changes. Identifying the cause of P accumulation requires a complete understanding of the tectonics, eustatic and oceanographic setting (Filippelli and Delaney, 1994; Hoppie and Garrison, 2001), and of the sedimentary flux (Sageman et al., 2003) and basin morphology (Dill et al., 1997). The first and second positive P anomalies correspond with significant reduction of Si (Fig. 3b), Al (Fig. 3c), Ti (Fig. 3d), Zr (Fig. 3e), and Ba (Fig. 3f) while the third anomaly corresponds with subdued, but perceptible reduction in detrital elements.

The trends of Ca (Fig. 3g) and Sr (Fig. 3h) generally follow the positive anomalies of P. While the magnitudes of P and Sr excursions seem to diminish from older to younger deposits (Fig. 3a and h), average Ca increases (Fig. 3g). Several recent studies have assumed that weathering and P input to the oceans are similar to the weathering and input of strontium (Raymo, 1994). Comparison of excursions of Sr and P showed that there is a corresponding positive excursion of Sr during the episodes of enrichment of P. However, occurrences of unrelated positive excursions of Sr and a marked decrease in detrital influx during periods of phosphorus enrichment as expressed by negative excursions of typically detrital elements such as Si, Al, Ti, Zr, and Ba negate the possibility of exclusively enhanced terrestrial influx (Raymo et al., 1997) as the cause for positive anomalies of phosphorus. To test the possibility of diagenetic enrichments and also due to the fact that rocks under study are either carbonates and or have calcareous matrix deposited under marine conditions, the Mn/Sr ratio was computed and the profile of this ratio was compared with excursions of P. These excursions do not correlate with the Mn/Sr ratio profile (Fig. 3i) and hence, diagenetic enrichment is not considered. For phosphorus to become mobile, acidic anoxic conditions are required and, it gets re-deposited in the oxic zones together with Fe-oxyhydroxides (Jaffe et al., 2002). Had this been the cause of positive anomalies of P in the rocks under study, Fe should show co-variation. This is not the case (Fig. 3j). Moreover, although Fe shows a general increasing trend from bottom to top, its enrichment is

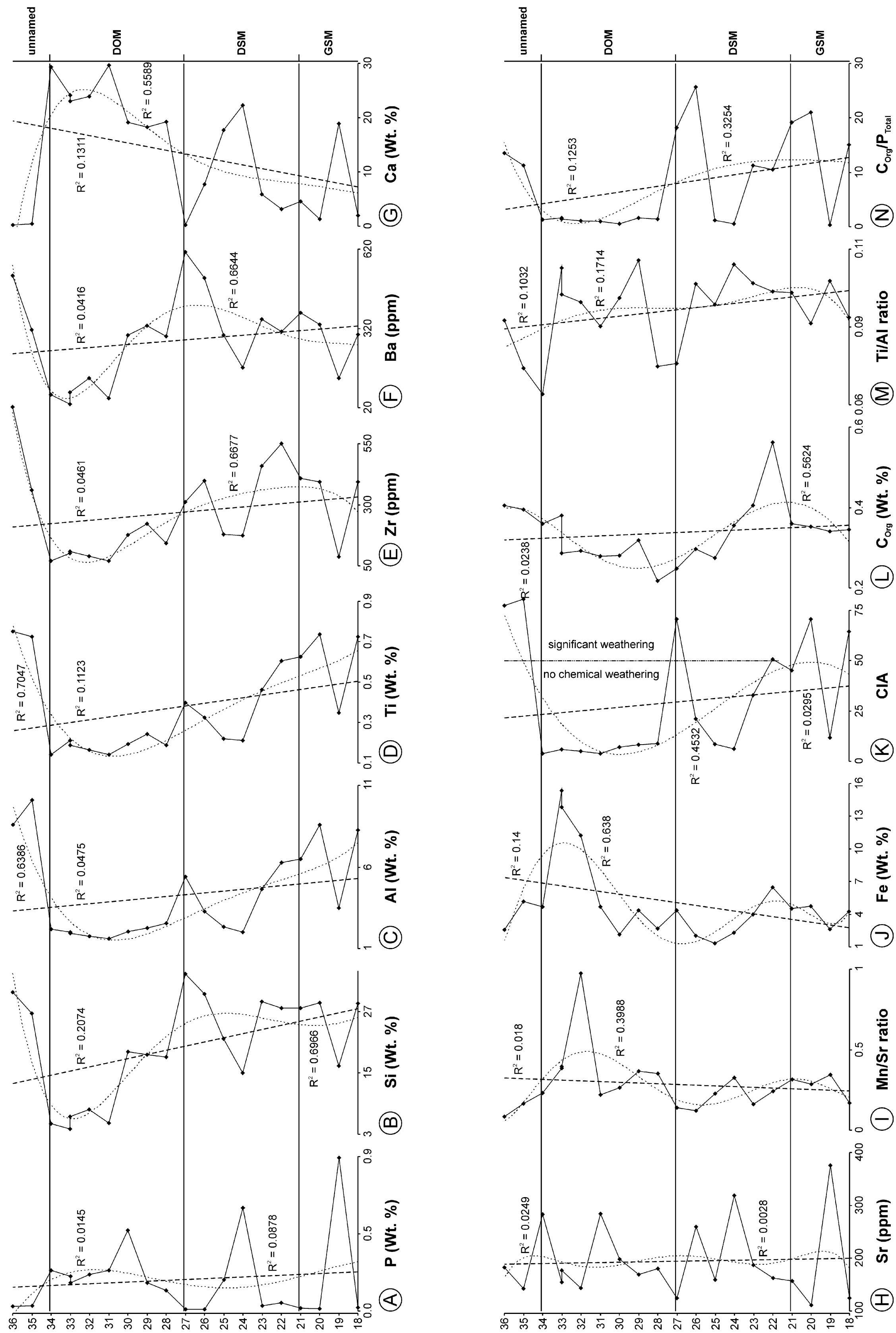

Fig. 3. Geochemical profiles of the Fakirwari section. Straight dashed line shows linear trend; curved dashed line shows the polynomial trend; solid line shows the absolute values. (GSM – Gypsiferous Shale member; DSM – Dhosa Sandstone member; DOM – Dhosa Oolite member). The positive excursions referred in the text are the first (at bottom of the profile), the second (middle of the profile) and the third (top of the profile) anomalies.

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associated with the resedimented bioclasts, ooids and lithoclasts of the "matrix" portion of cap beds of the DOM.

Occurrences of P anomalies in rocks that exhibit significant shell concentrations and either concretions (first anomaly), bioturbation (second anomaly) and/or recycled sediment (third anomaly) may relate them to sea-level changes and low sedimentation rates. The third anomaly that occurs in the DOM precedes the perceived fall in sea-level (Singh, 1989; Alberti et al., submitted for publication) that produced significant reworking of biogenic hardparts, extensive syn-depositional erosion and re-sedimentation, and deposition of the chaotic "matrix" of the Dhosa cap bed, etc. and supports the interpretation of enrichment of phosphorus as a result of sea-level fluctuation (rise or fall). It is interesting to note that the periods of enhanced P accumulation coincide with periods of significant reduction of chemical weathering in the source area as indicated by the corresponding negative anomalies of the Chemical Index of Alteration (CIA – Fig. 3k) that normally result during periods of sea-level rise. Rangel et al. (2000) and Ramkumar et al. (2009) documented the enhanced concentration of phosphorus in sediments deposited immediately after sea-level fluctuation (either rise or fall). Hoppie and Garrison (2001) opined that excursions of P can be directly related to individual eustatic and tectonic events. According to Filippelli and Delaney (1994), fluctuations in sea level cause changes in shelf area which in turn alter the oceanic P mass balance, resulting in re-distribution of P within a sedimentary basin. Periods of sea-level rise/highstand promote enhanced concentrations of P (Hoppie and Garrison, 2001) due to strong coastal upwelling, which in turn normally result in higher primary productivity (Derry et al., 1994). Prevalence of these events could be verified through either strong positive correlation of P with C_{Org} or similar proxies. Absence of any significant correlation with C_{Org} (Fig. 3l), occurrences of very low Ba_{excess} (sectional mean: 0.230; first anomaly: 0.090; second anomaly: 0.147; third anomaly: 0.272) and the very low Mn/Al ratio of the rocks (sectional mean: 0.022; first anomaly: 0.037; second anomaly: 0.052; third anomaly: 0.026) when compared with the Mn/Al ratio of anoxic basins (31.2) or PAAS [Post Archean Australian Shale – Taylor and McLennan, 1985] (8.5) negate the possibility that these positive anomalies are related to sea-level highstands and enhanced primary productivity. It is also inferred that the Mn/Al ratios of the studied samples indicate reduction in oxygen but are not comparable with the highly depleted nature that could be found in anoxic basins.

Hoppie and Garrison (2001) and Spalletti et al. (2001) suggested that phosphorus could become concentrated in oxygen minimum zones in areas of reduced detrital influx. The very low Mn values (129, 103, 51 ppm with reference to first, second, and third P anomalies, respectively) of the rocks in which P anomalies are recorded may indicate oxygen-poor conditions (Sageman et al., 2003). However, redox-sensitive elements such as Cr and V do not indicate corresponding changes in oxygen levels during the positive excursions of P. While the significant reduction of detrital influx shown by negative anomalies of Si, Al, Ti, Zr, and Ba could indicate a likely deficiency in oxygen levels due to sea-level highstand, intense bioturbation of the rocks associated with the phosphorus anomaly and a very low Mn/Al ratio when compared with that of anoxic basin or PAAS do not support the influence of the oxygen minimum zone or anoxic conditions. In contrast, occurrences of negative anomalies of detrital anomalies could indicate restricted circulation and thereby reductions of available oxygen near the sediment–water interface. The Ti/Al ratio, an indicator of siliciclastic influx into depositional sites (Sageman et al., 2003) does show a slight increase at the first and second anomaly of P, but a decrease at the third positive excursion (Fig. 3m). However, throughout the observed section, the change is within a short range, signifying smaller-scale sea-level fluctuations and resultant subdued detrital influx within a larger-scale sea-level cycle and detrital influx. Most importantly, this ratio shows significant negative shift "immediately after" the third positive excursion of phosphorus, implying phosphorus enrichment before sea-level maximum/highstand. Sageman et al. (2003) suggested that an increase in the Ti/Al ratio can be interpreted as the result of basinward movement of the shoreline. In this context, slight changes in sea-level and consequent shoreline shifts towards continental regions "after" the positive anomalies of phosphorus can be inferred. Considering the broad, but comparatively shallow nature of the depositional basin (e.g., Singh, 1989), it is perfectly possible to envisage significant impact on the sedimentation pattern, type of sediment and geochemical composition of sediment by changes in sea-level. Dill et al. (1997), stated that the stagnation model and the productivity model as important while analyzing the enrichment of phosphorous. These models involve transport of phosphorus by coastal upwelling to regions where the water circulation is restricted by submarine swells and local sinks, and controlled by small-scale changes of the sea-level. These observations, together with the non-correlated nature of phosphorus anomalies with maximum flooding, anoxic conditions and detrital elements, suggest redistribution of phosphorus during periods of sea-level fluctuations, possibly during sea-level rise, but not necessarily associated with sea-level highstand and/or sea-level lowstand.

Sageman et al. (2003) advocated sea-level rise as the principal cause of termination of siliciclastic influx and organic matter preservation due to reduction of seasonal or extended periods of ocean water-column mixing and creation of a conducive environment for nutrient re-distribution. Sageman et al. (2003) utilized the ratio of C_{Org}/P_{Total} to understand sea-level fluctuations and resultant redox condition changes based on the surmise that this ratio provides a conservative estimate on remineralization of P and terrestrial organic matter influx to the marine regime. Accordingly, an anti-sympathetic relationship is observed when the trend of the C_{Org}/P_{Total} ratio (Fig. 3n) is compared with the phosphorus excursions. It means that there was no terrestrial organic matter influx, the P excursions preceded periods of enhanced burial of C_{Org}, and by implication, preceded sea-level maximum/highstand. At two instances in the FWS, the value of C_{Org}/P_{Total} is around 25. It is comparable with the reported C_{Org}/P_{Total} value of well preserved grey mudstones (Sageman et al., 2003) that contain unaltered organic carbon and deposited under rapid burial conditions associated with periods of significant siliciclastic influx. By implication, it affirms the interpretation that the periods of enhanced accumulation of P in the study area could have been created during sea-level rise by sediment reworking (an observation that also explains the non-correlated nature of P, Fe, Mn, etc.), but not necessarily associated with maximum flooding/highstand.

It is interesting to note that all these three anomalies occur in bioclastic packstones/arenaceous bioclastic packstones in stratigraphic successions characterized predominantly by rock types dominated by mud matrix, signifying a change in energy conditions during the enhanced P accumulation. This observation, along with the general association of P anomalies with sea-level fluctuations, could strongly indicate a change of depositional energy condition as a result of sea-level fluctuation and resultant re-distribution of P. Sediment re-distribution as a cause of phosphorus accumulation has been suggested by Compton et al. (1993) and reported in the Cauvery Basin (Ramkumar et al., 2009). This inference is also supported by the occurrences of recycled sediments, particularly bioclasts in these rocks. It is further ascertained by the non-correlation of episodes of P with C_{Org} (which suggests a source of P other than primary productivity), but correlation with Ca, Sr, C_{Inorg} and bioclasts (which means, the source of P was purely marine, the influx of terrestrial organic matter was low and the enrichment of organic matter in the sediments was due to recycling).

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The prevalence of sea-level rise during these periods and the absence of chemical weathering in the source area provide insights in the prevailing palaeoclimatological conditions. Sea-level rise and coeval absence of chemical weathering result in deprivation of detrital influx to depositional sites, all of which are recorded by the rocks under study. Such a situation goes hand-in-hand with higher pCO_2 in the atmosphere resulting in a warm climate. Repetitive occurrences of the P anomalies (i.e., in the Gypsiferous Shale member, Dhosa Sandstone member and Dhosa Oolite member) may support a cyclic phenomenon. By implication, these anomalies could be linked with short-term climatic sea-level cycles, which in turn formed part of a major cycle, the duration of which can be defined only with high-resolution biostratigraphic data. Elrick and Scott (2010) demonstrated the influence of high-frequency sea-level cycles of glacio-eustatic origin on geochemical cycles in marine strata. They have also documented that the geochemical signals do not exactly co-vary with the sea-level curve owing to the fact that the change is recorded by the chemical system before the facies is doing so, producing a mismatch. Changes in depositional energy conditions and low rates of sedimentation in the study area may support similar inference for the observed P excursions that preceded the sea-level maximum. The spatial distribution of the studied stratigraphic sections suggests that the phosphorus anomalies have been caused by processes that acted on a regional/basinal scale.

6. Conclusions

Three positive excursions of P in the Callovian-Oxfordian strata of the Kachchh Basin are being recorded in the present study. The excursions show a diminishing trend in magnitude in the stratigraphic order. All these three excursions are typically recorded in the FWS while the LDS shows the occurrence of two excursions, the JMS documents the third and smallest excursion. Analysis of the associated features in terms of fauna, sedimentary structure, and geochemical characteristics had led to the inference that these excursions were influenced by fluctuations in sea-level, which in turn were controlled by variations in palaeo-climatic and weathering cycles. Recurrence of these events across the basin (as indicated by the presence of positive excursions of P in geographically separated locations as well as at various stratigraphic levels) suggests a process of a cyclic nature.

It is also inferred that all the sea-level fluctuations were of relatively small scale superimposed on the larger-scale-sea-level trend. It is surmised that, owing to the large size and comparatively shallow nature of the depositional basin, the sediments and along with phosphorus were redistributed following sea-level changes and concomitant changes in water energy paving way for the anomalous concentrations of P. Taking into account that previous studies recorded global signals in the facies and faunal composition of these rocks (Fürsich and Oschmann, 1993) and that phosphorus is coupled with the global carbon cycles and climate, fixation of time frames for these cycles through high-resolution biostratigraphic data could provide further insights and permit a more precise correlation with coeval strata elsewhere.

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