CHAPTER 7
SULPHUR ISOTOPES AS TRACERS FOR SEA LEVEL VARIABILITY

$\delta^{34}S$

7.1 Sea level changes

Local sea level changes have been addressed by many workers with the help of various coastal geomorphic features (Pant and Juyal, 1993; Rust and Kershaw, 2000), stable isotopic variation (Lamb et al., 2006) and instrumental records (Douglas, 1991; Holgate, 2007). During glacial and interglacial period, sea level changed significantly and based on various studies and observations a global sea level curve has been generated (Kidson, 1982; Pluet and Pirazzoli, 1991; Fleming et al., 1998; Milne et al., 2005; Woodroffe and Horton, 2005; Angulo et al., 2006). However, Holocene didn't experience significant changes in solar insolation and polar ice sheets which resulted in marginal sea level variations. In view of aforementioned observations, it has been suggested that localised sea level curve may be preferred instead of generalised sea level changes generated for other regions (Hashimi et al., 1995).

Gujarat with a longest coastline in India (1600 km) comprises three physiographic features, Kachchh mainland, Gujarat mainland and Saurashtra peninsula. Among them Saurashtra peninsula has archived paleo sea strandlines in the form of inland miliolites (Baskaran et al., 1987) and other coastal features such as intertidal platform, tidal notch (Pant and Juyal, 1993) and relict mudflat (Banerji et al., 2015). The Saurashtra peninsula not only archived the traces of sea level changes but also the tectonic component in the form of preserved tidal notch (Pant and Juyal, 1993). Thus, the estimates of sea level change along the coastal Saurashtra can result from either due to local sea level change or tectonic component or both.

In order to address the tectonic component along the Saurashtra coast, the relict and active mudflats from southern Saurashtra coast were analysed for the stable isotopic analysis. Stable isotope ratios of organic matter can be used as naturally occurring tracers to trace its movement through the natural ecosystems (Jansson and Gearing, 1988). The elements carbon, nitrogen, sulphur and their isotopes are known to be involved with biological synthesis thereby their respective stable isotopic value can potentially characterise source contribution and secondary alterations at times (Peterson and Fry, 1987; Peterson and Howarth, 1987; McCutchan et al., 2003; Richards et al., 2003). Generally, reduced product of metabolism are enriched in light isotopes (Kaplan, 1975). Stable carbon and nitrogen isotopes have been extensively used as proxy to elucidate the source and fate of organic matter in the aquatic system (Peters et al., 1978; Gordon and Goni, 2003). Capability of measuring sulphur concentrations along with its isotopic anomaly ($\delta^{34}S$) certainly aids to better understanding of reaction pathways and source information of S cycle in addition of C and N cycle. However, such studies are still at formative level and need to be further explored. The present study attempts to use the stable sulphur isotope in combination with key geochemical proxies along with carbon and nitrogen isotopes for estimating the sea level change along the southern Saurashtra mudflats during last 5 ka.

7.1.1 Sulphur isotope

The sulphur isotope ratio ($^{34}S/^{32}S$) is indicative of variations during various inorganic and organic processes occurring in the atmosphere, hydrosphere, geosphere and biosphere. The transfer of sulphur among various reservoirs often involves alteration in the oxidation state that is mediated through biotic and abiotic induced processes (Strauss, 1997). Geologically, the precipitation of evaporites from seawater and the biologically mediated reduction of seawater sulphate and subsequent formation of sedimentary pyrite are considered to be the important processes in the sulphur geochemical cycle (Strauss, 1997).

High sulphate in the sea water results in comparatively high concentration of reduced sulphur in the form of pyrite during condition when sedimentary organic carbon concentration are high enough to stimulate the bacterial sulphate reduction (Berner, 1970; Raiswell and Berner, 1985). Due to kinetic fractionation, the sulphide produced by bacterial sulphate reduction is significantly depleted in ^{34}S compared to coexisting sulphate (Harrison and Thode, 1957; Habicht et al., 2002). Evaporites have largest concentration of sulphates and their $\delta^{34}S$ value range between +35 to +5 ‰, while in the case of sedimentary sulphides, it ranges between +40 to -50 ‰ (Thode, 1970). Ambient aerosols over polluted urban environments of USA and coastal marine environment of India (Goa) have been found very close i.e. 5 ± 1 ‰ (Norman et al., 1999; Agnihotri et al., 2015), which is similar to surface soils of north India (R. Agnihotri *personal communication*). Biogenic emissions of coastal marine environments (DMS or DMSP) have been reported to be significantly enriched to ~17.5 ‰. Therefore, the isotopic composition of sedimentary sulphur provides significant information on paleoenvironments and biogeochemical processes (Canfield, 2001).

7.2 Result and Discussion

Though nitrogen, carbon and sulphur isotopes have been extensively used as paleoclimatic proxy, use of sulphur isotopes for ascertaining the climate as well as sea level changes still needs to be addressed. Nitrogen isotopic composition of the marine sediment has been used to reconstruct the paleoproductivity changes (Altabet et al., 2002), while only a few studies have recorded significance of nitrogen isotope as a terrestrial proxy (Lorente et al., 2015). The carbon isotope has gained sufficient attention among the paleoclimate community for interpreting the provenance of organic carbon (terrestrial or aquatic) in a particular region (Meyers, 1994; Meyers, 1997).

Studies carried out along the Saurashtra coast have suggested that changes in the past sea level was induced by sea level change/tectonic changes (Gupta, 1972; Gupta and Amin, 1974; Pant and Juyal, 1993; Juyal et al., 1995). But there exists a paucity of continuous records of sea level changes for the region during mid–late Holocene. In view of this, the present study is an attempt to reconstruct the continuous record of the sea level change during the last 5 ka. Aiming towards achieving this objective, sulphur isotopes along with total sulphur have been used for the first time to ascertain the sea level change in the region supported by nitrogen and carbon isotopes. Three mudflat sediment sections from the Saurashtra region were studied to decipher the paleoclimatic record as well as the sea level changes with the help of stable isotopic variations. Towards this, two sediment cores from the active mudflats of Diu (DV), Rohisa (RH) and a lithosection of relict mudflat from Vasoj (VV) were retrieved from the Saurashtra coast.

7.2.1 The Relict mudflat (Vasoj: VV)

The relict mudflat section of Vasoj (VV) represents archived climatic and sea level history of the last 4710–1500 cal yr BP as discussed in Chapter-3. The lithological, geochemical and palynological studies of this section indicate various stages of climatic conditions along with high sea level during the last 1500–4710 cal yr. The tectonic activity has been interpreted based on the tidal notch located at Diu Island. Based on above analyses, this study indicates nearly 1 m sea level changes with nearly 1 m of tectonic overprinting (Banerji et al., 2015; Chapter-3).

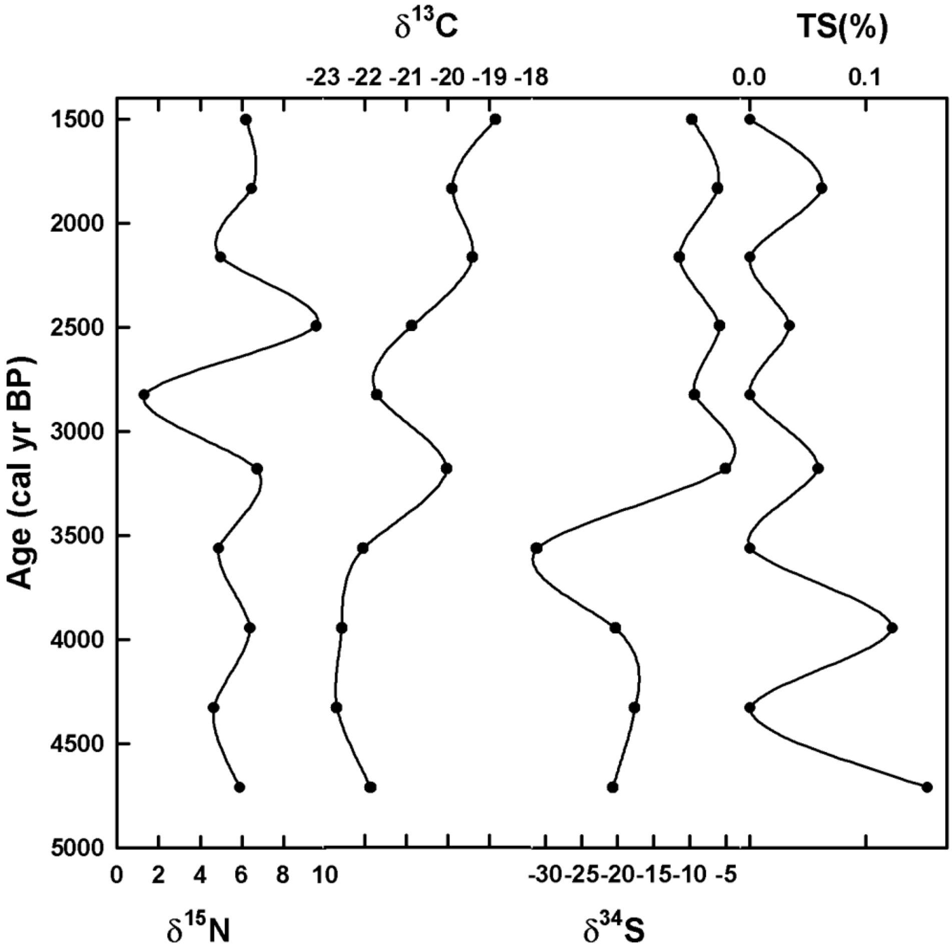

Figure 7-1. Downcore variations of nitrogen, carbon and sulphur isotope and total sulphur concentration for the litho–section of relict mudflat (VV).

The TS, δ^{34}S, δ^{15}N and δ^{13}C for the relict mudflat of Vasoj (VV) varies from 0.03 to 0.15 %, -20.7 to -5.1 ‰, 5.9 to 9.6 ‰ and -22.5 to -19.9 ‰ respectively (Fig. 7–1). The downcore variation of both δ^{34}S and δ^{13}C followed almost similar trend, wherein extremely depleted values are observed from 4710– 3560 cal yr BP followed by marked enrichment in the δ^{34}S after 3535 cal yr BP from -20 to -6 ‰ which fluctuated till 1500 cal yr BP. In the case of δ^{13}C, marginal fluctuation with enriched values has been observed till 1500 cal yr BP. δ^{15}N also followed a similar trend like δ^{13}C, wherein the values mainly varied between 4–8 ‰ with no major fluctuation except for a marked depleted value (1.3 ‰) observed between 3180–2495 cal yr BP.

For TS, high concentration was observed during 4710 cal yr BP with a decreasing trend till 1500 cal yr BP. The redox sensitive elements, enriched Mo/Al_2O_3 and V/Al_2O_3 during 4710–3200 cal yr BP has been observed with reduced values between 3200 and 1500 cal yr BP. For Mn/Al_2O_3, Cr/Al_2O_3 and Co/Al_2O_3 low values between 4710 and 3200 cal yr BP which got enriched during 3200–1500 cal yr BP (Fig. 7–2).

The depleted $\delta^{13}C$ values (-23 to -20 ‰) between 4710 and 2825 cal yr BP indicate increased contribution of terrestrial organic carbon (supported by high detrital tagged elements) as well as presence of mangrove forest as indicated by palynological study. On the basis of the study carried out by Yang et al., 2013, the average values of $\delta^{15}N$ and $\delta^{13}C$ for the mudflat sediment are nearly 6.85 ± 0.61‰ and -23.87 ± 0.58‰ respectively. In the case of relict mudflat of Vasoj (VV), the variations in the $\delta^{15}N$ (5.9–6.7 ‰) values support the presence of mangrove while, abrupt depletion in the $\delta^{15}N$ between 3180 and 2825 cal yr BP points to increased terrestrial contribution (Chapter-3), which is supported by marginal depletion in the $\delta^{13}C$ values. Such enhanced terrestrial contribution during 3180–2825 cal yr BP can be attributed to the intense monsoon in the region, which has also been observed in the active Diu (DV) mudflat (Chapter-4).

Depleted isotopic variations usually results due to biological activity. In the relict mudflat section VV, intense depletion in the $\delta^{34}S$ with high TS concentration during 4710–2825 cal yr BP suggest marine influence which is further supported by the mangrove forest, foraminifer linings and other marine elements discussed in Chapter-3. Reducing condition persisted in the mangrove forest as shown by the enriched values of Mo/ Al_2O_3 and V/Al_2O_3.

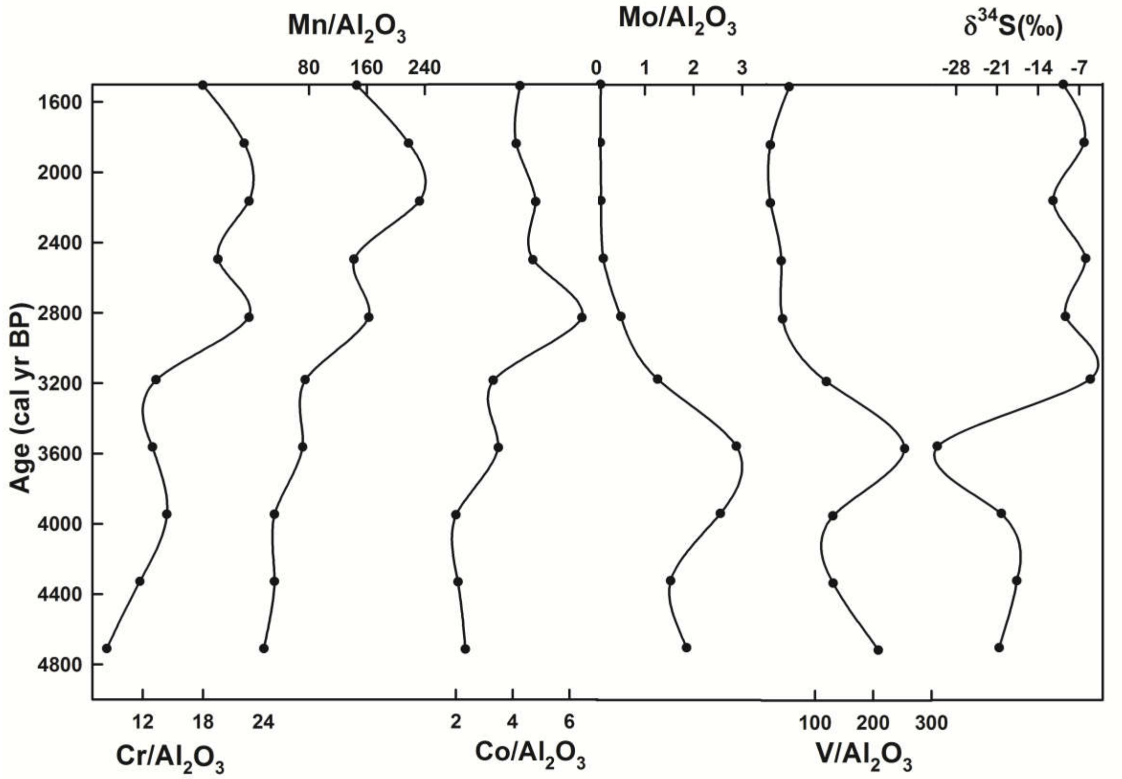

Figure 7-2. Downcore variation of redox sensitive element and $\delta^{34}S$ for the relict mudflat section (VV).

This results in the depleted values of sulphur isotopes due to enhanced productivity during 4710–3945 cal yr BP, and the region was experiencing lagoonal conditions. Reduced TS concentration and enrichment in the $\delta^{34}S$ implies sea regression after 3560 cal yr BP, which transformed the lagoon into mudflat. The top of the Unit-I of the litho section for the relict mudflat (VV) representing the period 3560–3180 cal yr BP (Chapter-3) shows weathered mottled clay with *Turritella sp.* shells at the top representing sea regression. The presence of *Turritella* shells (Banerji et al., 2015) with enriched sulphur values suggest that the lagoonal/estuarine condition transformed into the mudflat due to the sea regression caused by both sea level change / tectonic changes.

High sulphur concentrations (TS) is suggestive of continued marine influence till 1500 cal yr BP, and the low TS concentrations in the surface sediments indicate reduced marine influence. After 1500 cal yr BP marginal regression in sea (due to local sea level change or tectonic component) ceased the sedimentation process in the region and active mudflat was transformed into relict mudflat.

7.2.2 The Active Mudflat of Saurashtra

Based on the approach of isotopic data interpretation of the relict mudflat, the active mudflat has been investigated for its isotopic variation during the past. The sediment core collected from the active mudflat of Diu (DV) is the contemporary record of relict mudflat of Vasoj (VV) that has archived paleoclimatic history of last 4000 yr BP. Another active mudflat investigated in the southern Saurashtra coast is Rohisa (RH) representing a climatic history of last 2000 yr BP.

I. Diu mudflat (DV)

The TS, $\delta^{34}S$, $\delta^{15}N$ and $\delta^{13}C$ contents vary from 0.0–0.4 %, -28.6– 8.53 ‰, -2.58– 7.2 ‰ and -26.4 to -18.3 ‰ respectively (Fig. 7–3). The sediment core raised from the active mudflat of Diu (DV) records a climatic and sea level history of last 4000 yr BP. It can be considered to be of contemporaneous to the relict mudflat as it is situated in the close proximity of ~3.5 km SW of relict mudflat.

Enhanced concentration for the TS has been observed during 4000–3200 cal yr BP followed by negligible concentration till 70 cal yr BP. Similarly, for $\delta^{34}S$, depleted values are recorded between 4000 and 3400 cal yr BP followed by an abrupt enrichment after 3400 cal yr BP till 70 cal yr BP. $\delta^{15}N$, along with marginal fluctuation show consistently enriched values during 4000–2355 cal yr BP followed by an abrupt depletion. The latter fluctuated marginally till 70 cal yr BP. The redox sensitive elements viz. Co/Al_2O_3, Mn/Al_2O_3 and Cr/Al_2O_3 show enriched values during 4000–3400 cal yr BP following which reduction with marginal fluctuation has been discerned till 70 cal yr BP. The $\delta^{13}C$ for the entire core show fluctuating values with mixed marine and terrestrial signatures.

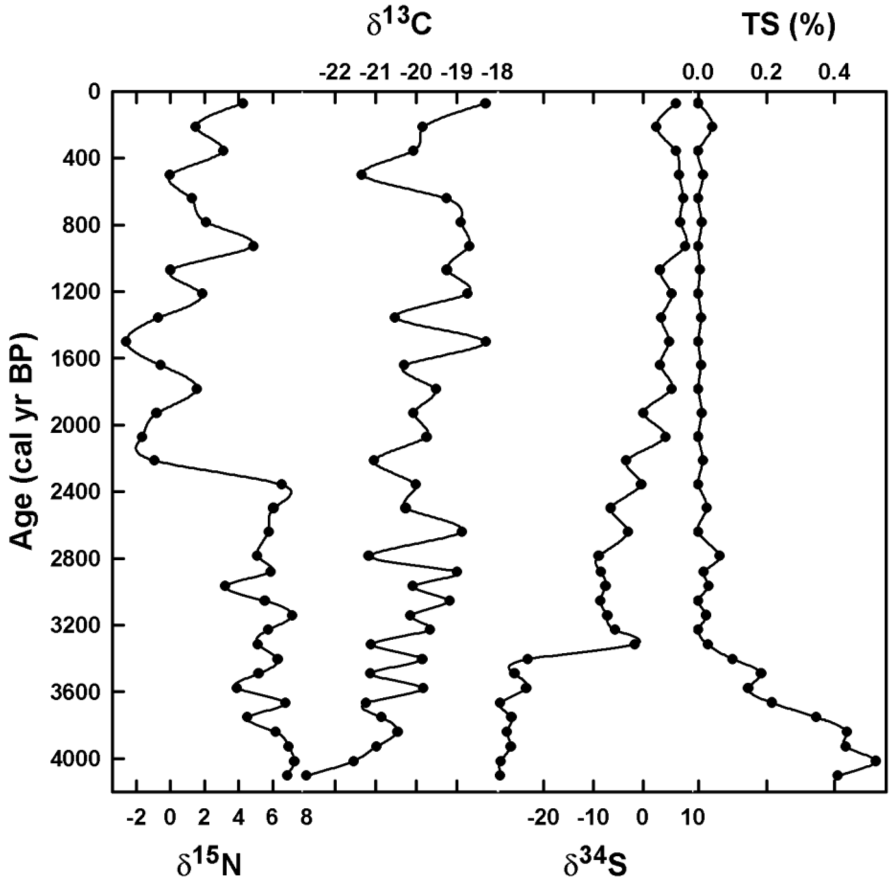

Figure 7-3. Downcore variations of nitrogen, carbon, sulphur isotope and total sulphur concentration for the sediment core of active mudflat (DV). Note, sudden shift of $\delta^{34}S$ after 3400 cal yr BP supported reduced TS.

The depleted values of $\delta^{34}S$ along with high TS during 4000 and 3400 cal yr BP indicate persistence of reducing conditions which is also supported by enhanced values of Co/Al_2O_3, Mn/Al_2O_3 and Cr/Al_2O_3 (Fig 7–4). During this period, the relict mudflat section (VV) indicates persistence of estuarine condition in the region with marginally high sea level suggested by presence of mangrove pollens and foraminiferal linings (Chapter-3).

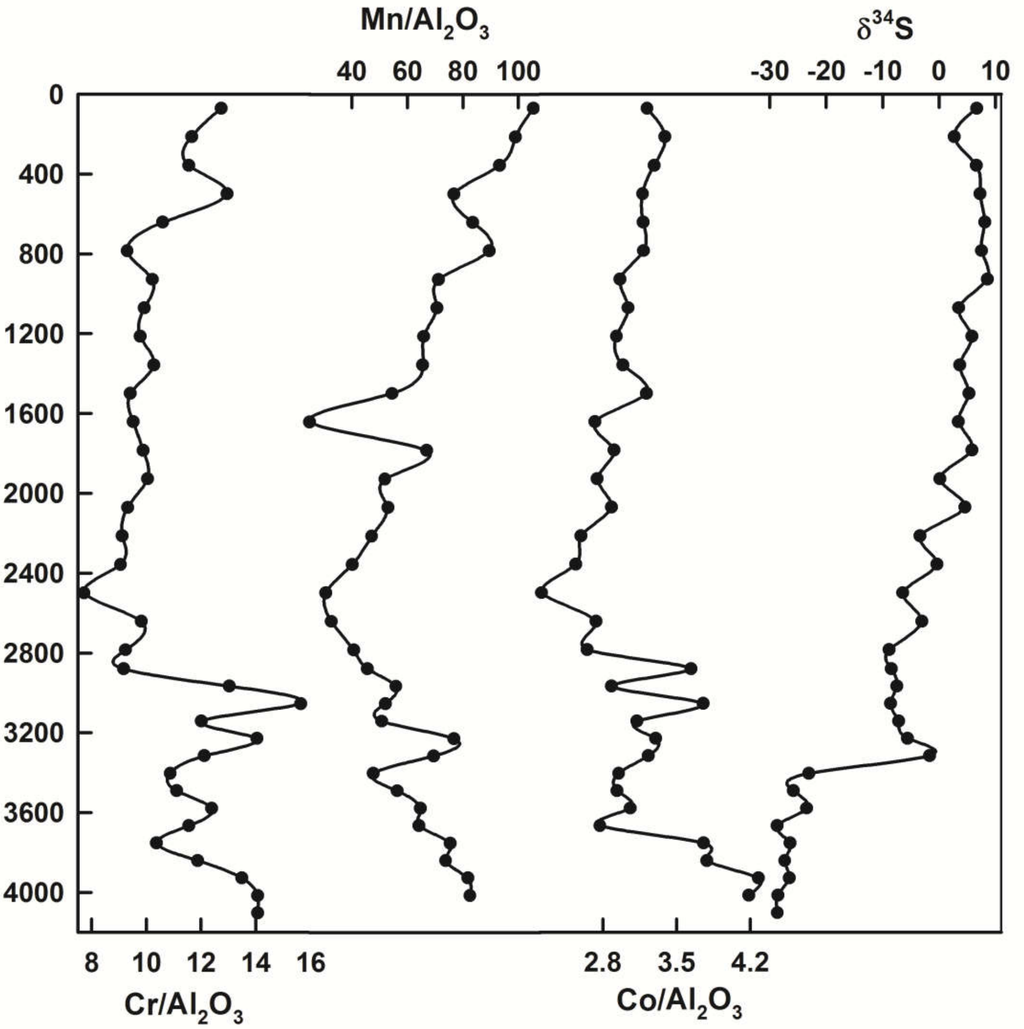

Figure 7-4. Downcore variation of redox sensitive elements for the sediment core Diu (DV). Note, sudden shift in the $\delta^{34}S$ in Unit-I supported by enhanced values for the redox sensitive elements.

Thus, depleted sulphur isotopic composition with increased TS suggests that the region was experiencing estuarine/lagoonal conditions with marginally high sea level. An abrupt increase in the sulphur isotope during 3400–3315 cal yr BP has been noted, while in relict mudflat (VV), such shift was seen between 3560 and 3180 cal yr BP.

This shift in the sulphur isotopic value for the relict mudflat was interpreted as marginal sea regression supported by the presence of *Turritella* sp. shell and mangrove pollen.

The shift in the $\delta^{34}S$ from depleted to enriched values within a period is common in active (DV) and relict mudflat (VV) implying sea regression. Thus, during 3404–3180 cal yr BP, the lagoonal/estuarine condition was transformed into active mudflat due to marginal sea regression caused by local sea level change/tectonic alteration.

II. Rohisa Mudflat (RH)

The sediment core raised from the active mudflat of the Rohisa (RH) records a climatic history of last 2000 yr BP. The TS, $\delta^{34}S$, $\delta^{15}N$ and $\delta^{13}C$ contents vary from 0.028–1.00 %, -25.13 to 8.40 ‰, 2.9– 15.62 ‰ and -21.35 to -18.44 ‰ respectively (Fig 7–5).

Enhanced concentration of TS has been noticed between 2000–1400 cal yr BP followed by very low values of TS till present. In the case of $\delta^{34}S$, depleted values during 2000–1500 cal yr BP followed by an abrupt enrichment after 1430 cal yr BP till present has been observed. The redox sensitive elements viz. Co/Al_2O_3, Mn/Al_2O_3, V/Al_2O_3 and Cr/Al_2O_3 (Fig 7–6) are enriched during the period between 2000–1500 cal yr BP followed by negligible fluctuation during 1500 cal yr BP–2012 AD. The $\delta^{13}C$ and $\delta^{15}N$ follow a similar pattern indicating a fluctuating trend during last 2000 yr BP.

Depleted values for $\delta^{15}N$ has been noticed during 1970–1550 cal yr BP followed by an abrupt enrichment which remained nearly consistent ranging between 10–15 ‰ excepting three major shifts between 1275–1120 cal yr BP, 890–735 cal yr BP and after 200 cal yr BP. The values of $\delta^{13}C$, though followed a similar trend of

$\delta^{15}N$, remain within mixed terrestrial and marine values. Only the major fluctuation has been observed between 1970 and 1750 cal yr BP. The depleted values in the sulphur isotope along with high sulphur concentration during 1970–1500 cal yr BP indicate reducing conditions. This is supported by the enhanced concentration of redox sensitive elements caused by high productivity. Such high productivity also resulted into depleted $\delta^{34}S$.

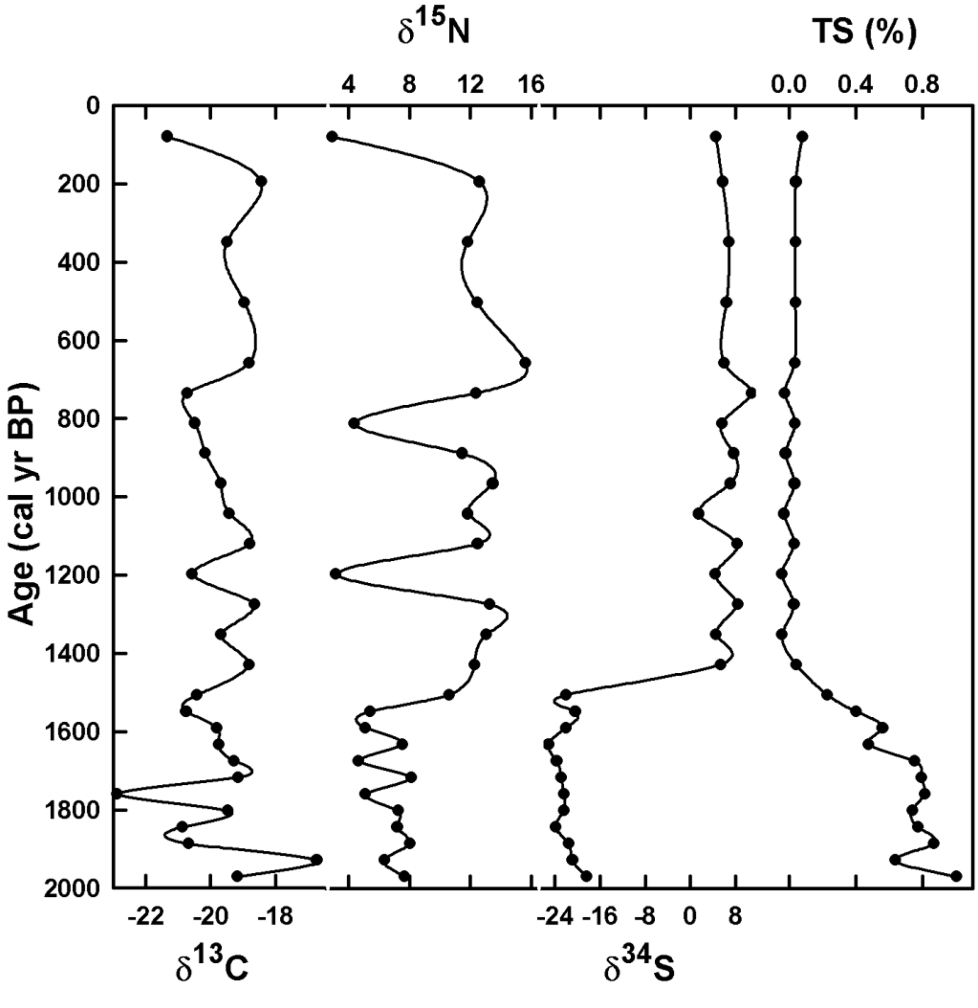

Figure 7-5. Downcore variations of nitrogen, carbon, sulphur isotope and total sulphur concentration for the sediment core of active mudflat (RH). Note, sudden shift of $\delta^{34}S$ after 1500 cal yr BP supported by gradual shift in TS.

High concentration of TS suggestive of presence of sea water in the region, indicates marginal high sea level experiencing lagoonal/ estuarine conditions between

1970 and 1500 cal yr BP. The abrupt enrichment in the $\delta^{34}S$ after 1500 cal yr BP with low TS values has been observed. This low TS can be attributed to the sea water ingression only during high tides and the enriched $\delta^{34}S$ resulted due to reduced productivity.

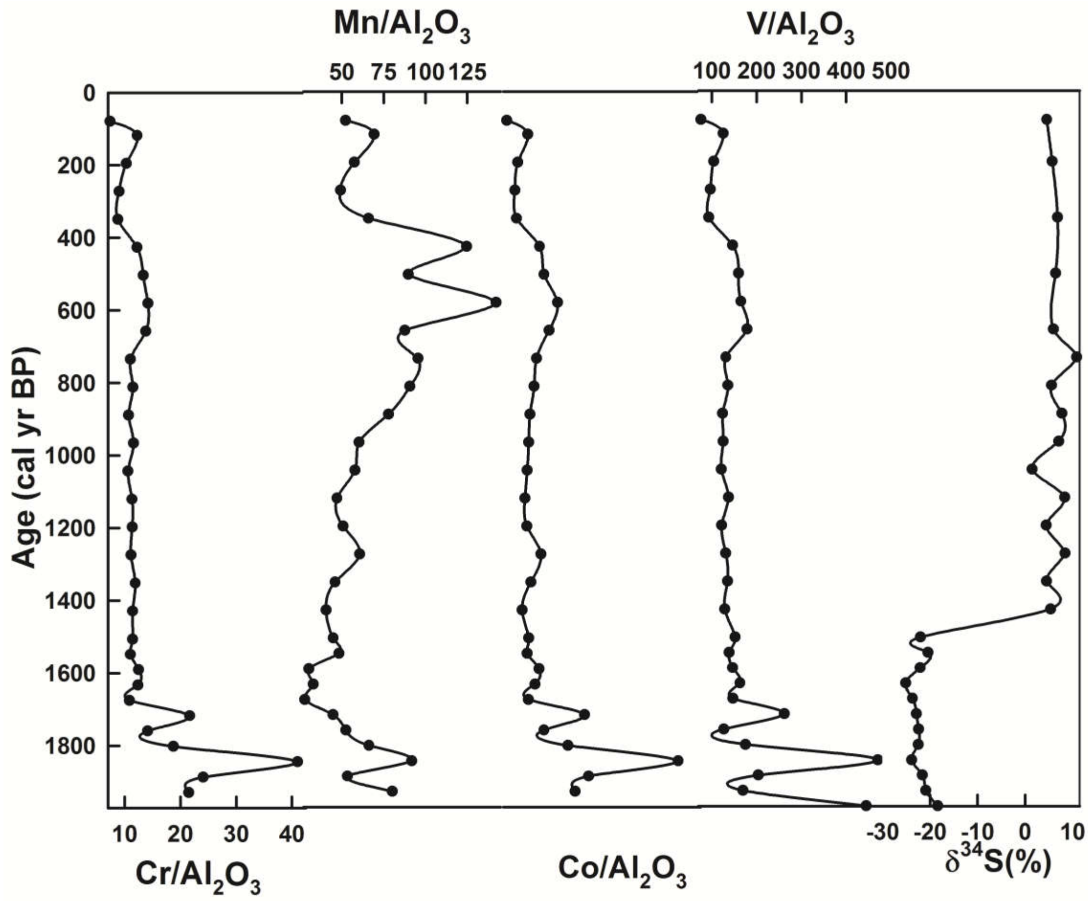

Figure 7-6. Downcore variations of redox sensitive elements for the sediment core of active mudflat (RH).

Evidences thus tend to indicate that the lagoonal conditions were transformed into mudflat region. The depleted values for $\delta^{13}C$ and $\delta^{14}N$ during 1970–1550 cal yr BP indicate enhanced terrestrial influence resulted due to intense monsoonal activity as well as enhanced productivity (discussed in Chapter-5).

7.3 Comparison between $\delta^{34}S$ and TS for the active and relict mudflats

In all the three sections (VV, DV and RH) are depleted in $\delta^{34}S$ with enhanced TS and redox sensitive elements during initial phase of the sediment deposition, followed by enriched $\delta^{34}S$ low values of TS and redox sensitive elements. Abrupt shift from extremely depleted $\delta^{34}S$ to enriched values supported by changes in the redox sensitive elements implies change in redox conditions from high productivity to extremely reduced productivity.

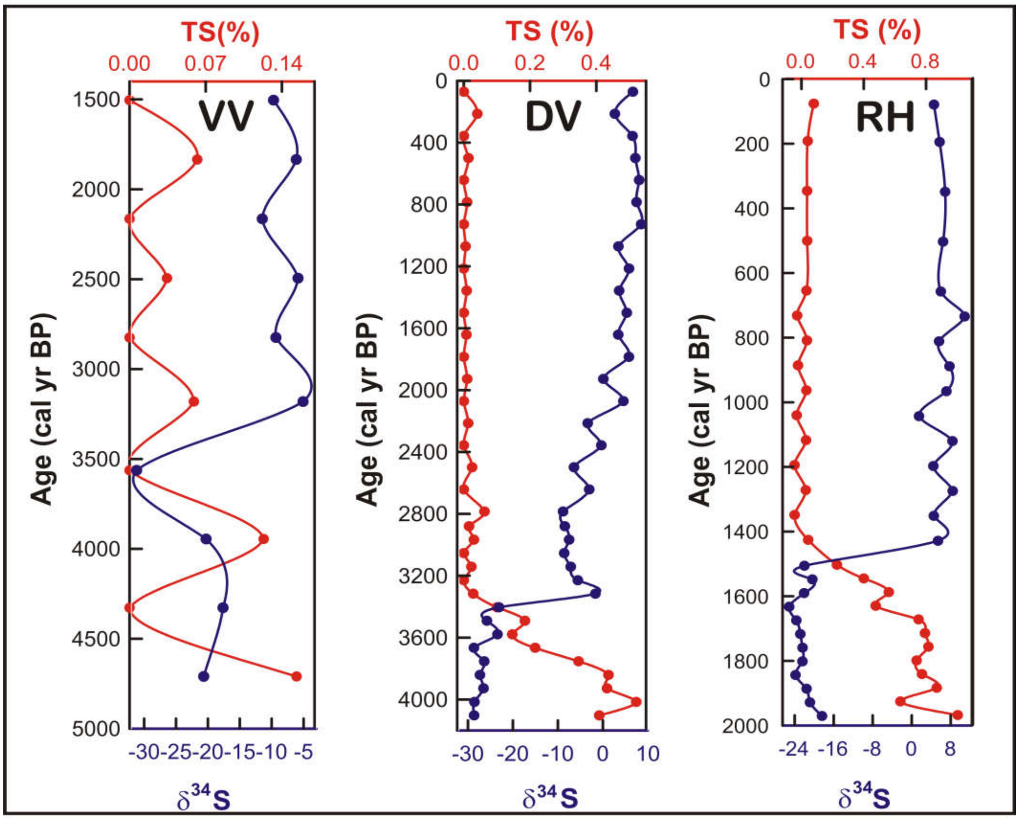

Figure 7-7. Comparison of Total sulphur (TS) and $\delta^{34}S$ variation for relict (VV) and partially active (DV) and active mudflat (RH) of Vasoj village, Diu and Rohisa respectively.

Extreme reduced TS concentration implies decrease in the sulphate deposition. These portray regressive phase of the sea and is corroborated by the presence of

Turritella shells and reduced mangrove pollen in the case of relict mudflat section (VV).

Generally, lagoon and estuaries are more productive compared to mudflats therefore, enhanced redox sensitive elements, TS and extremely depleted sulphur isotope shows persistence of lagoon/ estuarine conditions which transformed into mudflats with the sea level lowering. Both relict mudflat (VV) (Fig.7–7) and its contemporary active mudflat (DV) indicated abrupt shift in the δ^{34}S around ~3200 cal yr BP. The relict mudflat has shown that there were both sea level and tectonic components of ~1 m each during last 5 ka (Chapter-3). Based on the sulphur isotope, it can be suggested that mudflats (VV and DV) were initially experiencing a lagoonal condition which later transformed into mudflat after 3200 cal yr BP. Such abrupt change in the sulphur isotope (DV: -23 to -1.6 ‰ and VV: -30.5 to -5.1 ‰) is unlikely to be caused solely by sea level change, and thus there is another component which playing a significant role. This may be attributed to tectonic component that uplifted the region and transformed it into mudflat after 3200 cal yr BP. Radiocarbon dating of calm shells from southern Saurashtra coast testify elevated sea levels of nearly 2 m which was followed by regression masked by tectonic component (Juyal et al., 1995). The active mudflat of Rohisa (RH) representing depositional history of last 2000 yr BP indicate change in the sea level after 1600 yr BP as shown by the enriched δ^{34}S and reduced TS.

The abrupt shift (-22 to +5.4 ‰) of δ^{34}S for the RH core within a short span of 100 yr (1500–1400 cal yr BP) is not likely to be induced by local sea level change alone, and a tectonic component must have played a momentous role in transforming the estuarine/lagoonal environment to mudflat region. A paleoenvironmental study carried out at lower Mahi basin suggested a high sea level during 3500–1700 yr BP along with the tectonic component that resulted into sea level lowering (Kusumgar et al., 1998).

It is interesting to note that the sulphur isotopic variation for the Southern Saurashtra mudflats show the $\delta^{34}S$ values for the mudflat ranges between -8 to +10‰ while for estuarine/lagoonal conditions it ranges between -30 and -8 ‰ (Fig 7–8).

7.4 $\delta^{34}S$ as an indicator of sea level change caused by tectonics along South Saurashtra Coast

Stable isotopes have been efficaciously used as a potential tool for paleoclimatic reconstruction. Both carbon and nitrogen isotopes have been extensively used in various studies but application of sulphur isotopes has remained limited for climatic reconstruction. The present study attempts to utilise sulphur isotopes for the first time in ascertaining the sea level changes in the Saurashtra region. Based on $\delta^{34}S$ for the active and relict mudflat of Diu Island, it has been suggested that the region experienced a tectonic upliftment after ~3500 yr BP leading to the transformation of lagoon to mudflat region (Fig 7–5). The Rohisa active mudflat experienced this transformation after 1600 yr BP (Fig 7–5).

The sedimentation in the relict mudflat of Diu ceased after 1600 yr which could also be attributed to the tectonic upliftment. However, the partially active mudflat of Diu (DV) being situated near the coast didn't get considerably affected by the tectonic uplift after 1600 yr BP as during this period the region was already transformed into mudflat from lagoon therefore a negligible shift in the $\delta^{34}S$ values are observed. Based on these observations it may be inferred that there happened to be two phases of tectonic upliftment i.e. ~3500 yr BP and ~1500 yr BP during last 5 ka that might have developed the present configuration of the southern Saurashtra coast.

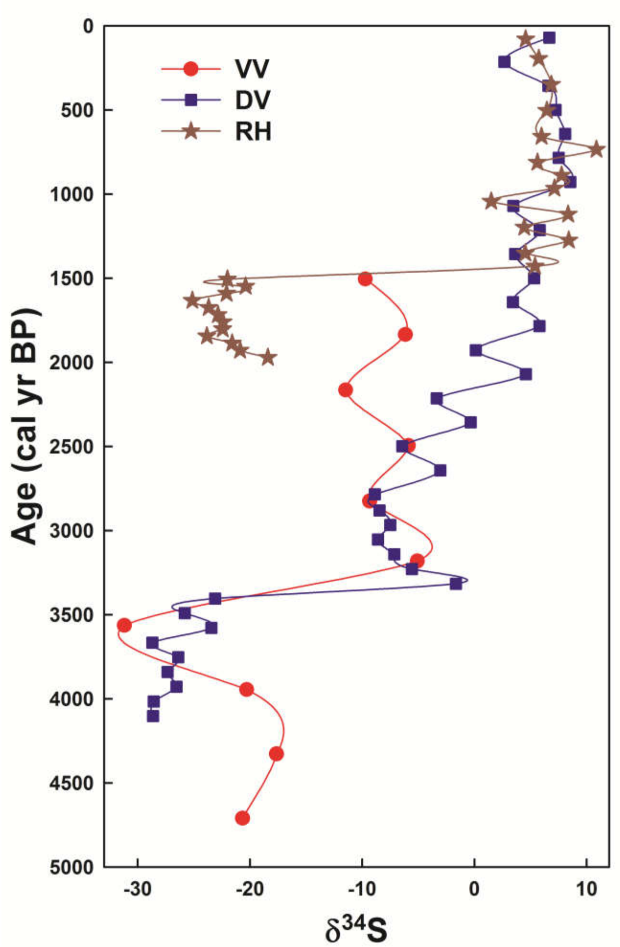

Figure 7-8. Variation in sulphur isotope along southern Saurashtra coast during last 5 ka assertained from active and relict mudflat.

The application of sulphur isotope in studies related to sea level changes is still in a preliminary stage, and the present work for the first time demonstrates that sulphur isotopes can be used as a potential tracer in the studies of land-sea interaction, sea level changes and tectonics. Further geomorphic features along with sulphur isotopes of other mudflat along the Saurashtra coast need are awaited to understand the tectonic as well as local sea level changes in the region.