# Abstract

This thesis presents a systematic geochemical study of the Western Continental Margin of India and the Sambhar salt lake in Rajasthan. The first study (Part-A) is aimed at understanding the biogeochemical processes occurring in the margin sediments and their role as a sink or source for trace elements to the open ocean. Part-B focusses on the evolution of chemical and isotopic composition of the Sambhar lake during the annual wetting and drying cycles and attempts to place contraints on the source of salt to the lake basin.

## Part–A: Geochemical study of sediments from the Western Continental Margin of India (WCMI)

Six sediment cores of about 20–25 cm length have been analyzed for selected U-Th series radionuclides ($^{238,234}$U, $^{232,230}$Th, $^{226}$Ra and $^{210}$Pb) and major and trace elements. These sediment cores are from the upper slope (water depth $\sim$ 300 m) and lower slope (water depth $\sim$ 2500 m) regions which transect through the sub-oxic and oxic environmental conditions across the WCMI. The objective of this study is to understand the spatial and temporal variations (on a century time scale) of $CaCO_3$, organic matter (OM), particle reactive ($^{210}$Pb, $^{232,230}$Th) and redox sensisitive (U, Mn and Fe) elements.

The chronology of the sediments has been determined based on the $^{210}Pb_{excess}$ method which provides a good handle to describe the temporal variations in the deposition of lithogenic and biogenic components of the sediment. The sediment accumulation rates range from 0.25–1.83 mm/y which corresponds to a time span of about 100–800 years BP for the core lengths. In one of the cores, the depth profile of $^{137}$Cs concentration is also measured which yields a sediment accumulation rate consistent with that derived from the $^{210}Pb_{excess}$ method. The contents of $CaCO_3$ and OM are relatively higher in the upper slope region. $CaCO_3$, though biogenic in nature, its abundance in most of the cores is dominated by relict calcareous materials as evidenced by "older" $^{14}$C ages in both surface and deeper sections. Such an observation limits the use of $CaCO_3$ in the cores to obtain information on the temporal changes in the water column productivity. The relatively high abundance of organic matter in upper slope sediments results from a combination of high biological productivity and high sedimentation rate. A uniform distribution of $CaCO_3$ over the length of core sampled in upper slope region indicates that

environmental conditions have remained unchanged during the time span represented by the core length. However, in the lower slope sediments, $CaCO_3$ increases by as much as 60% in the deeper sections indicating its relatively higher deposition in the past which may be due to increased contribution of the relict calcareous materials.

The $^{210}Pb$ inventory shows a positive correlation with the rate of sediment accumulation. This implies that $^{210}Pb$ (and other similar particle reactive nuclides) gets focussed and deposited in regions of high sediment accumulation. For this reason, the depositional flux of $^{210}Pb_{excess}$ shows spatial variation along the WCMI sediments with values in some cores considerably in excess to that expected from atmospheric fallout and water column production.

The Mn concentration (on a $CaCO_3$ free basis) and the Mn/Al ratio in upper slope sediments (averaged over entire core length) is low by a factor of about three compared to that transported by Narbada/Tapti river suspended particles ($\sim$ 1000 ppm). This has been interpreted in terms of its mobilization in reducing conditions. The amount of manganese mobilized from the upper slope sediments from an area bounded by the four cores analyzed is about $\sim 5.0 \times 10^{10}$ g/y, nearly same order of magnitude as the supply of dissolved Mn by world rivers to the ocean. In contrast, some of the upper slope sediments show uranium enrichment by a factor of five compared to open ocean sediments. These sediment cores are characterized by the $^{234}U/^{238}U$ activity ratio typical of seawater, suggesting that the dominant source of U to these sediments is seawater. The removal flux of uranium suggests that nearly 3% of its dissolved supply by the world rivers is sequestered in the WCMI region. Furthermore, the depth profiles of Mn concentration and U/Th ratio in these sediments do not show any significant variations indicating that the redox conditions prevailing over the region have not changed during the last few centuries. Thus, it can be concluded that the upper slope sediments of WCMI act as a "sink" for oceanic uranium and "source" for dissolved manganese to seawater.

The distribution of Mn in the lower slope sediments shows definite structure with high concentration near the sediment-water interface. This high concentration could result from (i) the diagenesis occurring in sedimentary column which mobilizes the Mn from the bottom sections to the surface where it is reprecipitated, (ii) transport of soluble Mn from the upper slope region. The profile of U/Th weight ratio in the lower slope sediments shows a continuous increase with depth indicating U removal deeper in the sediments from seawater due to reducing/sub-oxic conditions prevailing in the sub-surface layer.

The metal/Al ratios in WCMI sediments have been found to be in the same range as that reported in the Narbada/Tapti river particles. Also, there is no significant increase in Cu/Al, Zn/Al, Pb/Al and Ni/Al ratios at the core tops relative to the bottom sections. These results reflect metal abundances in margin sediments to be dominated by fluvial sources and there is no significant anthropogenic inputs of these elements during the last century.

## Part–B: Geochemical and isotopic study of the Sambhar lake, Rajasthan (India)

The oxygen isotopic composition, major ions and selected U-Th series radionuclides ($^{238,234}U$, $^{226,228}Ra$, $^{210}Po$ and $^{210}Pb$) have been studied in various reservoirs of the Sambhar lake viz. groundwaters, river waters, lake brines and sub-surface brines to characterize them in terms of their chemical and isotopic composition. In addition, attempt has been made to identify the source water composition of the brine, possible source of salt to the lake basin and mixing of water bodies in the region.

The oxygen isotopic composition ($\delta^{18}O$) of lake and river waters during monsoon and the groundwaters in most of the seasons is in the range of meteoric precipitation ($-6.4$ to $-3.2$ $^o/_{oo}$) indicating that oxygen isotopic composition of these reservoirs is dominated by atmospheric precipitation. A good correlation between $\delta^{18}O$ and salt content (TDS) in groundwaters from the region collected during monsoon and winter seasons reflects a two component mixing between low TDS, low $\delta^{18}O$ and high TDS, high $\delta^{18}O$ endmembers. The lowest $\delta^{18}O$ ($-5.5$ $^o/_{oo}$) observed in the lake during July 92 indicates that the lake is recharged by atmospheric precipitation and surface run-off. The effect of recharge is also seen in the $\delta^{18}O$ content in some of the sub-surface brines which decreases from $\sim$+5 $^o/_{oo}$ to $-1$ $^o/_{oo}$ in some of the wells immediately after the monsoon, caused by recharge either from atmospheric precipitation or from the lake waters during the monsoon season. The $\delta^{18}O$ of the lake water increases from $\sim -5^o/_{oo}$ immediately after the monsoon to $\sim+21^o/_{oo}$ during summer and remains steady at this value. The isotopic evolution trend in the lake is broadly of Rayleigh fractionation type, however, the saturation in $\delta^{18}O$ during the late stage of evaporation is explained by the Craig-Gordon model which suggests isotopic exchange by back condensation of isotopically depleted atmospheric water vapour. The $\delta^{18}O$ data in the lake and sub-surface brines differ significantly during most of the seasons. The $\delta^{18}O$ in lake saturates at a mean value of 21 $^{o}/_{oo}$ beyond TDS of 100 g/l during annual evaporation cycle. Sub-surface brines, on the other hand, show a linear trend between $\delta^{18}O$ and TDS, the $\delta^{18}O$ increases from $-1$ to about 7 $^{o}/_{oo}$ for TDS in the range of 39 to 270 g/l suggesting a two component mixing.

The chemical composition of groundwaters adjacent to the lake, lake waters and sub-surface brines is of Na-Cl type. The dominance of NaCl in these water reservoirs indicates general presence of halite in the drainage basin. All the groundwaters, river waters, lake waters and sub-surface brines are saturated with respect to calcite and dolomite minerals but undersaturated with respect to gypsum. The precipitation of minerals such as calcite and dolomite in the lake basin favours an alkaline path of brine evolution. The evolution of the Sambhar lake brine has been modelled based on the Hardie-Eugster model by evaporating various initial endmembers. The evaporation of lake water collected during October, immediately following the monsoon, yields brine similar in composition to that observed. The evaporation of river water, though yields an alkaline brine similar to the lake brine, it differs from the lake brine in terms of Na/Cl, Na/Alk and $Cl/SO_4$ ratios. The Na/Cl ratio in the lake brine is generally lower but the $Cl/SO_4$ ratio is higher than that produced from river water evaporation. The low Na/Cl and high $Cl/SO_4$ ratios in the lake brine are attributed to recycling of salts from the salt-encrustation during the recharge period. Similar calculation using typical groundwater from the region as the initial endmember shows that their evaporation cannot yield the alkaline brine similar to the lake. This suggests that groundwater alone cannot account for the type of brine available in the lake.

The results on abundances of uranium ($^{238,234}U$), radium ($^{226,228}Ra$), $^{210}Po$ and $^{210}Pb$ radionuclides in various hydrologic systems of the Sambhar lake are such that these water reservoirs can be distinctly characterized. The concentration of U vs. salt content and reciprocal of U vs. $^{234}U/^{238}U$ activity ratio in groundwaters show linear trends suggesting a two component of mixing. This observation is consistent with the $\delta^{18}O-TDS$ relationship. In lake waters, U behaves generally conservative upto a stage before halite cystallization and thereafter the concentration rises sharply in the residual brine due its evaporative enrichment and preferential retention in the aqueous phase. Compared to groundwaters and river waters, the U/TDS ratio in the lake water is low during most of the seasons. Such an observation indicates that the uranium input from surface run-off is diluted by the salt present in the lake bed. The amount of recycling of salt from the lake bed during the recharge period based on the result of U/TDS ratio in river and lake water is calculated to be 95% of the total salt which is also consistent with an estimate from the Na/Cl ratio.

The NaCl content of rain water from the location is about 2 mg/l. An upper limit on estimate of NaCl depositing over whole catchment area of the lake based on the measured NaCl content in rain water is calculated to be ~5000 tons which is less than $\leq 3\%$ of the current salt production from the lake basin. The inventory of salt in the Sambhar lake after monsoon (Oct 92) is about $10^6$ tons. The annual supply of salt via rains is $<1\%$ of the inventory. These estimates, therefore, suggest that rains are not a major source of salt to the lake at present. An estimate of the input of salt to the lake basin from river and groundwaters collected during recharge period (based on the geometric mean of Cl concentration and assuming 50% of water in lake derived from them) is about 6% of the salt inventory in the lake. These estimates, therefore, suggest that rains and surface/sub-surface run-off are not major source of salt to the lake in present day condition. Another hypothesis of the source of salt to this area is via aeolian transport of marine aerosol particles from the Gulf of Kutch. The study of uranium and its isotopic ratio places some constraints on the importance of the source of salt to the basin. As mentioned earlier, uranium shows a strong positive correlation with TDS and has a uniform $^{234}U/^{238}U$ ratio $1.65\pm0.03$ during the annual evaporation cycle. If there is significant contribution of marine aerosols with associated uranium then the U/TDS and the $^{234}U/^{238}U$ activity ratio are expected to decrease since seawater is characterized by U/TDS and uranium activity ratios ~0.1 $\mu$g/g and $1.14\pm0.02$ respectively. As this is not observed, importance of aeolian transport of marine aerosol particles as a source of salt to the lake appears to be negligible.

A very low Ra/TDS ratio (lower by two to three orders of magnitudes) in the brines compared to the groundwaters and river waters suggests that Ra isotopes have been removed from these waters. Such an observation consistent with low concentrations of Ca and Mg ions in the lake brines. The radium isotopes also show saturation in their activities during evaporation in salinity range of 100–370 g/l. These results, therefore, suggest that Ra isotopes have been removed during early stages of evaporation by co-precipitation with Ca-Mg minerals and in the later stages the concentration saturates because of equilibration with the clay minerals. The distribution of $^{210}$Po and $^{210}$Pb nuclides in various water reservoirs has indicated their difference in particle reactivity. The groundwaters show $^{210}$Po/$^{210}$Pb activity ratio far less than unity indicating preferential removal of $^{210}$Po onto particulates. However, in lake and pan waters, the $^{210}$Po/$^{210}$Pb activity ratio is greater than one which is rarely observed in natural waters. This has been explained by the preferential complexation of $^{210}$Po relative to $^{210}$Pb by the algal material present in these waters. On the other hand, the $^{210}$Po/$^{210}$Pb activity ratio is nearly one in most of the sub-surface brines suggesting that particle reactivity of both the nuclides in these waters is identical.

The chemical and isotopic composition of the Sambhar lake and its source waters analyzed in this study, as stated above, place constraints on the source of salt to the lake basin. The present annual amount of salt contributed by surface/sub-surface inflow waters and atmospheric precipitation is 1–2 orders of magnitude lower than the inventory of salt in the lake. Also, contribution of salt from atmospheric transport of marine aerosol particles does not seem to be a significant source to the lake. The important processes occurring currently in the lake are recycling of the salt from the lake bed during recharge period followed by evaporation and precipitation of Ca-Mg minerals which result an alkaline Na–Cl type of brine.