

ON THE IMPORTANCE OF STUDYING PARTICULATE MATTER IN THE OCEANS*

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OCEANS represent an aqueous solution of a very complex and ancient history. The recycling of the ocean water between the atmosphere and the continents over periods of the order of 100-200 m. y. is accompanied by a variety of physical and chemical processes, both on the land and within the oceans. It is no wonder, therefore that the ocean water as well as the marine deposits have become the focus of study for scientists of various disciplines, chemists, physicists, etc. Particularly in the last two decades, as our knowledge of marine phenomena increased, scientists in other disciplines quickly joined in. In the discussions today, I would like to consider particular aspects of investigations in the marine environments which highlight this interaction between oceanographers and scientists of other fields.

It has been recognised for long time that the spatial and depth distribution of trace elements in different oceans and even within a given ocean is very variable, inspite of the ancient age of the oceans. Practically the concentrations of none of the trace elements, in the dissolved and particulate form are uniform vertically and laterally. The *distribution*, which is usually most variable in the case of elements present in trace concentrations, does in fact quite often represent a steady state condition. What brings about variations in the trace element concentrations within short distances (or depths) of the order of metres or kilometres? The processes responsible for this are a variety of physical, chemical and biological reactions occurring within the sea. Only in recent years, with the advent of nuclear techniques, one has begun to understand these processes as well as their rates. Below, we consider few illustratory examples in which natural radionuclides, belonging to the uranium and thorium decay series as well as those produced by cosmic radiation, artificial radionuclides introduced by nuclear weapon's testing and those accreted from the interplanetary space by the earth for studying these processes. The application of radionuclides as tracers in marine environments has become popular in recent years and the amount of interesting work in this field is indeed large. I will therefore concentrate only on a few aspects relating to the suspended particulate matter in the oceans - extraterrestrial, terrestrial and biogenic. Even here I will largely confine to work in which members of the Geophysics Research Group of the Tata Institute of Fundamental Research have been involved.

At first we will very briefly consider the interaction of solids with sea water; which is important at all depths within the oceans. The important reactions in which these solids take part are adsorption, leaching, and dissolution. These reactions which continuously alter the trace element concentrations in the oceans vary with time and space and hence the trace element concentrations are often not in a steady state. Even if we neglect the seasonal variations, the resulting distributions of trace elements because of these processes is highly variable, both laterally and vertically.

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In Fig. 1 we show, a highly simplified picture of the important processes as well as some of the trace elements and radionuclides involved, in them.

As examples, let me discuss in some detail two important cases of physico-chemical reactions caused by the marine suspended matter. Activity of the short-lived Th^{234} (half-life = 24 days) was found to be in marked radioactive disequilibrium with respect to the concentration of its parent, U^{238} in the top hundred metres of sea water column (Bhat *et al.*, 1969). Observations of Th^{234} activities in surface waters have indicated that thorium is chemically very active and is quickly adsorbed on to suspended materials. Even in the open ocean sufficient amount of particulate matter exists so that often the Th^{234} activity is very low in surface waters. At depths of about 100 metres, excess Th^{234} activities above secular equilibrium are

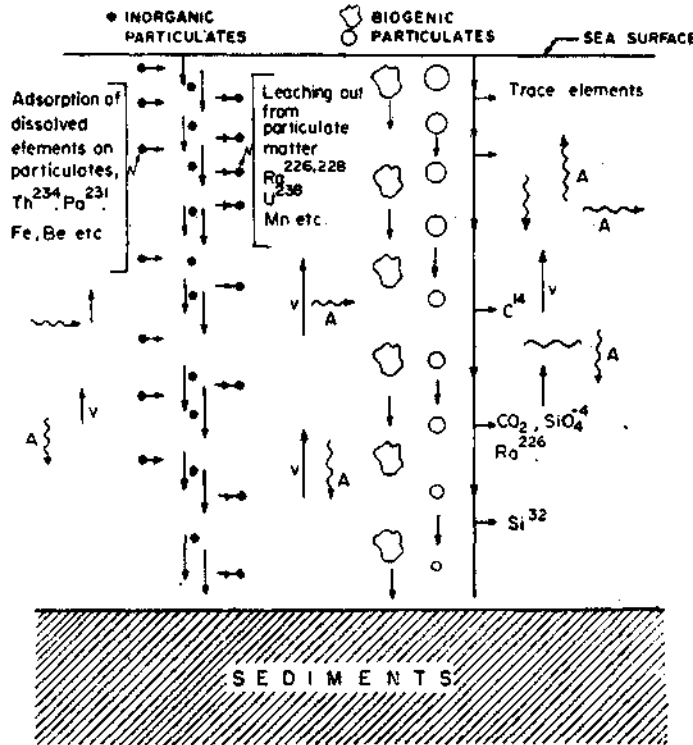


Fig. 1. "Over simplified picture of the chemical processes associated with "inorganic" and "biogenic" particulate matter in sea water. Depending on their chemical reactivity, elements get adsorbed or leached out from the inorganic particulates transiting through the sea water column. R. H. S. of the diagram depicts the role of biogenic materials in transporting radioactive and stable elements from surface to deep ocean.

found. Fig. 2 shows some of the observed $\text{Th}^{234}/\text{U}^{238}$ profiles in sea waters. As shown by Bhat *et al.* (1969), it seems that these results can only be understood by invoking particulate settling of both inorganic and organic materials onto which Th^{234} has been adsorbed. The latter is invoked to explain the super-secular equilibrium values. The theoretically calculated $\text{Th}^{234}/\text{U}^{238}$ activity ratios for

the case of a pure particulate settling is shown in Fig. 3. The measurements so far on Th^{234} are consistent with a mean settling velocity of the order of $(1-2) \times 10^{-3}$ cm/sec (Bhat *et al.*, 1969). It should be added here that similar studies on depth variation in the concentration of Be^7 and other chemically active elements where radioactive isotopes (man-made) exist should prove very valuable for delineating the role of particulates in regulating the concentrations of these active elements.

It would be expected that radioisotopes of chemically active elements, such as Be^7 , Fe^{56} will show a very different depth distribution compared to, say, Cs^{137} where only a small amount is expected to be removed by particulate settling. The effective velocity for downward mixing in the mixed layer, due to eddy diffusion $= A/Z = 5/10^4 = 5 \times 10^{-4}$ cm/sec is smaller than the mean particulate settling velocity of $1-2 \times 10^{-3}$ cm/sec deduced on the basis of Th^{234} . (A = eddy diffusion constant $= 5 \text{ cm}^2 \text{ sec}^{-1}$ and Z = thickness of the mixed layer, taken to be 100 m).

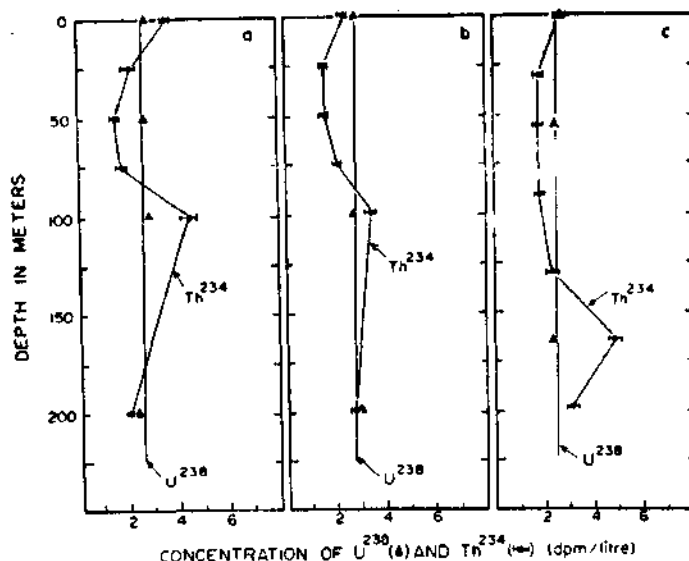


Fig. 2. Measured Th^{234} and U^{238} concentrations in three profile samples; curves a, b and c refer to stations $13^\circ 04' \text{ N}$, $65^\circ 28' \text{ E}$ (Arabian Sea); $18^\circ 42' \text{ N}$, $65^\circ 12' \text{ E}$ (Arabian Sea) $13^\circ 4.8' \text{ S}$, $114^\circ 4.7' \text{ E}$ (Wharton Sea) respectively. Note the marked deficiency of Th^{234} in the 25-100 m depth regions and an excess immediately below this depth. (after Bhat *et al.*, 1969).

As another example, I would like to quote here the recent observations of man-made C^{14} for both inorganic and organic phases which could be separated from the sea water, up to depths of 3000-4000 metres (Somayajulu *et al.*, 1969; Williams *et al.*, 1970). This observation clearly reflects sinking of biogenic calcareous skeletal material and with it the associated organic remains of the organisms of recent origin in surface waters where C^{14} levels are considerably high because of exchange with the atmosphere (for relevant data, see Somayajulu *et al.*, 1969). It is quite clear that, similar to the cases of C^{14} , the depth distribution of a host of

stable and radioactive isotopes is controlled by the particulate sinking (Fig. 1). It would be very instructive to examine the concentrations of Ra²²⁶, Th²³², manganese, etc. in these particulate materials.

Finally, let me discuss a few aspects of the particulate matter of extraterrestrial origin.

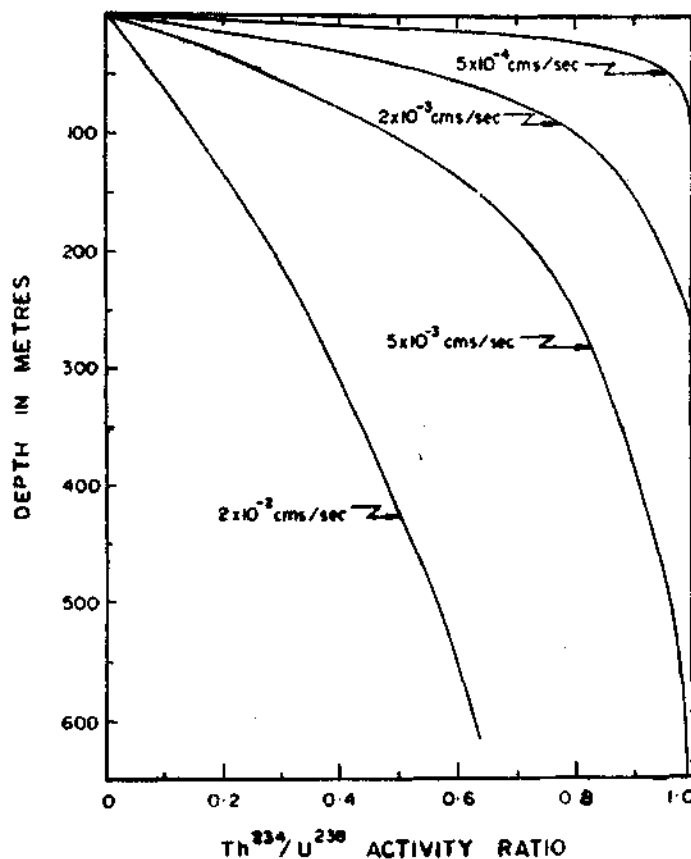
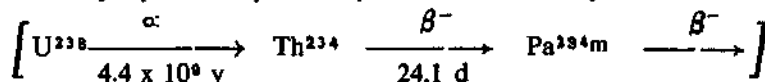


Fig. 3. Theoretically expected disequilibrium profiles for Th²³⁴ activity



in the surface layers of sea water for the case of their removal by adsorption on particulate matter settling with velocities 5×10^{-4} , 2×10^{-3} , 5×10^{-3} and 2×10^{-2} cms/sec corresponding to particles of radii 1.2, 2.4, 3.8 and 7.7 microns respectively (density of 2.6 gms/cc); after Bhat *et al.*, 1969.

The sediments contain mainly clays, about 70-80 per cent depending on the location (Griffin and Goldberg, 1966). The sediments are largely made up of terrestrial matter (river-borne and eolian) and authigenic deposits like manganese nodules and submarine volcanic products. Of course, one also expects a non-

appreciable part to be contributed by extraterrestrial accreted materials but it is difficult to calculate this contribution, particularly since our knowledge of the influx rates of cosmic dust and larger extraterrestrial particles is very uncertain at present. In view of the fact that deep sea sediments accumulate slowly, their usefulness towards a study of extraterrestrial components and time variations in their accretion rates, has been realised for quite some time (Murray and Renard, 1891). Since then several attempts have been made to quantitatively ascertain the contributions due to cosmic dust and meteoroids/ meteorites by studying nickel and noble metals (Au, Ir, or Pd) concentrations in deep sea sediments (Barker and Anders, 1968; Venkatavardan, 1969) as well as the frequency of occurrence of spherules due to ablation of meteorites. A special situation arises in the case of cosmic dust alone where one expects it to be fairly enriched in certain radioactive elements, in comparison to meteorites, due to interaction of low energy cosmic ray particles in space (Lal, 1962). Theoretical estimates of Wasson (1963) and Lal and Venkatavardan (1967) show the feasibility of characterising cosmic materials by the radioactive nuclides, Al^{26} , Mn^{53} and Ni^{60} which are either not produced on the earth or in only small quantities; these nuclides therefore serve as "signatures" of cosmic dust. Positive results have been reported in the case of Al^{26} by Lal and Venkatavardan (1966) and this result seems to have been confirmed by the work of Wasson *et al.* (1967). However, the subsequent work of Tanaka *et al.* (1968) in a deep sea sediment core and of McCorkell *et al.* (1967) in Greenland ice does not confirm the above observations. In the former case, Be^{10} measurements have not been made and the negative result could be a manifestation of high sedimentation rate. The latter of-course represents short term accumulations. In the case of Mn^{53} and Ni^{60} , the experimental sensitivity is not yet high enough to check on the expected influx rates (Venkatavardan, 1970).

It should be pointed out here that so far all analyses of sediments have been mostly confined to sediments deposited during the last 1-2 m. y. Now with the availability of "Joides" sediment cores, the study of particulate matter in the marine environment can be extended back to about 50-100 m. y.

In addition to the pelagic sediments such ancient geological records have been suspected to exist in the slowly depositing marine accumulations, the so called ferromanganese nodules, basing on the results of Th^{230} and Pa^{231} dating methods (for a comprehensive review see Ku and Broecker, 1969). However, since the half lives of these radionuclides, Th^{230} and Pa^{231} are short ($< 80,000$ years) the deduced accumulation rates refer only to the top 200-500 micron regions of these nodules, doubts have been cast on the validity of these dating techniques. Now with the application of the Be^{10} technique (Somayajulu, 1967; Bhat *et al.*, 1970) the evidence is indeed compelling that the nodules in open oceans, at least do grow at a slow rate, 1-4 mm/10⁶ yrs. Nodules of about 10-15 cm thickness could thus correspond 50-150 m. y. of age. Their growth is probably not a continuous one, however. As a matter of fact Bhat *et al.* (1970) argue in favour of intermittent growth of these nodules; growth periods averaging to only 10% of their life time. Herein probably lies the answer to the very often asked question "what keeps the nodules floating on the ocean floor". We believe that the bottom currents could provide the physical mechanism to support the nodules above the sediments.

Clearly, a great deal of work remains to be done in the field of particulate matter in the marine environment. These studies seem important towards delineation of the complex physical and chemical processes controlling the trace element distribution in the oceans as well as the history of influx of cosmic materials on the earth.

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DISCUSSIONS

S. SAMBE GOWDA: Were the manganese nodules collected from different latitudes?

D. LAL: Yes. The nodules analysed derive from different locations in Pacific and Indian Oceans.

ANIL LYALL: Was the area from which the large nodule was retrieved, surveyed by means of underwater camera or TV? What is the average size of the nodules? One such immense nodule supplied by Scripps to Smithsonian Institution was found to be dolomite. Have you measured the concentration of A¹²⁶ in 'Tertiary clays' or in sediments where a high rate of deposition prevails?

D. LAL: I am not sure whether they had any underwater camera or TV operating while dredging the large Zetes nodule. Almost all nodules we have analysed were principally composed of Mn and Fe hydrous oxides and vary in size from few millimetres to tens of cms. There are few reports about manganese-oxide coatings on shells and calcareous skeletal materials. Generally these are recovered from shallow water depth. The dolomite nodule you have mentioned could belong to this class.

Regarding your second question, I would say that the best material for analysis of Al^{26} is low accumulating authigenic deposits *e.g.* red clays and manganese nodules. Al^{26} which has a half-life of only 0.8 m. y. and hence would be absent in tertiary clays. Its specific activity in fast depositing sediments would also be small, due to a large dilution by terrestrial alumina.