

REMARKS ON THE CHEMICAL PROBLEMS IN RELATION TO THE MARINE RADIOACTIVITY

by Rinnosuke FUKAI

1. Introduction.

In the course of attacking the problems concerning marine radioactivity, it is highly important to utilize known information in the field of oceanography as effective as possible, since a lot of labours and expenses are required to accumulate any oceanographical information. However, in general, the existing knowledge is not sufficient for the full understanding of the problems, thus, new studies in specific aspects are required. In the present note the author intends to point out some aspects of chemical oceanography, or marine chemistry, which are specially important for the scientific understanding of the problems of marine radioactivity.

The ultimate goal of the chemical oceanography is to know the law, which governs the distribution of all chemical elements and isotopes in marine environments. A number of studies have been conducted along this line up to now. Especially in recent years, the distribution of trace elements in marine environments are being clarified by using modern techniques in analytical chemistry. The results obtained by these studies are highly valuable as the basic data for the understanding of chemical behaviours of radionuclides in marine environments. However, only a little is known about the physico-chemical status of trace elements in sea water.

In the Oceanographic Congress at New York in 1959, SILLEN presented a valuable lecture (6). He predicted ionic species of various elements existing in sea water on the basis of thermodynamical properties of ions. These predictions are very useful as the theoretical guides for marine chemists who are engaging in field studies, although they should be backed up by *in situ* measurements.

It seems quite certain that many contributions to the chemical problems of marine radioactivity will be offered through studies in this aspect. Including the problems of ionic species in sea water, the author believes that the most urgent chemical problem concerning marine radioactivity is to get the quantitative knowledge about the physico-chemical status of elements, especially, trace elements, in sea water.

In order to demonstrate the complexity of the problems some examples are given below.

2. Chemical forms of iodine in sea water.

FROMM, who stayed in Oceanographic Museum of Monaco from 1963 to June 1964, made the experiments on the uptake of iodine-131 by rainbow-trauts before he came to Monaco (1). He proved that iodine-131 in the form of iodide is taken up by fish very rapidly in fresh water media. On the basis of these experiments he expected that, if the similar experiments are carried out in sea water media, effects of isotope dilution of iodine-131 by stable iodine in sea water should be recognized, since the iodine content of sea water (about 50 $\mu\text{g/l}$) is several ten times greater than that of fresh water. However, when he conducted those experiments by using marine fish, he obtained the results practically similar to those obtained for

fresh water fish (2). This means that the stable isotope of iodine (iodine-127, 100 %) in sea water did not serve as the carrier for iodine-131. That is, the stable iodine in the sea water used for the experiments should be present in a chemical form other than iodide.

As to iodine in sea water *in situ*, SUGAWARA and TERADA (7, 8) reported that there are two chemical forms of iodine, iodide and iodate, and the thermodynamically more stable form in sea water should be iodate. From this point of view, apparently Fromm's experiments can be interpreted by the consideration of iodite-iodate equilibrium in sea water used for the experiments. This leads to the conclusion that, when the chemical behaviours of radioactive iodine is to be considered, it is not sufficient to consider total iodine in sea water as the whole, but different behaviours of different ionic species have to be taken into consideration. Similar situation will be applied to some of other elements. This example can demonstrate the importance of the information concerning the chemical form of elements in sea water for the understanding of the behaviours of radionuclides in marine environments.

3. Behaviour of manganese in sea water.

The authors has found out recently a remarkable peak in gamma-spectrograms taken for ashes of marine plants. This peak may quite possibly be identified from its energy as that of manganese-54, although radiochemical separations of the samples have not yet been completed.

As to manganese in sea water studies were carried out by HARVEY (4) and RONA *et al.* (5), and it is believed that the majority of manganese in sea water exists in the particulate form. GOLDBERG (3) assumed that particulate manganese dioxide plays a role of the chemical scavenger in the sedimentary processes.

Taking this information into consideration, manganese-54 found in the ashes of marine plants is likely to be attached on the surface of the plants. In order to remove the contamination in the surface, the plants were soaked with 0.1 N hydrochloric acid for 1 hour and rinsed with distilled water before drying. After the samples were ashed, the gamma-spectrograms of washed plants were compared with those of unwashed plants. There was practically no difference. This means that manganese-54 in marine plants seems to be bound tightly with plant tissues. To interpret this fact, it seems reasonable to think that at least some parts of manganese-54 were taken up through metabolic processes of the plants, although manganese dioxide is very difficult to leach out by diluted acid.

On the other hand, tracer experiments prove that divalent manganese is not easily precipitated at the pH of sea water, even when hydroxide of iron is present.

On these experimental results, it seems possible to think that at least some fractions of manganese-54 in fall-out may be brought into sea water in a soluble form and could be ingested by marine plants, although it is too early to draw any conclusion. This interpretation is not necessarily contradict the existing information. That is, particulate manganese found in sea water could be considered as the results of the long-term cycle of manganese in marine environments or as that formed before it was brought into sea water, whereas manganese taken up into the plant tissues could be soluble manganese, which is the fraction of total manganese. In connection with this, it should be stated that RONA *et al.* (5) pointed out the occurrence of organic-bound manganese in sea water. This could be considered as the metabolic products or decomposition products of some marine organisms. Anyhow, this example reveals the fact that even the simple existence of manganese-54 in marine plants implies appreciably complex problems and that, again, the quantitative information concerning physico-chemical status of the elements is required.

4. Conclusion.

As repeatedly stated above, the author believes that for the full understanding of the chemical behaviours of radionuclides in marine environments, the information concerning

ionic species as well as state of dispersion of trace elements in sea water is essential. And the author also believes that quantitative evaluation of the role played by the organo-metabolic compounds in the cycles of the elements in marine environments should be made.

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