

ately strong base with a pK_b of 5.2 (9), an acid-base reaction between stearic acid and the basic nitrogen group of the drug may occur. The accessibility of the carboxyl group should strongly determine the extent of this interaction. Harkins (8) has reported that for mixed films of stearyl amine and stearic acid an acid-base interaction does indeed take place.

In addition to ion-ion interactions, interactions resulting from short-range van der Waals forces between the film and drug molecules, are also present; by their very nature, these interactions depend on the proximity to each other of the molecules in the surface film. Consequently, when the film is attenuated, the acid-base reaction should predominate, but as the film is compressed and the molecules are aligned, the van der Waals forces become increasingly prominent.

The problem of film instability can best be explained by postulating a process of "interfacial-dissolution" which sometimes occurs in films whose regular arrangement is disrupted when an irregularly shaped molecule penetrates the film (10). The lateral cohesion arising from the van der Waals forces, which enhance film stabilization in the case of the stearate films, is disrupted when veratrine (a bulky and irregularly shaped entity) is the penetrating molecule. The facts that no signs of film collapse (that is, film striations and an abrupt decrease in film pressure) were observed and that a film pressure of about 35 dynes was obtained on rapid compression of the film are other indications that this is a true "dissolution" process. Consequently, both veratrine and stearate leave the interface, perhaps as the salt, and are dissolved in the substrate. This process also accounts for the small limiting area as well as the instability of the film. When Ca^{++} is added to the substrate, the carboxyl groups are tied up as calcium stearate and the acid-base reaction cannot occur (11). This is also reflected in the lowering of the spreading pressure in the attenuated film. The fact that the limiting area for stearate is obtained on the Ca^{++} substrate indicates that here only the van der Waals forces predominate, and they are too weak to prevent the veratrine from being squeezed from the film.

The Ca^{++} antagonism for veratrine, then, is the competition for the acid groups of the film and is influenced by the relative interaction energies of these competing agents. One should also find that the antagonism is influenced by the Ca^{++} concentration, pH , and temperature. Evidence is already available for nerve that at low temperature (12) and pH (13) veratridine depolarization is weaker (14).

These findings provide further evidence that monolayers of stearic acid

are affected by drugs and ions at physiological and pharmacological concentrations and exhibit responses and antagonisms that are sufficiently distinctive to suggest interactions related to biological effects. These and related model systems certainly merit further exploration (15).

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15. We are indebted to W. A. Zisman and L. Jarvis for the loan of the film balance and for introducing one of us (N. L. G.) to the film balance technique.

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Metabolically Induced Precipitation of Trace Elements from Sea Water

Abstract. The presence of organic material in some manganese-rich nodules suggests that the nodules are of biological origin. This suggestion leads to the proposal that in sea water, heavy metals get protection from hydrolysis by organic complexing; parts of these complexes become metabolized, the remaining parts then precipitate. These processes would explain a number of interesting observations.

Two recent detailed papers (1, 2) discuss from the physicochemical standpoint the genesis of the commonly found (3) manganese-rich deposits on the sea floor. Adequate consideration has never been given, however, to the possibility that these deposits stem from biological processes.

I have recently been examining some

typical manganese-rich nodules from the Blake Plateau (collected in August 1957 at latitude 30° 51'N, longitude 78° 27'W in about 400 fathoms) and have succeeded in finding in them a fraction of a percent of organic material. A crushed and ground nodule, when rinsed with distilled water (pH 7), yields a bright yellow solution with pH about 4. If this solution is acidified, the color is eliminated. Ethyl acetate extracts from this colorless solution a fraction which can be recovered, by extraction into a weakly ammoniacal solution, and which then becomes yellow. Paper chromatography of this solution reveals at least three components. Extraction of the nodule with 7N NH_4OH yields further organic material which can be charred by heating it in an open dish. Some material having free amino groups has been detected with Ninhydrin. A further organic fraction can be extracted with 95 percent ethyl alcohol.

This organic material might have been adsorbed from sea water during the inorganic process of deposition of the trace elements, or alternatively, it could be accounted for directly if bottom-dwelling organisms are the agents by which the nodules are made. A nonphotosynthetic organism would be required for the latter interpretation, since manganese-rich deposits have been found throughout the depths of the oceans. A nonchemosynthetic organism also seems to be required by the fact that the deposits are found at all depths where adequate oxygen is available. Food would have to be derived from the several milligrams per liter of organic material that are present in sea water at most depths. The composition of this material is poorly known, but tyrosine analysis of hydrolyzed sea water assays this amino acid at a fraction of a milligram to a few milligrams per liter (4); many others should be present in comparable amounts. These amino acids and protein-derived compounds could serve as a valuable part of the nutrients of a great variety of organisms; if they were an important part, slow growth would be required for life on this starvation diet.

It is well known that by various types of chemical bonding, amino acids, peptides, and proteins form complex molecules with numerous metallic ions (5). Some of these complexes are sufficiently stable that the usual properties of the metallic ions in solution become effectively masked, and it is then impossible to treat their chemistry by the usual rules of solubility, pH sensitivity, and so forth, that apply to the simple inorganic ions in dilute solution. Many of these complexes are so stable that it seems quite certain that they must exist in sea water if the proper ingredients are available.

Unfortunately, not enough is yet

known to predict, with assurance, the metabolic fate of such complex compounds in biological systems. We may suppose, however, if bottom-dwelling organisms feeding on these complexes in the sea water are responsible for deposition of manganese and iron hydroxide along with appreciable quantities of numerous other trace elements, that these organisms are able to metabolize the organic part of the complex molecule and reject the inorganic part. It can be imagined that by this process a concentration of inorganic ions is built up within or in the neighborhood of the living organisms. The ions, freed of their organic complexing agent which protected them from hydrolysis, then precipitate as hydroxides in the sea water. The metabolic processes of the organisms might not be able to compete successfully with all reactions involved in forming especially stable complexes, but it would seem from the variety of trace elements present in these deposits that complexes of appropriate stability are common.

From this hypothesis, a number of inferences can be drawn.

1) If manganese-rich deposits are being formed today by living biological agents, it should be possible to detect metabolic activity in fresh samples. A generation time of about 2 weeks is suggested by calculations based on the following assumptions: rate of deposition, 1 mm/1000 years; organism 1 μ thick having the same composition as *Escherichia coli*; 2 moles of amino acid used per mole of manganese deposited. Faster deposition, as advocated by Goldberg and Arrhenius (2), would reduce the generation time proportionally.

2) If temperature has no limiting effect on quality or quantity of nutrients, then, as in any other biological system, there should be an optimum growth temperature.

3) If the rate of growth is solely a function of the rate at which nutrients are supplied by the moving bottom currents, then it should be possible to recognize differences in abundances in areas swept by currents and in areas where the currents are known to be minimal. On a small scale, this effect might be detected by detailed examination of the geometry of individual samples.

4) If the various organic complexes that provide material for trace-element deposition have a sharp inverse dependence of their stability on temperature, then, in general, the detailed composition of the deposits should become simpler with increased temperature of formation.

5) Elements that do not form organic complexes or that already are strongly complexed inorganically will be missing from the deposits.

6) If it is correct that complex molecules are required for trace-element de-

position on the sea floor, then their importance in other chemical and biological processes in the sea is to be expected.

This hypothesis affords plausible explanations for a number of well-established facts about the manganese-rich deposits of the sea floor. (i) A mechanism is provided for effecting vast concentration of a wide variety of trace elements from sea water. Fluctuations in composition reflect changes in the nutrients. (ii) The concentrated product is poorly organized crystallographically, partly because of the variety of elements in it, but more particularly because of the manner of disperse formation on a minute size-scale basis. (iii) From an analysis of the Challenger Expedition report (6) it is seen that the probability of finding manganese-rich deposits is high (.45) in water between 34° and 38°F and low (.076) in water that is now warmer than 38°F; no manganese nodules can be identified in the hundreds of photographs (7) of the Mediterranean and Red Sea floors where the temperatures are about 56° and 72°F, respectively. Such findings are consistent with the needs of an organism living on a starvation diet. Deposits of this type are thus naturally associated with an ice age. (The deposits on the Blake Plateau where the bottom temperature is now 45°F may no longer be increasing.) (iv) The presence of extensive adherent coatings of manganese-rich deposits on basic igneous rocks and their scarcity on lime, and, in nodules, the common nuclei of sharks' teeth, earbones of whales, fragments of previous nodules, and so forth, merely reflect the needs of the organisms for certain types of materials on which to attach (8, 9).

Note added in proof: In *Nature* (in press), J. W. Graham and S. C. Cooper give additional evidence bearing on the hypothesis of this report.

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Spiral Capillary Plastic Scintillation Flow Counter for Beta Assay

Abstract. Tracer counting of beta emitters in aqueous solution was performed with a detector fabricated from a plastic scintillator capillary. The detector exhibits low gamma background and reproducible detection efficiency, and it requires minimum sample preparation. Counting efficiencies were determined for aqueous solutions of P^{32} , Na^{22} , and C^{14} and for $C^{14}O_2$ gas.

Efforts to achieve rapid and reproducible methods of sample preparation for measurement of low-energy alpha and beta emitters in gaseous form or in solution are often fraught with difficulties. For scintillation counting it is usually necessary to have the sample in a form soluble in, or miscible with, a liquid scintillator solution. Obtaining such samples presents problems of solubility and quenching action which are frequently difficult to circumvent. The suitability of various solvent systems has been investigated by Hayes (1), while Kallmann has suggested the use of naphthalene to reduce quenching (2). Furthermore, liquid scintillators which will accommodate small percentages of aqueous solution have been developed (3). Davidson (4) has recently reviewed the practical aspects of internal liquid scintillation counting. For very low C^{14} activities the synthesis of organic samples to give suitable solvents or diluents has been reported (5). The counting of suspensions of insoluble active samples in liquid scintillators (6) and scintillating gels (7) avoids many of the problems inherent in internal liquid scintillation counting but is not generally applicable to aqueous solutions. Schram (8) has recently counted aqueous solutions on plastic scintillator sheets.

Nevertheless, most of these methods require additional sample preparation and standardization of the scintillator solution with respect to efficiency (1). Significant and often variable amounts of quenching are encountered in the use of different samples or special solvent mixtures (4, 9).

In the work discussed in this report we investigated the use of a plastic scintillator capillary for direct counting of aqueous solutions containing weak beta emitters such as C^{14} . By a suitable choice of geometry, a wall thickness sufficient to interact with most of the beta energy can be employed, with a bore diameter which will not give serious self-absorption at low beta energies. Increasing the wall thickness limits the length, and hence the volume, of the capillary but increases the height of the pulse from high-energy emitters. Decreasing the bore of the capillary decreases self-absorption but reduces the volume and hence the total counting rate.