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SOME BIOLOGICAL ASPECTS OF THE STRONTIUM CYCLE

Introducing a new tool of Paleoecology

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The main overall problem being undertaken is the Bio-geochemistry of Strontium. The amounts are determined in rocks, soils, sediments, lakes, rivers, ocean, and organisms so as to form a coherent picture of the rate of flux of the element between its sites of occurences. This whole complex of distribution and movement of an element may be visualized as a unit as done by Vernadsky. Like other species or units in nature, this complex qualifies as an entity because of stability with time even though material and energy are continually passing through the system. A system of balanced rates may have self correcting mechanisms which maintain the stability. A water wave, an organism or a bio-geochemical complex are all cases of at least partial stability. Natural selec tion can act on any self propagating entity organic or inorganic.

This overall problem as stated above has several parts that have assumed major importance. It is one such part that is presented in this paper.

Strontium by its close chemical similarity to the far more abundant calcium goes along with calcium wherever that element goes. But it is just different enough so that it is more or less partially excluded or included relative to calcium depending on the nature of the journey. Thus the ratio of the amounts of the two elements is an ever present indicator of the past history of the material.

This paper may be summarized briefly as follows: Because the strontium in skeletons and shells of organisms reflects the amount in the medium in which the animal lived, it is possible to tell from fossil shells the type of habitat in which the animal lived. The following may be inferred:

1. The constitution of ancient seas may be determined.
2. Some marine and fresh water material may be separated.
3. Physiological evidence may be acquired on ancient organisms.
4. Evidence may be had as to the stability of Bio-geochemical complexes.

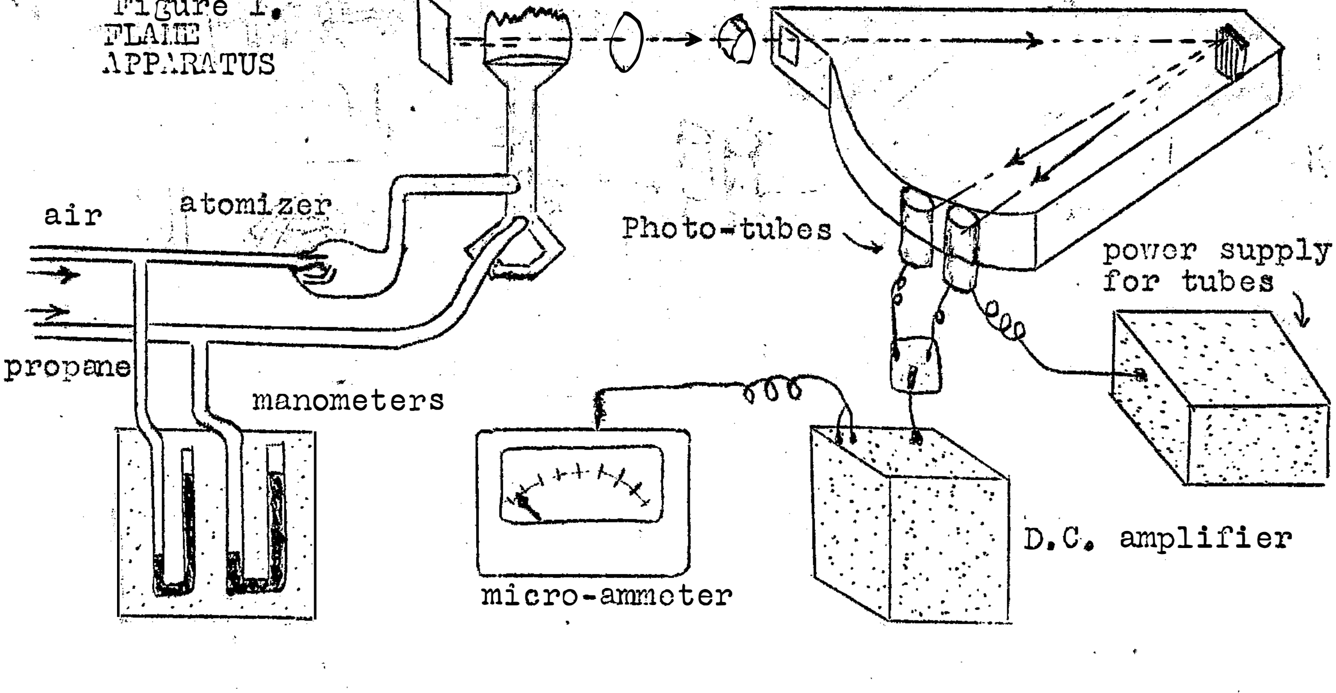
Method

First let us consider the technique. The accurate determination of strontium where calcium is a thousand times more abundant requires a spectrographic technique where the excited ions in an arc, spark, or flame emit characteristic light that is in part proportional to the amount. Thus strontium has been estimated for many years in these ways. But the big problem in such determination has been interference since any other ions present influence the strontium emission by unknown interactions in the excited state. Reliable values are obtained only when the total composition of the standards used corresponds to the unknowns.

Because of this difficulty and the tediousness of the methods, good reliable values have been scarce indeed. In spectro-graphic work errors of 1000% have crept into much published work where precautions were not taken. Due to these difficulties the accumulated data has been too contradictory for generalization to be made.

In the analyses to follow, it is believed that many of the difficulties have been overcome by three technical steps. First of all a Lundergardh flame spectroscopic method is used. A solution of the material is atomized by a jet of compressed air and injected into the base of a Bunsen burner. The strontium and calcium ions are excited in the flame and emit their characteristic wave lengths of light. This light is passed through lenses to a diffraction grating wwhich acting as a prism spreads the wave lengths apart into a spectrum. This flame technique invented in 1929 by Lundergardh has advantages of steadiness of light. Also it does not excite many elements other than alkali and alkaline earth elements. Thus there is no difficulty in separating lines of the spectrum. In addition there is no change in characteristics of the light source with time during the excitation since new fresh material is always coming into the flame. The apparatus is abbreviated in figure 1.

Figure 1.
FLAME
APPARATUS



The second difficulty of tediousness accompanied by all the difficulties of the photographic method used in many spectrographic techniques has been overcome by the use of photoelectric measurement. A photomultiplier tube is placed opposite the best strontium line and another opposite the best calcium line. The electric current from these tubes is proportional to the amount of light striking them. The currents are passed through a D.C. amplifier and registered on a micro-ammeter. By turning a switch the calcium and then the strontium deflections are observed in turn. These readings give the amounts of both elements when taken to a curve made from standard solutions. This speed increases accuracy by allowing constant checks to be made with the Standards and with the background light of the gas flame alone.

The third technical step overcomes the greatest difficulty of interference. All analyses are made on calcium carbonate dissolved in 20% Hydrochloric Acid. When the Calcium and strontium are in any other form or associated with anything else, standard gravimetric technique is used to separate and convert them into the carbonate form. These elements are precipitated as oxalate and ashed to convert to carbonate.

Analysis of variance on 120 samples shows 5--20% reproducibility for the strontium/calcium ratio. For a spectrographic mmethod this is good and where the variation in occurrence is of the order of 100,000%, this is quite adequate. Like all spectrographic methods the percent reproducibility does not decrease with the quantity. The measurement is as accurate for tiny quantities as for the larger ones.

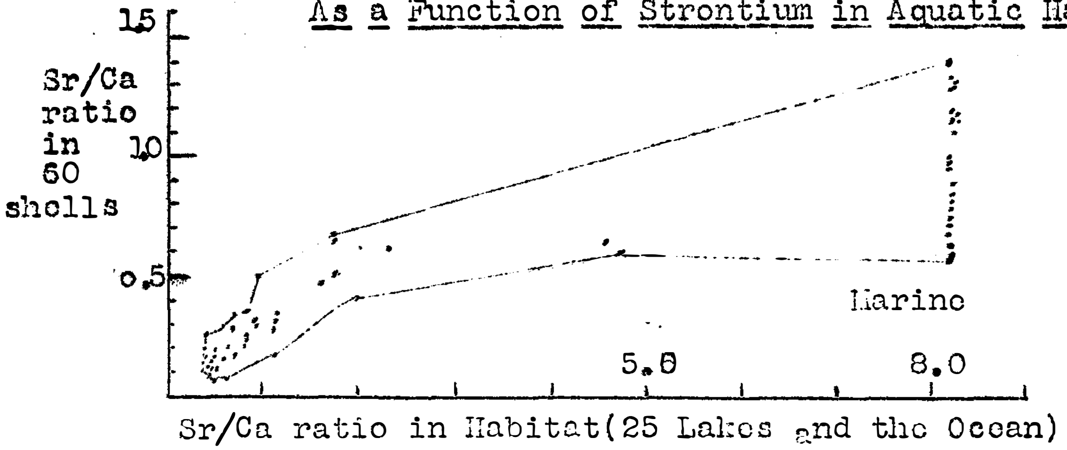
RESULTS

In order to get oriented to the story, the following basic facts must be remembered. In the ocean there are 8.16 atoms of strontium for every 1000 atoms of calcium. This is written 8.16/1000. But when skeletons and shells are laid down, some of the strontium is left behind so that in shells and skeletons the ratio by atoms of strontium to calcium is between .6/1000 and 5.5/1000. The degree of exclusion has a definite taxonomic pattern.

In contrast to the ocean most ordinary fresh waters have lower Sr/Ca ratios with a range: .3/1000 to 5.0/1000. Correspondingly the ratio in the shells is less than the water and thus less than the marine shells. That this is true is demonstrated in <u>figure 2</u>. The data in Table 1 show that the same differences exist between fresh and salt water for calcareous algae, crustacea, and otoliths of fish as well as molluscs.

Figure 2

Strontium in Shells of Pelecypod and Gastropod Molluscs As a Function of Strontium in Aquatic Habitats



These basic data lead us to the most interesting result in Table 2. The Sr/Ca ratio is not radically different in the Cretaceous, Miocene, and Pleistocene marine shells. Thus it is inferred that the oceanic chemical condition was similar in these respects during this period. This can be called Paleochemistry.

Table 1. Comparisons of Strontium Distribution

	Marine		Fresh Water	
	Sr/Ca	number of samples	Sr/Ca	Number of samples
Water	8.16	120	1.09	28
Mollusca	1.01	25	.37	72
Crustacea	2.82	5	.37	1
Calcareous algae	2.45	10	.29	3
Otoliths of fish	2.25	7	.33	2
Arid lake Mollusca	--	--	.90	3
Mollusca from pool, Rosendale, N.Y.	--	--	3.75	3

Table 2. Mollusca During Geologic Time

Modern	1.01	25	.37	72
Pleistocene --Fla.	1.24	6	--	--
Miocene --Austria & France	1.16	10	--	--
Cretaceous--Tenn, N.J.,& N.D.	1.42	19	--	--
Mazon Creek, Ill.	--	--	.60	1
Oldman River, Alb.	--	--	.84	1

The second big use of the Sr/Ca ratio as a paleoecological tool is the determination of the differences between fresh and marine fossil shells. As shown in figure 2 for the Molluscs the fresh water values grade into and overlap with the marine values. But the marine values never get below .6/1000. Fresh waters get high Sr/Ca ratios only under certain conditions. This is not completely worked out yet but promises to be a tool in itself as an indicator of lake paleochemistry. At present it may be said that Sr/Ca ratios are high in three conditions. One occurs wherever the calcium is very low so that the ratio tends to be high. The selective removal of Barium by organisms may aid this process. It most certainly does in laboratory culture.

The second condition is in Arid lakes. This was first pointed out by Hutchinson in 1943 for Tibetan lakes. The high values averaging 1.9/1000 for snails in Table 1 support this idea. The third condition for high Sr/Ca ratio occurs where the water is peculiarly situated over rocks and minerals which for special geological reasons are high in Sr. In the table 1 there is a case where this is suspected for a pool near Rosendale, N.Y.

In Table 2, two fresh water localities in the Cretaceous were analyzed. The values are in agreement with the generalizations above. The Alberta value of .84/1000 is too much on the border between fresh water and marine organisms to be conclusive alone. But the .60/1000 for a gastropod from Mazon Creek, Ill is plainly indicative of Fresh water since the only marine forms this low are Pecten, Brachiopods, and Pteropods.

The data for the Paleozoic as yet is very limited because good unreplaced fossil material has not been obtained. But in the process of study, although the evidence is not yet extensive, it seems likely that Sr/Ca ratios can give information bearing on replacement and history of rock formation.

The evidence in table 2 from the geologic periods suggests that since the ionic constitution of the oceans is strongly interrelated, the maintenance of the ssame order of magnitude of Sr/Ca ratios over considerable time is a support for the idea of a chemical complex of some stability. Just as Natural selection as a Maxwell Demon has guided organic evolution toward the more complex, so has it here perhaps guided the evolution of the bio-geochemical complex toward higher survival value. Can we wonder that there might be more total organization in the modern oceanic complex than in ancient oceans??

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