The Stability of the World Strontium Cycle[1]

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THE CHEMICAL ELEMENTS that make up the biosphere circulate in systems driven by radiant energy and in patterns described as biogeochemical cycles. The study of the structure and progress of such cycles has been a fruitful approach to earth science.

A fundamental property of these cycles is the degree of stability. A stable cycle is one that maintains an unchanging rate of circulation and constant standing concentrations in the various parts of the system. Although the stability principle of Fechner (*1*) suggests that a system should trend toward a stable state, it has not yet been possible to determine whether any of the cycles are actually stabilized. Major obstacles are the lack of quantitative data on present cycles, and the absence of direct evidence about the cycles in the past.

Historically, the sedimentary cycle as a whole was visualized as in a complete circulation at an early date by Hutton (*2*). Later, Blackwelder (*3*) described the phosphorous system as a closed cycle. More often, however, authors making geochemical studies have proposed that evolution and progressive changes are occurring in the cyclic patterns. Thus, for example, changes in the concentrations of the oceanic elements have often been postulated, as in the studies of Clarke (*4*), Conway (*5*), Kuenen (*6*), Hutchinson (*7*), Rankama and Sahama (*8*), and Rubey (*9*). Specifically, changes in the oceanic strontium concentration have been postulated by Delecourt (*10*) and Conway (*5*). Even the biogeochemical cycles of those elements that circulate through the atmosphere, such as oxygen, carbon, and nitrogen (atmophilic elements), have often been postulated to be unstable and in transition while circulating.

Stable systems are characterized by self-regulating mechanisms, and Lotka (*11*) has shown that a cycle can possess such a mechanism. His theory states that if a cycle consists of a constant quantity of some variable moving from stages A to B to C, and so forth, and finally back to A, and if the rate of movement from one stage to the next depends on the quantity or concentration at each step, the whole cycle retains a steady pattern, with the amount at each step inversely proportional to the rate of passage through that step. Such a steady state is similar to the radioactive equilibrium, except that in this case the cycle is closed with respect to matter. Kostitzin (*12*) discussed this theory in terms of the atmophilic elements, and Hutchinson (*13*) has quantitatively considered the carbon cycle from the point of view of self-regulating mechanisms. Evidence is now needed to indicate directly the degree of stability of biogeochemical cycles in the past.

The purpose of this communication is to describe quantitatively the world strontium cycle and to present some direct evidence bearing on the stability of this cycle during the geological past. By way of comparison, some rough calculations are made of the flux of some other nonatmophilic biogeochemical cycles.

THE STRONTIUM CYCLE

Strontium, like the somewhat similar and more abundant calcium, has been found in all the phases of the biosphere in which analyses have been made. Although resembling calcium chemically, the ionization constants, solubility products, and other properties differ usually by a factor of from 2 to 100, so that most natural processes act on the two elements differentially. Strontium moves in a cycle qualitatively resembling that of calcium but quantitatively different, and is about 1/500 as concentrated in most phases. The ratio of Sr/Ca by atoms is used in presenting information on strontium, because the ratio makes possible the comparison of the strontium content and the more familiar calcium content, and because the ratio changes during a process only when there is a differential action on the two elements.

By being excluded from ultrabasic and basic rocks, strontium works upward in the lithosphere during fractional crystallization because of its large ionic radius. It is found abundantly along with potassium in volcanic rocks, alkali rocks, and pegmatites, as shown by Noll (*14*). From these and other igneous rocks and from sediments strontium, along with calcium, is removed in weathering and passes down the rivers partly in solution and partly in the crystalline particles of silt. The crystalline fraction is immediately deposited in marine argillaceous sediments, and the soluble fraction tends to increase the strontium concentration in the sea. However, the incorporation of strontium into the carbonate and phosphatic skeletons of organisms removes strontium from the sea, together with calcium, in about the same Sr/Ca ratio as in the materials coming down the rivers. The strontium-bearing calcareous and argillaceous deposits are elevated in the course of orogenesis and are subsequently eroded, so that the strontium and calcium return again to the sea. Some sedimentary strontium is probably incorporated into magmas, from which it is returned to the continental surfaces as volcanic or plutonic igneous rock, and thus the cycle is at least partly closed. The circulation of strontium through

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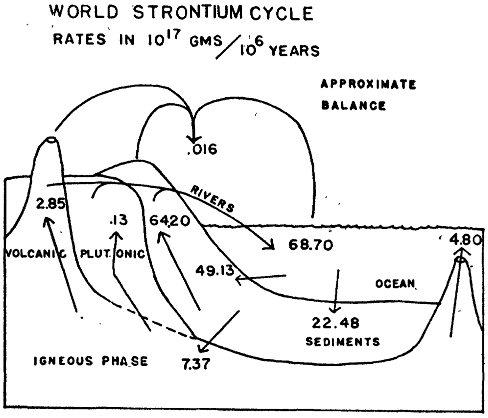

FIG. 1. Flux of strontium estimated according to the assumptions in Tables 1 and 2.

the atmosphere in dust is quantitatively unimportant. The strontium cycle is shown in condensed form in Fig. 1.

One suspects that the cycle may be closed and stable, because 95 per cent of all matter draining to the sea is estimated by Conway to be of sedimentary origin and is again being deposited as sediments. If the 5 per cent of igneous matter draining to the sea is equalled by the sedimentary matter incorporated into igneous rock each year, the cycle will be stabilized and closed, not only for strontium and calcium, but possibly for other elements also.

EVIDENCES OF STABILITY

One may test this hypothesis of a stable strontium cycle in four ways: (1) by determining whether the Sr/Ca ratios of the inflow balance the Sr/Ca ratios of the outflow in phases of the cycle; (2) by calculating the rates of flow between the phases, to see if there is a balance; (3) by finding whether there is a self-regulating mechanism; (4) by devising a paleochemical method to estimate directly the past nature of the cycle.

Analyses of samples representing the major phases of the sedimentary cycle have been used to make rough estimates of the Sr/Ca ratio (Table 2). In the table the Sr/Ca ratios of the materials entering the ocean are close enough to the ratios of those materials deposited from the ocean to indicate that a steady state in the relative relationships of the strontium and calcium cycles in the ocean is reasonable. Thus, the first line of approach does not contradict the hypothesis of stability for the strontium cycle.

Since estimates have been made of the Sr/Ca ratio in the main phases of the strontium cycle, the rates of flow of strontium can be obtained by multiplying the concentrations by the rates of flow of rivers, rates of sedimentary deposition and uplift of rocks, and rates of erosion. Because the sedimentary cycle is not known to be closed and balanced, only the rates of flow of matter down the rivers and of sedimentary deposition can be estimated. Generally, most geochemical calculations have dealt with these phases and have ignored the rate of return (*4, 6, 15, 16*). In the absence of direct estimates of the rate of return of matter from the sediments to the continents, for purposes of calculation the sedimentary cycle is assumed to be balanced and stable. In Table 1 are presented the crude approximations of estimations of the rates of flow of matter through the various phases of the sedimentary cycle. In Table 2 the concentrations of the various elements in the different phases are multiplied by the total flow through each phase to obtain the rates of flow of the separate elements, including strontium. The balance in the separate elemental cycles that is achieved suggests that the hypothesis of a closed stable cycle for sedimentary elements, including strontium, is quantitatively reasonable, but the estimates and results are much too rough and uncertain to constitute certain proof.

TABLE 1

SOURCES OF THE ESTIMATES OF FLUX OF MASS IN THE SEDIMENTARY CYCLE ON THE ASSUMPTION THAT THE CYCLE IS IN A STEADY STATE
($Gg/10^6$ years)

Entering ocean		
Water	370,000	—Wust (*17*)
Dissolved salts	54	—146 ppm, Conway (*5*)
Silt	130	—438 ppm, Conway (*5*)
Volcanic (directly from magma to the sea)	10	—Extension of estimates on the basis of ocean area; compromise between Verhoogen (*18*)—5 $Gg/10^6$ yrs., and Sapper (*19*)—41 $Gg/10^6$ yrs.
Total solids	194	
Leaving ocean		
Deep sea sediments		Averages from Kuenen (*26*) corrected for water
Blue mud	46	
Globigerina ooze	15	
Red clay	5	
Total	66	
Shallow sediments		By difference between inflow and deep-sea sedimentation; divided into a 5 : 1 : 1 ratio of shales, sandstones, and limestones as reported by Kuenen (*6*) for a Tertiary deposit
Shales	88	
Sandstones	20	
Limestones	20	
Total	128	
Weathering of igneous rock	20	1/20 of total weathering after Conway (*5*)
Igneous rock emerging at surface	20	Assumed to balance the weathering for calculation purposes
Materials absorbed into igneous	20	Assumed to balance the materials brought to the surface
Sediments uplifted in earth movements	174	Amount required to balance the sedimentary cycle

TABLE 2

Flow Rates through World Phases on the Assumption of Steady State

(Crude Approximations of Rates in Gg—10^{20} g/10^6 years)

Phase	Mass[a]	Magnesium		Calcium		Strontium		Potassium		Sodium		Modified sodium		Carbonate		Silicon		Aluminum		Iron	
		%	Flux	%	Flux	Sr/Ca (Atoms/ 1,000 atoms)	Flux (10^{17} g/10^6 years) %	%	Flux	%	Flux	%	Flux	%	Flux	%	Flux	%	Flux	%	Flux
Into ocean																					
Dissolved	54	3.41[b]	1.84	20.39[b]	11.01	2.19[d]	50.61	2.12[b]	1.14	5.68[b]	3.07	2.90[l]	1.57	39.08[b]	21.10	5.46[b]	2.94	1.48[b]	.80[m]	—[m]	—[m]
Silt	130	.61[e]	.79	1.87[e]	2.43	3.40[f]	18.09	1.26[e]	1.64	.78[e]	1.01	.78[e]	1.01	1.90[e]	2.47	32.00[e]	41.60	7.00[c]	9.10	2.40[e]	3.14
Volcanics	10	4.59[c]	.46	5.98[c]	.60	3.66[g]	4.80	2.16[c]	.22	1.31[c]	.12	1.31[c]	.12	?	?	25.90[c]	2.60	8.26[c]	.81	6.10[c]	.61
Total	194		3.09		14.04		73.50		3.00		4.20		2.70		23.57		47.10		10.71		—
Sedimentation from ocean																					
Blue mud	46	1.30[b]	.60	1.46[b]	.67	3.40[f]	4.99	1.87[b]	.86	.78[b]	.36	.94[n]	.43	(3.0)[o]	1.38	26.60[b]	12.23	9.12[b]	4.20	5.32[b]	2.44
Globigerina ooze	15	.83[b]	.12	20.62[b]	3.09	1.86[h]	12.59	1.10[b]	.17	.73[b]	.11	.88[n]	.15	31.0[o]	4.65	12.40[b]	1.86	5.16[b]	.77	2.62[b]	.42
Red clay	5	1.99[b]	.10	1.40[b]	.70	3.20[f]	4.90	2.36[b]	.12	1.45[b]	.07	1.74[n]	.09	—	—	25.40[b]	1.27	8.45[b]	.43	6.72[b]	.27
Limestone	20	4.74[b]	.95	30.50[b]	6.10	2.50[h]	33.37	.27[b]	.05	.04[b]	.01	.04[b]	.01	56.7[o]	11.34	2.42[b]	.48	.43[b]	.09	.38[b]	.08
Shales	88	1.47[b]	1.29	2.22[b]	1.95	2.80[f]	11.95	2.69[b]	2.37	.97[b]	.85	.97[b]	.85	(3.0)[o]	2.64	27.10[b]	23.85	8.16[b]	7.18	4.69[b]	4.13
Sandstones	20	.70[b]	.14	3.93[b]	.79	2.20[f]	3.81	1.09[b]	.22	.33[b]	.07	.33[b]	.07	6.9	1.38	36.50[b]	7.30	2.53[b]	.50	.98[b]	.20
Total	194		3.20		13.30		71.61		3.79		1.47		1.68		21.39		47.00		13.17		7.54
Sedimentary incorporation into igneous phase																					
	20	1.65[i]	.33	6.88[i]	1.37	2.45[i]	7.37	1.90[i]	.38	.76[i]	.15	—	—	11.0[i]	2.20	24.22[i]	4.84	6.79[i]	1.35	3.88[i]	.78
Igneous exposure to weathering																					
Volcanic extrusion	16	4.59[c]	.73	5.96[c]	.95	3.66[g]	7.62	1.86[c]	.30	1.76[c]	.28	—	—	—	—	24.60[c]	3.94	8.39[c]	1.34	6.70[c]	1.07
New exposure of plutonics	4	.13[j]	.01	1.5[j]	.06	1.00[k]	.13	.46[j]	.02	2.36[j]	.09	—	—	—	—	34.78[j]	1.39	6.52[j]	.26	1.23[j]	.05
Total	20		.74		1.01		7.75		.32		.37						5.33		1.60		1.12
Uplift	174	1.65[i]	2.87	6.88[i]	11.97	2.45[i]	64.2	1.90[i]	3.30	.76[i]	1.32	—	—	11.0[i]	19.4	24.22[i]	42.20	6.79[i]	11.80	3.88[i]	6.75

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[a] The basis for flux of mass is explained in Table 1.

[b] Clarke (*4*).

[c] For composition of volcanic extrusions, an average of the values given by Kuenen for volcanic ash (*6*) computed on a rhyolite : andesite : basalt : 1 : 2 : 4 basis and a mean of 8 basalts in Clarke (*4*) were used.

[d] Mean of five rivers.

[e] Average from silt of Mississippi, Nile, and Vistula (*4*).

[f] Average of some argillaceous marine sediments.

[g] Average from the literature, using scheme outlined in footnote *c*.

[h] Average of modern calcareous sediments.

[i] Weighted average of all sediment components fluxes above.

[j] Granites in Clarke (*4*).

[k] Fenno-Scandian values for Precambrian ancient granites (*20–22*).

[l] Corrected for chlorides after Conway (*5*).

[m] Measure of colloidal component unavailable.

[n] Deep-sea sediments with pore space sodium ; 20% added.

[o] Values equivalent to calcium content assumed.

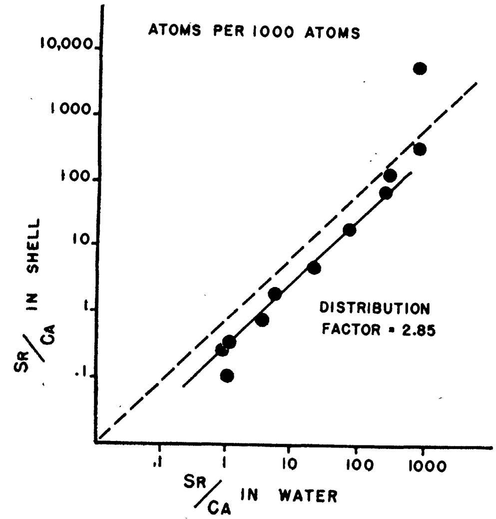

FIG. 2. Sr/Ca in shells of *Physa* as a function of the Sr/Ca in aquaria.

In Figs. 2 and 3 data are presented indicating that in nature, as in the laboratory, the Sr/Ca ratio in the shells of mollusks is proportional to the Sr/Ca ratio in the environmental medium. This relationship is the basis of a self-regulating mechanism controlling the strontium concentration in the ocean. If the inflow of strontium into the ocean increases relative to calcium, the Sr/Ca ratio of the water will increase; this in turn will increase the Sr/Ca ratio in the shells and thus tend to lower the ocean Sr/Ca and maintain a steady-state equilibrium concentration of the elements. This situation, in which the rate of flow of strontium is dependent upon the concentrations of strontium, fits the conditions described by Lotka (*11*) for a closed self-regulating cycle. It seems reasonable that the

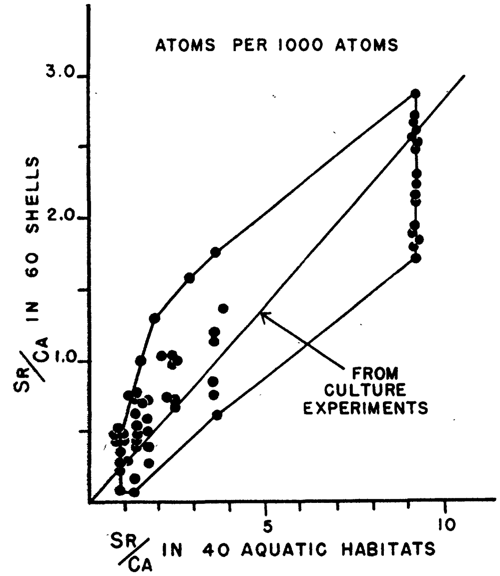

FIG. 3. Sr/Ca in aragonite mollusks as a function of Sr/Ca of the habitat.

TABLE 3

STRONTIUM IN FOSSILS OVER GEOLOGIC TIME
(Most specimens were generously provided by the Yale Peabody Museum)

Sr/Ca in atoms/1,000 atoms

Age and material	Cases	Sr/Ca	Sr/Ca of similar modern material	Percentage of the modern
Cambrian				
Obolus matinalis conglomerate	1	2.60	3.60[a]	72
Dicellomus pellitus[m]	1	2.32	3.60[a]	65
D. appalachia[m]	1	3.70	3.60[a]	103
Ordovician				
Carbonate brachiopods[n]	2	1.40	1.75[b]	80
Mississippian				
Mollusks	2	3.80	2.61[c]	145
Pennsylvanian				
Aragonite nautiloids in	1	3.57	3.87[d]	92
asphalt	1	2.46	3.87[d]	63
Brachiopods; highest values	4	1.64	1.87[b]	88
all others	5	1.02	1.75	58
Mollusks	2	3.43	2.61[c]	131
Permian				
Eryops tooth	1	2.69	2.40[e]	112
Jurassic				
Ichthyosaur tooth	1	3.41	3.29[f]	103
Cretaceous				
Terebratula	1	2.03	1.80[b]	113
Bacculites (aragonite)	1	2.96	3.87[d]	76
Scaphites	1	3.94	3.87[d]	102
Hyposaurus bone	1	2.05	3.29[f]	62
Belemnites	2	2.09	—	—
Cretaceous Coon Creek formation, Tenn.				
Ostrea	1	1.80	1.33[g]	135
Turritella	1	5.18	3.00[h]	165
Other mollusks	9	4.44	2.61[c]	170
Miocene				
Venus	2	3.08	2.39[i]	129
Corals	2	10.50	10.60[j]	101
Ostrea	1	1.43	1.33[g]	108
Pecten	2	2.50	1.75[k]	143
Dentalium	1	2.37	2.34[l]	100
Other mollusks	9	2.89	2.61[c]	110
Pleistocene				
Pecten	1	1.90	1.75[k]	109
Other mollusks	5	2.54	2.61[c]	103
Mean				105

Values used in comparisons above:

[a] *Crania*.

[b] Two species of *Terebratula*: Sr/Ca: 1.75, 1.87.

[c] Mean of modern; possibly unrepresentative. Sr/Ca varies more in mollusks than in most other groups.

[d] *Nautilus*.

[e] Marine fish bones.

[f] Loggerhead turtle bone.

[g] *Ostrea*.

[h] *Turritella*.

[i] *Venus*.

[j] Average of corals furnished by J. Wells, Cornell University.

[k] Average of three species of *Pecten*: Sr/Ca: 1.32, 1.87, 2.08.

[l] *Dentalium*.

[m] Furnished by the Cambrian Research Laboratory, Statesville, N. C.

[n] Furnished by W. F. Prouty, University of Pittsburgh.

rates of flow in the other phases of the strontium cycle, such as sedimentary uplift and erosion, may be dependent on concentration, also. It seems safe to propose that a self-regulating system is in operation.

The next procedure is to find whether the strontium cycle has actually held its pattern over long periods of time. It has been possible to get some fairly direct evidence by the analysis of the Sr/Ca ratio in unaltered fossils. Since Sr/Ca in the calcareous skeleton reflects Sr/Ca in the water (Fig. 2), the analysis of the Sr/Ca ratio in unaltered fossils is a valid method of measuring the Sr/Ca ratio of past waters. Dieulafait (*23*), in 1877, by semiquantitative analyses of strontium in fossil brachiopod shells, inferred that the ancient ocean must have had as high a strontium concentration as the modern ocean. Table 3 gives the results of some quantitative analyses of selected materials that confirm Dieulafait. The spectrophotometric method that was used on oxalate precipitates of strontium and calcium has been shown to possess 17 per cent, or better, accuracy at the 5 per cent probability level.

The values in Table 3 constitute strong evidence that the oceanic Sr/Ca ratio has been of about the same order of magnitude at least since the early Paleozoic, because the Sr/Ca ratios of the fossil materials resemble those of the modern taxonomic counterparts. Since the ocean is a dominant part of the strontium and calcium cycles, the implication is that the two cycles have had the same relative position through 600 million years.

Thus, the application of all four approaches listed above suggests that the strontium cycle is stable. As a stable steady-state pattern in nature involving both living and nonliving components, the strontium cycle seems to qualify as one of the large entities which in ecological literature are known as *ecosystems* as defined by Tansley (*24*). It is suggested that the "strontium ecosystem" is a proper application of the term.

OTHER CYCLES

The evidence on the strontium cycle and the calculations in Table 2 on other cycles suggest the possibility that other elemental systems may be closed and stable. Possibly the whole sedimentary cycle is in a steady-state equilibrium.

The apparent discrepancy in Table 2 between the sodium flux down the rivers and the sodium flux into the sediments, when estimated on the assumptions of Tables 1 and 2, is not an indication of imbalance but is another support for the criticisms that have been already leveled at the analytical estimates of sodium in sedimentary rocks from other evidences by Kuenen and others (*5, 25*). The discrepancy is much greater than could be accounted for by the maximum estimate on the old assumption of sodium accumulating in the ocean at the present time. Actually, there is no real proof that the sodium cycle is not now nearly balanced, since most of the material entering the sea is from raised sediments and therefore, on any theory, should almost balance the sodium leaving the sea in sediments. If the cycle is completely closed, with igneous sodium being derived from incorporated sedimentary sodium, the calculations on age of the ocean from estimates of sodium lost to the ocean during the weathering of crystalline rock are, of course, invalidated.

In a system with a definite number of elements, the degrees of freedom are limited, so that the quantitative solution of one cycle helps in understanding the others. Thus, the calculations of the rates of circulation of the elements in the sedimentary cycle can be used to find inconsistencies in data now available, as in the case of sodium. If the cycle is anywhere near being closed and balanced, the calculations provide ways of estimating hidden parts of the sedimentary cycle, such as rate of uplift and magmatic incorporation of sediments. With increasing accuracy of estimates from new data, calculations more refined than those ~~in~~ Table 2 should provide other checks in the future. Even if the sedimentary cycle is undergoing progressive changes in its patterns, it is at the same time turning rapidly enough so that the flow rates should balance in part.

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