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Strontium in Natural Waters

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Introduction

HISTORICAL SKETCH

Not long after the discovery of strontium in 1790, search for the element in nature revealed a widespread distribution of the element in waters. During the early nineteenth century many qualitative and a few quantitative determinations were made indicating considerable quantities of strontium in mineral springs and brines (Mellor, 1923). Forchhammer in 1865 and Dieulafait in 1877 discovered much strontium in the ocean also, which subsequently led to a series of varying estimates for the strontium content of normal sea water of salinity 35 parts per thousand.

Desgrez and Meunier (1926) found 8.7 mg/l with arc spectrograph of sulfate precipitate; Thomas and Thompson (Thompson and Robinson, 1932) found 13.2 mg/l; Ramage (1936) reported 40–50 mg/l with a flame method; Noll (1934) found 7.0–7.8 mg/l with x-ray spectral methods on oxalate precipitates; Miyake (1939) found 14.4 mg/l gravimetrically after separation with nitrate; Vinogradov found 8.0 and

10.0 mg/1 (Vinogradov, 1938; Vinogradov and Borovik-Romanova, 1945). Then at about the same time several new studies fixed the value for the ocean within a small range of uncertainty. Smales (1951) found 10.0 mg/1 with flame and radioactive methods; Chow and Thompson (1955) found 8.0 mg/1 with flame methods directly on sea water; Bowen (1956) found 8.5 mg/1 by neutron activation; Hummel and Smales (1956) found 8.0 mg/1 with radioactive and stable isotopes; and Odum (1950b, 1951b) reported 8.1 mg/1 with flame methods on oxalate precipitates. Thus it seems agreed that the Sr/Ca ratio of sea water is close to 8 mg/1 (Sr/Ca Ratio, 9.0 atoms/1000 atoms).

Reliable modern analyses of fresh waters have been few. Lohammar (1938) reported a series for Swedish lakes, Odum (1951c) reported data from Florida, Wilska (1952) from Finland, and Borovik-Romanova, Korolev and Kutsenko (1954) from Russia. Further analyses were reported by Straub (1950) and McGrain and Thomas (1951).

In saline waters some uncertain and fragmentary data on water residues are reported by Clarke (1924). Francis (1923) observed some high strontium values in natural brines which he interpreted as due to the increased solubility of saline water. Delecourt (1946) interpreted some analyses of high strontium in ground brine by Camaran (1946) as an indication of little changed ancient ocean water with a hypothesis that strontium had decreased in recent geological ages. This is doubtful since the Sr/Ca ratio of this brine 4.6/1000 by atoms was actually lower than that for the present sea (9.23/1000).

Increased interest related to atomic energy due to the difficulties in dealing with strontium 90, a long lived by-product of fission led to new studies. Alexander, Nusbaum, and MacDonald (1954) analyzed surface waters and ground waters relative to 50 municipal water supplies in the United States. The widespread coverage of these data help permit generalizations regarding the geochemical distribution of strontium in waters.

If the trace element contents of fossils and rocks are to be used to indicate something of the nature of aquatic depositional environments paleoecologically, the relationship of the strontium/calcium ratio to regional water types must be understood. This was one motivation which led to further analysis.

METHODS

New analyses of waters in this paper were made with a flame photometric determination on calcium and strontium chloride solutions. These solutions were prepared from evaporates of 4 liter samples of fresh water as follows. After ashing and extracting with hydrochloric acid, ammonium oxalate 5 to 10 times in excess was added to the acid solutions which were then adjusted slowly at boiling temperatures to basic conditions with ammonium hydroxide. The resulting oxalate precipitates of calcium and strontium were collected on filter paper, ashed at 600 deg. to carbonates and redissolved in 20% HCl at approximately 0.1 M Calcium.

The intensity of the flame emission at 4607A for strontium and 4227A for calcium was estimated from flame in which moist air was passed through a nebulizer and into the air intake of a Fisher burner lined with a glass inner jacket. A flame photometer was devised from a qualitative, classroom, Cenco grating spectrograph by mounting a photomultiplier tube opposite the calcium line and another opposite the strontium line. The output of the photomultiplier tubes was passed into a D. C. amplifier and read on a 10 inch, zero to 50, microameter. With this apparatus it was possible to read strontium, calcium, and the background blue flame successively in a few seconds by tilting the nebulizer and by throwing a circuit switch to indicate first the calcium emission and then the strontium emission. Standards were made from known carbonate concentrations also dissolved in 20% HCl. Laborious as these methods are, they have insured that all interference of foreign substances was eliminated.

In the course of development of these techniques, it was found that direct flame analysis of extracts of evaporate residues was not feasible as indicated by Table 1 where analyses before oxalate separation were widely in error. The strontium values reported by Braidech and Emery (1935) in an arc spectrographic study of a number of elements in evaporates were simmilarly erratic and about 10 times too high presumably because of interference of other ions.

TABLE 1

Distortion of Analyses of Lake Waters Because of Different Composition of Standards and Evaporates

Evaporates		Oxalate Precipitate		Rough Gravimetric
Sr/Ca atoms/1000 atoms	Spectrographic calcium mg/l	Sr/Ca atoms/1000 atoms	Spectrographic calcium mg/l	Calcium mg/l
0.25	10.5	1.32	21.4	23.6
1.92	11.6	1.32	31.8	......
1.30	14.3	0.91	20.7	23.7
2.82	17.6	1.32	28.7	32.2
3.73	14.3	1.08	28.4	28.4
24.6	1.47	1.67	5.5	5.4
32.8	5.2	2.88	1.2	2.1
10.7	5.4	2.05	11.4	13.3
5.84	1.24	1.27	6.8	7.4
37.7	8.3	2.44	2.8	4.0
5.3	0.41	1.44	2.9	3.1

Sea water analyses were made with ammonium oxalate precipitations from 100 cc samples processed similarly. As indicated in Table 2 occlusion of sodium occurred in two series which also registered slightly higher strontium values. It was presumed that these values were too high due to stray light from sodium emission. The values for double precipitations were presumed to be too small because of some strontium loss in the extra precipitation.

ACKNOWLEDGMENTS

Data are from a Ph.D. dissertation, The Biogeochemistry of Strontium, 1950, Yale University with additional analyses made in 1952 in the Biology department, University of Florida, Gainesville, Florida. The inspirational direction of George Evelyn Hutchinson is gratefully acknowledged. Thanks are expressed to R. Hellman, Claude Adams, Willard Hartman, M. Passano, B. Ross Livingston, and R. Benoit for collection of samples. A. D. Hasler made available the residues from Wisconsin and Philippine lakes.

More Data on Strontium in Waters

The new data are presented in Table 3 in a classification into springs, rivers and streams, lake regions, and closed basins. Included are some published data of others

TABLE 2

Strontium Analyses of Sea Water

Location, Method	Number of Analyses	Sr/Ca Atoms Per 1000 Atoms	
		Mean	Range
LONG ISLAND SOUND, 1943–48, Salinity, 28–33 ‰;			
Temp., 0.0–20° C.; top and bottom samples:			
Arc spectrograph, log sector, oxalate precipitates, 1948	12	8.8	6.8 –12.3
Flame spectrophotometer, oxalate precipitates, some occluded sodium; concentration of solutions, 0.1 molar calcium; two analyses from each sample bottle, 1949*	120	9.21	6.72–12.0
Flame spectrophotometer, oxalate separations twice precipitated, concentration of solutions 0.1 molar calcium	16	8.72	7.91–10.00
Flame spectrophotometer, oxalate separations varied precipitation procedures; 0.1 molar calcium solutions*	12	8.90	8.32–10.00
Flame spectrophotometer, carbonate precipitations, 0.1 molar calcium solutions	5	11.34	4.9 –13.3
ATLANTIC OCEAN STATIONS			
30° 54′ N Lat., 62° 10′ W Long., Dec. 19, 1947; 31° 34′ N Lat., 36° 29′ W Long., Dec. 27, 1947; 35° 23′ N Lat., 10° 22′ W Long., Jan. 4, 1948; Off Hatteras, N. C., January, 1950; Depth, 1–4415 meters; Salinity, 34.9–36.9 ‰; Temperature, 0.02–22.3° C. Flame spectrophotometer, much occluded sodium, 1950			
Concentration of solutions, 0.2 molar calcium	47	10.96	10.22–11.08
Concentration of solutions, 0.05 molar calcium*	39	9.76	8.78–12.09
*Preferred value, mean of starred values, reported previously (Odum, 1951)		9.23	

for comparison as indicated. Because strontium is most nearly related to calcium among chemical elements it tends to be correlated in distribution. By expressing the data as Sr/Ca ratio by atoms some idea of the behavior of strontium relative to the better known calcium can be easily determined.

In Figure 1 are plotted representative data from Table 3 on coordinates of Sr/Ca ratio and approximate chlorinity. In Figure 2 coordinates of Sr/Ca and Ca are used. The relationship of strontium to some general classes of natural waters is indicated. These patterns can be explained in part by consideration of some aspects of the strontium cycle as described in the following paragraphs.

Whereas Rodhe (1951) found strontium in fresh waters of Sweden to bear a constant ratio to the conductivity and to the major ions, this relationship breaks down when waters from more diverse regions are compared (Figures 1 and 2).

Factors Controlling Strontium Content in Waters

THE EDAPHIC GEOCHEMICAL FACTOR

When acid rainwater falls and percolates soil and rock, it acquires strontium and calcium especially from those minerals and deposits which are both soluble and rich

TABLE 3

Strontium in Natural Waters

Name of Body of Water	Ca Milligrams Per Liter	Sr/Ca Atoms/1000 Atoms	Sr Micrograms Per Liter
FLORIDA SPRINGS			
Fanning Springs, Old Town, Levy Co., May 6, 1951	66.0	1.16	168
Blue Springs, Bronson, Levy Co., May 6, 1951	28.0	0.80	49
Troy Springs, Lafayette Co., May 6, 1951	54.7	0.79	95
Manatee Springs, Chiefland, Levy Co., May 6, 1951	31.7	2.50	173
Ichatucknee Springs, Columbia Co., May 13, 1951	50.3	1.25	137
Hart Springs, Wilcox, Gilchrist Co., May 13, 1951	66.7	0.85	124
Silver Springs, Marion Co., Nov. 25, 1950	71.6	5.0	784
Poe Springs, Alachua Co., Dec., 1950	63.7	3.0	418
Blue Springs, Gilchrist Co., Dec., 1950	53.3	1.78	208
Crystal Springs, Pasco Co., Dec., 1950	52.8	4.1	474
Orange Springs, Marion Co., Nov. 25, 1950	40.5	3.3	293
Chassahowitzka Springs, Citrus Co., Feb. 23, 1951	43.7	3.5	335
Mud Spring, Welaka, Putnam Co., March, 1951	44.4	8.0	778
Beecher Spring, Welaka, Putnam Co., March, 1951	42.6	5.7	485
Magnesia Springs, Alachua Co., Jan. 21, 1951	35.9	3.4	268
Rainbow Springs, Marion Co., Feb. 23, 1951	18.9	2.0	83
Juniper Springs, Marion Co., Nov. 25, 1950	13.7	4.9	147
Glenn Springs, Alachua Co., Jan. 15, 1950	14.6	1.35	43.2
Devils Mill Hopper, Alachua Co., April, 1950	24.4	2.0	107
Iron Spring, Hawthorne, Alachua Co., May, 1951	0.52	10	11
Salt Springs, Marion Co., Nov. 25, 1950	240	9.3, 12.3	4890
Silver Glen Springs, Marion Co., Nov. 25, 1950	87	7.9	687
Homossassa Springs, Citrus Co., Feb. 23, 1951	52.2	5.2	595
RIVERS AND STREAMS			
Housatonic River, Conn., Dec., 1949	22.9	0.91	45.6
Roundout Creek, Rosendale, N. Y., Dec., 1949	12.2	3.48	93.
Hudson River, Poughkeepsie, N. Y., Dec., 1949	18.6	2.65	107.9
James River, Richmond, Va., Feb. 17, 1950	10.5	1.80	41.4
Roanoke River, Henderson, N. C., Feb. 17, 1950	......	2.74	......
Delaware River, Newcastle Ferry, Feb., 1950	21.3	3.10	144
Withlacoochee River, Gulf Hammock, Fla., Feb. 23, 1951	43.2	3.7	350
St. Johns River, Welaka, Fla., March, 1951	38.5	8.1	683
Dunn Creek, St. Johns River, Welaka, Fla., March, 1951	36.4	10.5	837
Hogtown Creek, Gainesville, Fla., Jan., 1951	12.9	2.6	73.4
Prairie Creek, Gainesville, Fla., March, 1951	4.4	1.86	17.9
Appalachicola River, Chattahoochee, Fla., April, 1951	13.1	1.08	30.9
Suwanee River at Fanning Springs, Fla., April, 1951	28.6	1.80	111
Black Warrior River, Tuscaloose, Ala., April, 1951	5.1	1.76	19.1
Hatchet Creek, Gainesville, Fla., July, 1951	3.3	2.00	14.5
Boulder Creek, Colo. (Platte River) Clarke (1924)	6.7	4.2	61.5
Platte River, Colo. (Cache La Poudre) Clarke (1924)	31	3.8	258
LAKES			
Florida			
Sinks			
University of Florida (milk plant) Jan., 1951	34.6	2.20	167
Green sink (after rain) Aug. 29, 1951	12.6	1.18	33
Seepage lakes			
Newman's Lake, Gainesville, Jan. 21, 1951 Hawthorne, March, 1951	3.5	3.8	29
Lake Wauberg, Alachua Co., Jan., 1951	3.4	2.31	17
Hampton Lake, Bradford Co., June, 1951	1.7	3.22	12
High calcium lakes			
Lake Kanapaha, Gainesville, Jan., 1951	65.2	1.80	256
Fowler's Lake, Hawthorne, May, 1951	15.5	3.2	108
Bivin's Arm, Gainesville, Jan., 1951	37.6	2.10	173
Kentucky			
Devon Park Pond, Covington, Dec. 27, 1949	30.0	1.25	82
Wisconsin			
Trout Lake, June 27, 1925	8.8	2.31	44.4
Helmut Lake, Aug. 27, 1934	1.9	2.56	10.6
Helen Lake, Aug. 24, 1934	1.2	2.24	5.9

Lake Mary, Aug. 24, 1934	1.7	2.83	4.8
Lake Adelaide, Aug. 24, 1934	2.2	2.59	12.5
Nebish Lake, July 25, 1934	1.8	1.84	7.3
Lake Mendota, July 18, 1927	22.9	1.77	88.6
Lake Mendota (uncentrifuged)	20.2	2.10	92.7
Lake Mendota, July 25, 1928	25.3	1.16	64.2
Lake Erie, June 17, 1929	23.2	2.70	137.0
Maine			
Sabethday Lake, Cumberland Co., Dec., 1949	9.3	2.44	49.7
Sebago Lake, Cumberland Co., Dec., 1949	3.0	1.84	12.1
Range Pond, Androscoggin Co., Dec., 1949	3.0	1.47	9.7
Connecticut			
Low calcium lakes draining ancient crystalline rock			
Lake Quassapaug, Nov., 1949	2.1	2.88	13.2
Mt. Tom Pond, Nov., 1949	5.4	1.67	19.9
Westover School Pond, Nov., 1949	4.0	2.44	21.4
Beseck Lake, Nov., 1949	3.1	1.44	9.8
Monastery Pond, Nov., 1949	4.7	1.27	13.1
Lake Wintergreen Reservoir, Nov., 1949	4.0	2.50	21.9
Lake Waramaug, Nov., 1949	3.1	1.68	11.4
Bantam Lake, Nov., 1949	4.4	1.28	12.3
Seepage lakes			
Bethany Bog, May, 1950	1.9	2.01	8.5
Coldbrook Bog, Norfolk, May, Nov., 1949	1.6, 5.1	2.06	14.9
Moderate calcium lakes, more fertile, Triassic sediments			
Linsley Pond, Oct., 1949	13.3	2.05	59.6
Lake Quonnipaug, Nov., 1949	7.4	1.27	20.6
Clark Pond, Mill River, Nov. 25, 1949	15.8	1.31	45.3
Middletown Reservoir, Nov., 1949	14.2	2.46	76.5
Black Pond, Nov., 1949	11.3	1.73	42.8
Mt Carmel Pond, Nov. 25, 1949	10.0	0.86	18.8
Upper Linsley Pond, Dec. 15, 1949	......	1.92	......
Edgewood Park Pool, Nov., 1950	17.5	0.86	32.9
Wallingford Reservoir, Nov., 1950	20.1	2.02	88.8
Beardsley Pond, Conn., Nov., 1949	23.7	0.91	47.0
Bog Meadow Pond, Nov., 1949	28.4	1.08	67.0
Basalt drainage			
West Rock Park Pond (water film on mud) Dec. 1, 1949	21.9	2.10	100.7
High calcium lakes, limestone area			
Beeslick Pond, Nov., 1949	32.2	1.32	93.0
Lake Wononskopomac, Nov., 1949	23.6	1.32	68.2
East Twin Lake, Conn., Nov., 1949	31.8	1.32	91.9
North Carolina			
Piedmont, University Lake, Dec. 25, 1949	4.6	3.80	38.3
July, 1948	2.5, 3.2	5.90	32.2
Draining residual clays of ancient crystalline rocks			
Eastwood Lake, Orange Co., N. C., Dec. 25, 1949	3.8	3.57	29.7
Seepage lakes: Bladen Co., N. C.			
Jones Lakes, Dec. 24, 1949	0.32	4.30	3.0
Singletary Lake, Dec. 24, 1949	0.35	3.50	2.7
Lake Waccamaw (Miocene limestone outcrop) Dec. 24, 1949	6.3	2.39	33.0
Black Lake, Dec. 24, 1949	0.37	2.66	2.2
Sweden			
Average of 35 lakes (Lohammer, 1938)	20.60	1.35	......
Philippines			
Volcanic lakes			
Taal Lake, April 26, 1936	5.2	2.89	325.0
April 5, 1932	42.0	2.88	264.0
Laguna de Bay, March 16, 1932	8.7	4.72	89.7
Calibate Lake, March 4, 1932	68.4	5.00	750
April 3, 1932	......	5.00	......
CLOSED BASINS			
Ocean (see text)	400	9.23	8,100
Great Salt Lake, Utah (double precipitate) 1951	228	4.20	2,100
Utah Lake, data of Seidell (Clarke, 1924)	69	11.5	1,730

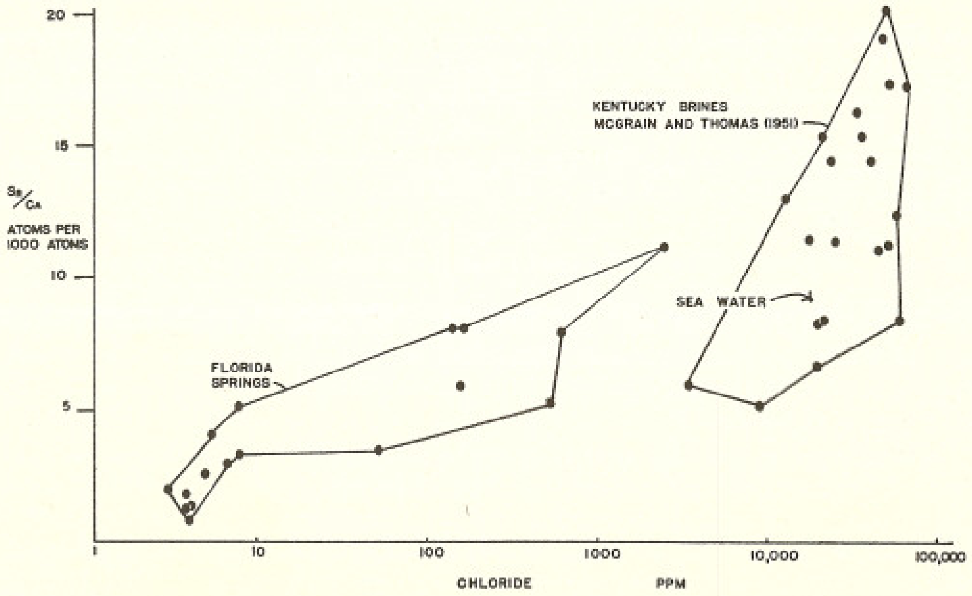

FIG. 1. Sr/Ca ratio of ground waters as a function of chlorinity in ppm. Data on Florida Springs are plotted as an example of a region with groundwaters at salinity less than sea water. Data on brines from Kentucky (McGrain and Thomas, 1951) are plotted representing ground waters with salinity greater than sea water. Several very high values of Sr/Ca ratio among the data on brines fall off the graph.

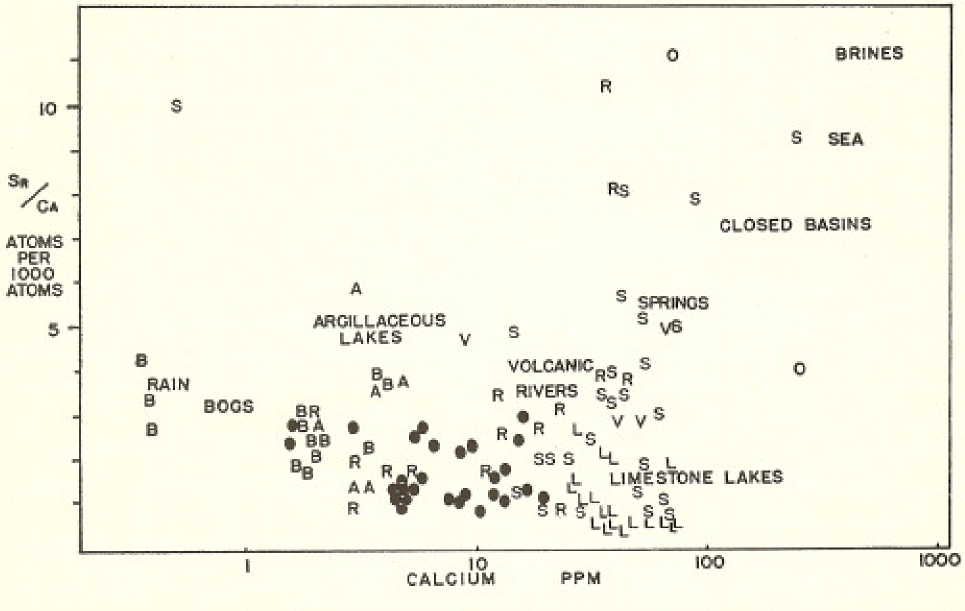

FIG. 2. Sr/Ca ratio of natural waters as a function of the calcium content. Data from this study are classified as follows: A, argillaceous lakes, turbid with clay, and low in calcium; B, bog and seepage lakes, mainly rain water, low in calcium; V, volcanic lakes; S, springs; R, rivers; L, lakes receiving drainage from old limestones; black circles are lakes with intermediate values; open circles are waters of closed lakes. Sr/Ca ratios of waters low in chloride decrease with increasing calcium content; Sr/Ca ratios of waters high in chloride increase with salinity.

in alkaline earth elements such as limestones of sedimentary origin or plagioclase, amphibole, and pyroxene of crystalline rock derivation. If the waters develop the Sr/Ca ratios of their substrates, the following patterns may be expected (Odum, 1957).

If the limestones are freshly deposited with direct precipitation involved or are made of reef coral, the Sr/Ca ratio may be as high as the sea (9.9/1000 by atoms). If, however, as is more often the case, the limestone is composed of shells of invertebrates the ratio is lower 1–6/1000 by atoms. If the limestone is replaced, especially if it is dolomitic, the Sr/Ca ratio may be much less than 1/1000. If the substrate is a soluble calcareous basic rock of non volcanic origin, a low Sr/Ca ratio is also derived (1–3.5/1000). In most calcareous substrates, high strontium contents are found with high calcium contents but the Sr/Ca ratio is low (example, Swedish lakes; Sr/Ca, 1.35 atoms/1000 atoms).

When the waters percolate non-calcareous substrates with less solubility of alkaline earth elements, a relatively larger proportion of the strontium may be derived from non-calcareous minerals which contain strontium. The larger ionic radius of strontium (1.27 A) relative to calcium (1.07 A) permits its inclusion along with potassium (radius 1.33 A) in such minerals as orthoclase feldspar as described by Noll (1934). Thus waters draining insoluble rocks tend to be low in total alkaline earths and to possess a fairly high Sr/Ca ratio (3.5 atoms/1000 atoms).

Among the igneous rocks as among the limestones there is a large range in strontium contents. Granites and other coarse grained rocks which formed slowly tend to be low in strontium, whereas rocks associated with rapid or late stages of fractional differentiations are high in strontium as in volcanic rocks or in pegmatites where strontium minerals themselves occur. Strontium more than calcium tends to remain volatile until the last stages of crystallization. Thus fine grained igneous rocks have more strontium than coarse grained rocks.

As described below in the discussion on closed basins, salt conditions, dry climates, and desert conditions tend to develop high Sr/Ca ratios so that rain percolating through such deposits will derive high ratios as well as high total concentrations.

Thus by way of summary, high Sr/Ca ratios may be expected in waters which drain evaporite deposits, pegmatites, volcanic rocks, those limestones with precipitation directly from the sea water, or fresh coral limestone. Low Sr/Ca ratios may be expected from consolidated limestones, replaced limestones, dolomites, non-volcanic basic igneous rock, and humid regions. The basis for the above summary and more complete data on the distribution of Sr/Ca ratio in regional rock types can be found elsewhere (Turekian and Kulp, 1956, Odum, 1950b, 1951a, 1957).

That the Sr/Ca ratios of surface waters actually do reflect in part the Sr/Ca of the regional substrates may be observed in Table 4. The high Sr/Ca ratios (4–10 atoms/1000 atoms) for western rivers of the U. S. reported by Alexander, Nusbaum, and MacDonald (1954) may be readily accounted for because of the known high strontium content of the Rocky Mountains, the widespread distribution of volcanic rock, and the arid climate. These authors also found a correlation between strontium content and the alkaline earth content of soils. Similarly the low values (mean 117 micrograms/liter; Sr/Ca ratio, 1.3 atoms/1000 atoms) in soft acid waters in Finland reflect the low regional Sr/Ca ratio (Wilska, 1952).

TABLE 4

Comparison of Strontium in Waters and Sources

Water and Source	Sr/Ca
5 bog lakes, Connecticut and North Carolina	3.53
Possible source: rain water, 2 samples New Haven, Conn.	3.78
N. C. reservoir lake, draining residual soils on precambrian rock	3.69
Representing source: clay sediment (acid extract)	3.30
Central Connecticut lakes; drainage from Triassic shales and intrusions	1.77
Representing source: 5 soils (acid extract)	2.12
N. C. Lake Waccamaw, seepage lake with limestone outcrop	2.39
Representing source: outcrop marl	2.71
Pond with limestone outcrop, Covington, Kentucky	1.25
Representing source: outcrop limestone	1.23
37 Swedish lakes (data of Lohammar, 1938)	1.35
Representing source: Swedish rocks (Landergren, 1943)	0.3–2
Drainage from a strontianite marl dump (Haselhoff, 1893)	30
Representing source: marl from dump	7–35
Lake Wononskopomac, Connecticut, Stockbridge Marble region	1.32
Representing source: sample of bedrock dolomite	0.22
Hudson River, Poughkeepsie, N. Y., draining sedimentary area	2.65
Representing source: mean of world sediments	2.08
Philippine lakes (3) in volcanic region (see Table 17)	4.21
Representing source: rhyolite: andesite: basalt, 1:2:4 Odum (1950b), and 7 volcanic glasses	9.77
Boulder Creek, Colo. Data of Clarke (1915); Platte River draining alkali igneous Front Range of Rockies	4.2
Representing source: 78 igneous rocks from Colorado Front Range	3.1–43.0

THE TURNOVER FACTOR, CLOSED BASINS

Although the chemical constitution of a stream is largely a function of the geochemistry of the sources of water, a lake, on the other hand, has internal self-regulating systems and cycles which strongly modify the edaphically controlled properties (Hutchinson, 1948). Matter and energy pass continually through a lake, but the concentrations maintained in the lake water may be of entirely different nature from those in the inflows.

As one extreme, consider the flow of a river into a closed basin in which there is no outlet like the ocean or Great Salt Lake in Utah. As the concentrations of strontium and calcium increase in the water, the solubility product of the calcium carbonate is reached and precipitation begins. By solubility product we do not mean the chemical solubility product but the biogeochemical product which is the effective one. The calcium concentration thereafter remains constant with a steady balance between inflow and outflow. However, since most depositional processes exclude strontium selectively relative to calcium, the mineral matter being sedimented has a lower Sr/Ca ratio than the water from which it is derived. Thus strontium does not deposit as readily as calcium and its concentration in the water increases until with rising concentrations, the amount of strontium included in deposition becomes proportionately great enough to match that flowing into the basin. Eventually the Sr/Ca ratio in the sediments balances the Sr/Ca in the inflow water and an equilibrium is reached with respect to strontium, calcium and the relative amount of the two. In this state the Sr/Ca in the water of the basin is considerably higher than that in the inflowing waters as in the ocean, for example. Eardley (1938) showed the manner by which Mg/Ca ratio was maintained at a high level in the Great Salt Lake by this mechanism.

In the ocean the Sr/Ca of the sea water is about 9.0/1000 whereas the Sr/Ca ratio of representative world rivers is about 2.2/1000 (Odum, 1951a). The Sr/Ca of the Great

Salt Lake, Utah, is 4.2/1000 whereas the Sr/Ca in the inflowing rivers is 2.93/1000 (Alexander *et al.*, 1954). In another closed basin Seidell reported Sr/Ca of 11.5/1000 (Clarke, 1924).

In lakes which are not completely closed but retain the water for much longer times than do rivers, the situation is intermediate and slight increases of Sr/Ca ratio might be expected. Alexander *et al.* (1954), believed this action may have been in operation in the Great Lakes. As suggested by the Sr/Ca ratios from Lohammar (1938) in Figure 3 there was a rise in Sr/Ca ratio during a time of least turnover (August). Data from Linsley Pond, Conn. (Fig. 4) suggest a similar pattern with considerable variability.

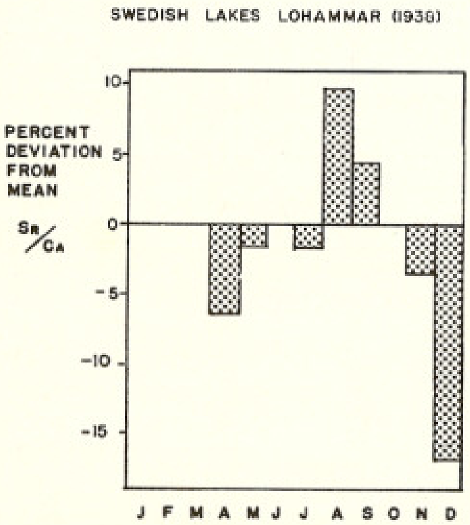

Fig. 3. Sr/Ca ratio in Swedish lakes at different times of the year based on data from Lohammar (1938). Data were not available for all months. The percent deviation of values from the mean for the particular lake is plotted. Higher Sr/Ca values occur in summer.

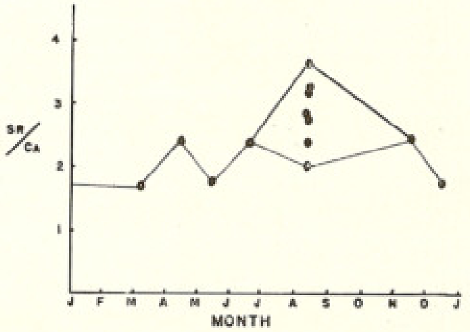

Fig. 4. Sr/Ca ratios in waters of Linsley Pond, Connecticut in 1949–50.

Illustrating the behavior of strontium during the evaporation of fresh waters is an analysis of calcium carbonate precipitate that resulted when 30 liters of water from Linsley Pond, Conn., was evaporated to 25 cc by Dr. Eva Low for another purpose. The precipitate that formed contained a Sr/Ca ratio of 1.25 atoms/1000 atoms, which is lower than most of the analyses of Sr/Ca ratio in Linsley Pond (1.65/1000) suggesting that strontium in comparison to calcium was excluded and left in the last 25 cc. Zeller and Wray (1956) found a similar increase in Sr/Ca ratio with successive precipitation.

The Sr/Ca values in closed basins will be especially high where the dilute inflowing drainage waters have high Sr/Ca ratios. For example the Lahontan Basin or the Southern California areas are much higher in strontium because of igneous, volcanic drainages than is the Bonneville basin with a predominantly sedimentary drainage.

GROUND WATER FACTOR

There are four processes which can produce higher Sr/Ca ratios in ground waters than in the surface waters from which they may be partly derived. The first process is the percolation through strata which contain pore space salt either from the ocean or from evaporite conditions in the source region. In Florida below the Suffolk Scarp at 25 ft. elevation, the land has been so recently beneath the sea that 25 to 10,000 ppm Cl still remains in the ground water (Odum, 1953; Black and Brown, 1951). As indicated in Figure 1 and Table 2, the ground waters and springs of Florida with high chloride contents have high Sr/Ca ratios, 5.7–9.3/1000. The Sr/Ca ratio for 9 Florida lakes is 2.62/1000 and for the springs including those without much chloride, 3.81/1000.

A second process which may produce higher Sr/Ca ratios in ground waters is the tendency for percolating waters to replace limestones and release strontium formerly held in the crystal lattices of the initial limestones. Evidence that this replacement process tends to lower Sr/Ca of rocks is summarized elsewhere (Odum, 1957).

A third process which may affect the Sr/Ca ratio in ground water is the differential behavior of the two elements in ion exchange processes in soils or clays. Both elements are bound by clays and organic matter. Apparently conditions exist which favor the relative retention of strontium in some cases and calcium in others. A discussion of this factor is included in the discussion of strontium content of some soils (Odum, 1957). There is little satisfactory evidence to indicate much consistent effect of soil exchange on the Sr/Ca ratio under steady state conditions.

A fourth process is the mixing of surface waters with hot solutions associated with thermal regions. Because of the high strontium content associated with vulcanism, such waters tend to have high Sr/Ca ratios.

Among mineral waters Francis (1923) found Sr/Ca 25.1/1000 and Clarke (1924) cites cases with a ratio of 28.7/1000. Such waters may have received strontium from several of these processes. M. Starr Nichols in a personal cummunication described some unusual well waters in eastern Wisconsin with 20 ppm strontium and Sr/Ca ratios up to 160 atoms/1000 atoms. Straub (1950) found up to 5.0 mg/1 strontium in mineral waters. Bororik-Romonova *et al.* (1954) found 4–390 ppm.

Among waters suitable for water supply, Alexander *et al.* (1954), believed that their data did not show indication of higher strontium in ground water than in surface waters. Such waters are selected for minimum mineralization. Many of the surface waters analyzed which had high strontium were in semi-arid regions or in areas of high geochemical strontium content. In spite of this selection an average of the 21 ground water values indicates a higher Sr/Ca ratio (3.8/1000) than 50 surface water values (Sr/Ca 2.5/1000). A diagrammatic picture of the relative behavior of strontium and calcium is shown in Figure 5 where representative values of solids and waters are given. The strontium removal into ground water is shown at a rate faster than that of calcium.

CORRELATION OF SALT AND STRONTIUM

It is well known that sodium and chloride are rapidly washed out of the sediments by percolating waters and that ground waters contain higher contents of these elements than other fresh waters (Conway, 1943). Thus waters percolating unreplaced sedi-

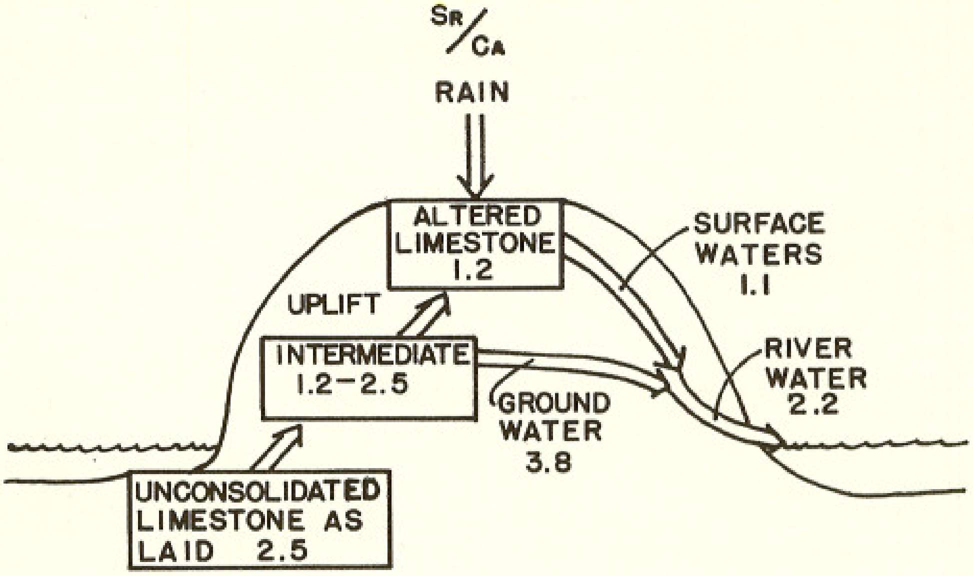

Fig. 5. The behavior of the Sr/Ca ratio in carbonate depositions during the sedimentary cycle. Values for various phases are means of data from this study. Strontium is more readily removed into solution during consolidation than calcium. This behavior accounts in part for low values af limestones and high values in ground waters.

ments like some in Florida yield high quantities of both sodium and strontium, whereas waters percolating older rocks like those in Connecticut yield lower amounts of salt and lower Sr/Ca ratios. Wherever salts of the sea or of arid basins are involved the Sr/Ca ratio tends to be high whether by direct mixture or from ancient deposits. Hydrothermal waters of volcanic regions are also rich in both strontium and chloride. Thus because of several mechanisms, there is a correlation of salt and strontium.

An example of the effect of ground-water salt in raising the Sr/Ca ratio is graphed in Figure 1. Data are plotted from the dilute ground waters of Florida (Odum, 1951c) and the brines of Kentucky (McGrain and Thomas, 1951). At salinities below that of sea water (1.9% Cl) the Sr/Ca ratio tends to decrease below the Sr/Ca ratio of sea water (9.0 atoms/1000 atoms) because of the solution of additional calcium from sedimentary rocks low in strontium. At salinities above that of sea water, the Sr/Ca ratio is observed to rise above the Sr/Ca ratio of sea water. Presumably deposition of calcium from the brines is occurring at the higher concentrations.

Regional differences in salt and strontium content are large. The difference in Sr/Ca ratio between hard waters containing salt (such as ground waters of the great plain) and hard waters low in salt (such as waters in Sweden) is striking. High Sr/Ca ratios also occur as discussed for igneous rocks where waters are very soft, or where substrates are volcanic.

Wherever waters receive little geochemical contribution but mainly elements from rain as in bog and seepage lakes a fairly high Sr/Ca ratio may be found as indicated in Table 1 for North Carolina, Connecticut, and Florida (Sr/Ca 2.0–4.5/1000). Two rainwater samples (Table 3) contained Sr/Ca ratio 3.8/1000. These moderately high values may reflect strontium of marine origin as well as of terrestrial dust origin. The widespread circulation of strontium containing dust is well known (Libby, 1956).

In surface waters close to the sea, high content of atmospheric transported salt may tend to raise the Sr/Ca ratios as it is known to do to chloride contents. It is difficul to separate this atmospheric factor from the space factor in low lying waters near th sea. In the Philippine lakes there is a volcanic factor also (Table 3).

VARIATION OF STRONTIUM IN SEA WATER

Although the strontium content of sea water seems established within small limits the question of variation needs consideration. Sr/Ca ratios of sea water are summarize in Tables 2 and 5.

TABLE 5

Analysis of Variance in Sea Waters of Long Island Sound

Variation Source	Degrees of Freedom	Sum of Squares	Variance	Variance Ratio	Significance
Within pairs from same bottle (analytical)	61	23.5241	0.3856	1.78	sig. P.05
Bottom vs. surface*	1	0.0661	0.0661	10.40	none
Between months*	11	4.2865	0.3897	1.76	none
Residual variation (includes analytical and any unaccounted water variation)	48	33.0047	0.6876	....	....
Total	122	60.8814			
Correction of mean	1			Mean = 9.21	

* Unequal numbers in each subclass.

The analytical error was large as indicated by a standard deviation of 0.6209 between pairs taken from the same bottle and run on the same day; 95% of the analyses were within 13.5% of the mean. On different days and different samples the errors were larger (standard deviation, 0.6876; 95% of the analyses within 18.1% of the mean).

Analysis of variance showed no significant differences within the limits of the methods used between the Sr/Ca ratios by season, or from top to bottom water. Chow and Thompson (1955) had less variation in data obtained by direct spectophotometry from surface to 2,000 meters in 3 series including Arctic, Pacific, and Atlantic oceans. From both studies it is apparent that strontium is a conservative element with a constant ratio to other major ions.

STRONTIUM IN THE ANCIENT OCEAN

A suggested pattern of evolution of the Sr/Ca ratio during the early history of the ocean is presented graphically in Figure 6. The proposed pattern is an elaboration of the idea presented previously that the present alkaline earth cycles of the world are in a steady state (Odum, 1951a). This hypothesis should be contrasted with a recent scheme proposed by Turekian and Kulp (1956) who suggest that the Sr/Ca ratio is a function of the present igneous drainage rather than of the cyclic sedimentary drainage now prevailing in the present era (Conway, 1943).

In Figure 6 the oceanic Sr/Ca ratio is at first fairly high and charactistic of basalt drainage. Then the ratio rises to a maximum while the first calcium carbonate is precipitating because of the elimination of strontium during carbonate deposition and consolidation. Finally, the Sr/Ca ratio drops again as the uplift of sediments begins

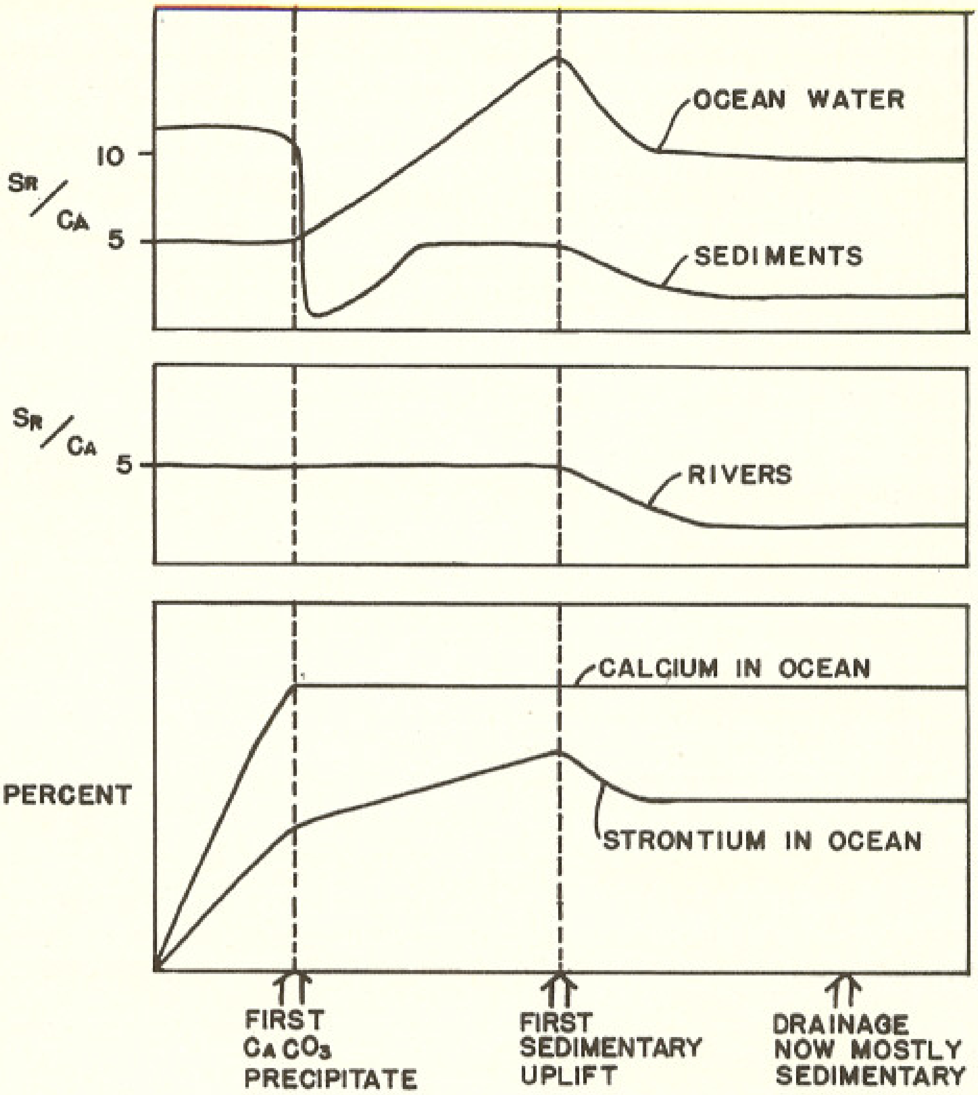

Fig. 6. A hypothesis of the behavior of the Sr/Ca ratio in the early history of the earth beginning with river drainage from a basaltic globe and an appreciable ocean with volatiles. Later a predominantly sedimentary drainage develops with a different steady state behavior of the Sr/Ca ratio. Sr/Ca ratios are given in atoms/1000 atoms.

because the rivers begin to draw much of their alkaline earth content from the uplifted sediments. By these schemes, the oceanic Sr/Ca ratio has decreased or been the same during the history of the ocean.

Summary

1. Three hundred analyses of strontium in natural waters are compared with published data in order to characterize the patterns and processes of the strontium cycle in the hydrosphere.

2. In non-marine waters, the Sr/Ca ratio of the region of water drainage is the mos important factor affecting the Sr/Ca ratio of waters. Sr/Ca values range fron 0.5 atoms/1000 atoms in areas draining replaced limestones to 5 atoms/1000 atoms o higher in areas of volcanic drainage.

3. Strontium is correlated with sodium chloride contents (a) because of the association of elements in waters deriving salt directly or indirectly from the sea; (b) because of the association of the elements in hydrothermal waters; (c) because of th tendency for both elements to be excluded from early sedimentary depositions anc secondary diagenisis to be deposited in late evaporites. These processes tend to produce high Sr/Ca ratios in ground waters.

4. In waters of closed basins which contain a steady state balance between th substances of inflowing river and the substances sedimented, the Sr/Ca ratio develops a higher value than in basins with outflows and high water turnover.

5. A discussion of the oceanic steady state between alkaline earth inflows and alkaline earth deposition does not support recently published ideas of increasing Sr/Ca ratio in the ocean.

6. In sea water all recent studies find strontium present as a conservative element with a constant Sr/Ca ratio of about 9.0 atoms/1000 atoms (8.0 mg/1 strontium in sea water of salinity 35 parts per thousand).

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