

STRONTIUM AND BARIUM IN SEA WATER AND MARINE ORGANISMS

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(Text-fig. 1)

Since the advent of nuclear fission, considerable interest has been aroused in the biological fate of strontium, as two isotopes of this element are among the longer-lived fission products of uranium. Strontium 90, in particular, constitutes the major hazard in old fission products because it is readily taken up by all kinds of plants and may then be concentrated in the bones of animals feeding on the plants. Strontium 90 contamination may be derived from fall-out from atomic explosions or from uncontrolled disposal of fission products. The oceans should receive more than twice as much Strontium 90 from fall-out as the continents because 70% of the surface area of the globe is covered by sea. The oceans are also used, though to a very limited extent at present, for the disposal of fission products from reactor wastes. Hence it is obviously important to study the behaviour of strontium in marine organisms in order to evaluate the health hazard caused by controlled or uncontrolled radioactive contamination of sea water. Barium has only relatively short-lived fission-product isotopes, but can readily be studied at the same time as strontium because of its similar chemistry.

Strontium and barium are elements which have long been known to occur in marine organisms and the sea. In the past, however, there have been considerable difficulties in the analytical determination of these two elements. Strontium, especially in trace amounts, is very difficult to separate from calcium, and while barium is more easily separated it is present in amounts so small as to tax the ingenuity of the conventional analyst. Spectrometric analysis has been used by several workers to determine these elements, but is not always sufficiently sensitive nor very precise. Recently, Harrison & Raymond (1955) and Bowen & Dymond (1955) have described the method of activation-analysis for these elements in animal and vegetable tissues respectively. In this work the same technique has been applied to determine strontium and barium in sea water and in various marine organisms.

METHODS

Collection and preparation of specimens

Sea water was collected and stored in polythene aspirators and all chemical manipulations were carried out using polythene apparatus. The chlorinity was determined by the Mohr titration method. Strontium was determined by activating 2 ml. samples of sea water sealed in polythene tubes with neutrons in the Harwell pile, BEPO. The associated activity, largely ^{24}Na and ^{38}Cl , after activation was considerable, and repeated precipitation with sodium carbonate was used to ensure complete decontamination from active sodium and chlorine. ^{139}Ba was separated from the ^{87}Sr , but could not be counted from such a small volume of sea water. Hence barium was concentrated from 1.5 l. samples of sea water using purified Zeo-Karb 225, sulphonated polystyrene resin. Columns of this resin, 15 cm long and 1 cm diameter, were set up in polythene tubes and were washed successively with 500 ml. 2N-NH₄Cl at pH 3.0, 500 ml. 6N redistilled HCl and finally 200 ml. redistilled H₂O. The NH₄Cl was made by passing cylinder ammonia into redistilled HCl in a polythene bottle. After this treatment samples of the resin left no residue after ashing at 500° C. Sea water 'spiked' with ^{140}Ba was then used to determine the break-through-volume of barium for the columns used. It was established that 88% of the barium in 1.5 l. of sea water was retained by the resin-column using a flow-rate of 2 ml./min. The losses were made up as follows:

| Passed through resin | Percentage Ba lost |
|-----------------------------------|--------------------|
| 500 ml. 'spiked' sea water | 0.4 |
| 1000 ml. 'spiked' sea water | 1.9 |
| 1500 ml. 'spiked' sea water | 8.3 |
| 500 ml. N/5 HNO ₃ wash | 3.8 |

After passing 1.5 l. of sea water through the column the resin was washed with 500 ml. of 0.2N redistilled HNO₃ and allowed to drain. Practically all the sodium, potassium and chlorine were removed in the eluent. The resin was then transferred to a silica basin and ashed at 500° C for 24 hr. The barium in the ash was determined by neutron-activation, taking care to remove sulphate ions from the activated ash by repeatedly boiling with saturated sodium carbonate solution and extracting the residue with hydrochloric acid. A 'blank' analysis of the clean resin showed no detectable barium.

Marine algae were collected in polythene bags and analysed as soon after collection as possible. Samples of tissue free from encrustations and parasitic algae were selected and washed with dilute choline chloride solution. They were then blotted dry and ashed in silica basins at 500° C: samples of the ash were used for activation-analysis.

Corals and mollusc shells were washed with distilled water, dried and ground in an agate mortar. They were not ashed before analysis.

Analytical methods

The method of activation-analysis has already been described (Harrison & Raymond, 1955; Bowen & Dymond, 1955). In this work ^{87}Sr was counted in liquid form in a scintillation counter as previously described, but ^{139}Ba was generally slurried on to a counting tray as the solid chromate, dried, and counted with an end-window EHM2 Geiger-Muller counter. Chemical yields were better than 95% for strontium and 90% for barium. Determinations of calcium were made by flame-photometry as described by Bowen & Dymond (1955).

RESULTS

Table I gives the strontium and barium contents of sea water from the English Channel corrected to 19.0‰ chlorinity.

TABLE I. STRONTIUM AND BARIUM CONTENT OF SEA WATER

| Vol. sea water taken | mg Sr/l. | Vol. sea water taken | $\mu\text{g Ba/l.}$ |
|-----------------------|-------------------|------------------------|---------------------|
| 400 ml. abs. on resin | 8.66 | 900 ml. abs. on resin | 5.8 |
| 2 ml. abs. on resin | 8.69 | 1500 ml. abs. on resin | 5.9 |
| 2 ml. abs. on resin | 8.30 | 1500 ml. abs. on resin | 6.8 |
| 2 ml. abs. on resin | 8.36 | | |
| Mean | 8.50 ₂ | Mean | 6.2 |

These figures should require a small correction because of the presence of uranium in sea water: ^{235}U undergoes nuclear fission on neutron activation and ^{92}Sr and ^{139}Ba are produced. The concentration of uranium in sea water is

TABLE II. ALKALINE EARTH CONTENT OF MARINE ALGAE

| Species | Where collected | p.p.m. dry wt. | | | wt./wt. | |
|-------------------------------------|-----------------|----------------|-------|------|---------|--------|
| | | Ca | Sr | Ba | Ca/Sr | Ca/Ba |
| Brown | | | | | | |
| <i>Fucus serratus</i> L. | Plymouth | 8,430 | 804 | 14 | 10.5 | 800 |
| <i>F. serratus</i> L. | Weymouth | 8,270 | 833 | < 23 | 9.9 | > 360 |
| <i>F. vesiculosus</i> L. | Weymouth | 8,180 | 702 | 9.5 | 11.6 | 860 |
| <i>Laminaria digitata</i> Lam. | Plymouth | 9,520 | 1,045 | 6.5 | 9.1 | 1,500 |
| <i>L. digitata</i> Lam. | Weymouth | 7,080 | 783 | < 23 | 9.0 | > 310 |
| <i>L. saccharina</i> Lam. | Weymouth | 7,720 | 698 | 11.3 | 11.1 | 680 |
| <i>Ascophyllum nodosum</i> Le Jol. | Weymouth | 8,320 | 428 | 5.6 | 19.5 | 1,500 |
| <i>Chorda filum</i> Lam. | Weymouth | 16,300 | 1240 | 18.6 | 13.2 | 880 |
| Mean | | 9,228 | 817 | 11 | 12 | 1,040 |
| Red | | | | | | |
| <i>Gigartina stellata</i> Batt. | Plymouth | 2,810 | 133 | 2.1 | 21 | 1,300 |
| <i>Chondrus crispus</i> Lyngb. | Plymouth | 6,420 | 131 | 5.6 | 49 | 1,100 |
| <i>Rhodomenia palmata</i> Grev. | Weymouth | 1,050 | 18.8 | 0.6 | 56 | 1,700 |
| Mean | | 3,427 | 94 | 2.8 | 42 | 1,370 |
| Green | | | | | | |
| <i>Enteromorpha compressa</i> Grev. | Plymouth | 10,300 | 87 | — | 120 | — |
| <i>E. intestinalis</i> Link. | Weymouth | 4,590 | 54.8 | 0.4 | 84 | 11,000 |
| <i>Ulva lactuca</i> L. | Weymouth | 3,840 | 38.2 | 2.5 | 100 | 1,500 |
| <i>U. lactuca</i> L. | Plymouth | 4,560 | 67.7 | — | 68 | — |
| Mean | | 5,822 | 62 | 1.45 | 93 | 6,250 |

about $1.5 \mu\text{g/l.}$ (Föyn, Karlik, Pettersson & Rona, 1939), and this would give rise to an apparent 0.0008 mg/l. of strontium and $0.2 \mu\text{g/l.}$ of barium.

Hence the correction is negligible for strontium and within the accuracy of the analysis for barium.

Tables II-IV give calcium, strontium and barium analyses for sea weeds, molluscan shells, and corals respectively.

TABLE III. ALKALINE EARTH CONTENT OF MOLLUSC SHELLS

| Species | Where collected | p.p.m. dry wt. | | | wt./wt. | |
|--------------------------------------|-----------------|----------------|-------|------|---------|-----------|
| | | Ca | Sr | Ba | Ca/Sr | Ca/Ba |
| Amphineura | | | | | | |
| <i>Acanthochitona crinitus</i> Penn. | Weymouth | 239,000 | 3,950 | < 10 | 60 | > 24,000 |
| <i>Lepidochitona cinereus</i> L. | Weymouth | 317,000 | 5,600 | 20 | 57 | 16,000 |
| Mean | | 278,000 | 4,775 | — | 58.5 | — |
| Gastropoda | | | | | | |
| <i>Patella vulgata</i> L. | Weymouth | 402,000 | 2,320 | < 4 | 173 | > 100,000 |
| <i>Littorina littoralis</i> L. | Weymouth | 388,000 | 1,720 | < 5 | 225 | > 80,000 |
| <i>Haliotis tuberculata</i> L. | Sark | 412,000 | 2,340 | < 7 | 176 | > 60,000 |
| <i>Rissoa parva</i> Da Costa | Lands End | 313,000 | 1,520 | < 6 | 206 | > 50,000 |
| <i>Bittium reticulatum</i> Da Costa | Kimmeridge | 361,000 | 1,420 | < 4 | 248 | > 90,000 |
| Scaphopoda | | | | | | |
| <i>Dentalium vulgare</i> Da Costa | Herm | 406,000 | 3,550 | 7.2 | 114 | 60,000 |
| Lamellibranchiata | | | | | | |
| <i>Arca tetragona</i> L. | Lands End | 353,000 | 3,260 | < 4 | 108 | > 90,000 |
| <i>Cardium echinatum</i> L. | Weymouth | 386,000 | 2,260 | < 1 | 170 | > 400,000 |
| <i>Pecten maximus</i> L. | Weymouth | 404,000 | 1,630 | < 3 | 247 | > 130,000 |
| <i>Lasaea rubra</i> Mont. | Kimmeridge | 375,000 | 1,820 | < 25 | 206 | > 15,000 |
| <i>Teredo megotara</i> F. & H. | Weymouth | 355,000 | 1,810 | 48 | 196 | 7,000 |
| Mean | | 377,700 | 2,150 | — | 188 | — |
| Cephalopoda | | | | | | |
| <i>Sepia elegans</i> D'Orbigny | Lands End | 243,000 | 2,910 | 20 | 84 | 12,000 |

TABLE IV. ALKALINE EARTH CONTENT OF RECENT CORALS

| Species | Where collected | p.p.m. dry weight | | | wt./wt. | |
|-------------------------------|------------------------------|-------------------|--------|------|---------|--------|
| | | Ca | Sr | Ba | Ca/Sr | Ca/Ba |
| <i>Millepora</i> sp. | Indian Ocean, 8 fm. | 323,000 | 7,360 | 8 | 44 | 40,000 |
| <i>Allopora norvegica</i> | N. Atlantic, 87 fm. | 303,000 | 7,760 | 18 | 39 | 17,000 |
| <i>Heliopora coerulea</i> | China Sea, 13 fm. | 325,000 | 6,520 | 85 | 50 | 4,000 |
| <i>Caulastraea furcata</i> | China Sea, 32 fm. | 324,000 | 13,400 | 11 | 24 | 30,000 |
| <i>Hydnophora polygonata</i> | China Sea, 6 fm. | 310,000 | 10,700 | 24 | 29 | 13,000 |
| <i>Pocillophora verrucosa</i> | China Sea, 13 fm. | 327,000 | 12,900 | 11 | 25 | 30,000 |
| <i>Psammocora planipora</i> | Indian Ocean, 60 fm. | 295,000 | 5,590 | 23 | 53 | 13,000 |
| <i>Seriatopora elegans</i> | China Sea, $\frac{1}{2}$ fm. | 332,000 | 12,500 | 11 | 27 | 30,000 |
| <i>Leptoseria solida</i> | Indian Ocean, 60 fm. | 326,000 | 8,680 | 12 | 38 | 27,000 |
| <i>Acropora</i> sp. | Persian Gulf, 63 fm. | 306,000 | 8,970 | 56 | 34 | 5,500 |
| <i>Alveopora</i> sp. | Indian Ocean, 39 fm. | 296,000 | 7,840 | 210* | 38 | 1,400 |
| <i>Merulina</i> sp. | China Sea, 30 fm. | 337,000 | 8,360 | 450* | 41 | 750 |
| <i>Stylopora</i> sp. | Muscat, 1 fm. | 323,000 | 8,490 | 43 | 37 | 7,500 |
| <i>Montipora</i> sp. | | 345,000 | 9,290 | — | 37 | — |
| <i>Amphihelia</i> sp. | | 345,000 | 10,650 | — | 32 | — |
| Mean | | 321,100 | 9,267 | 29.5 | 36 | 16,860 |

N.B. The two starred barium figures were omitted in taking the mean.

Fossil corals were also investigated and the results are collected in Table V.

TABLE V. ALKALINE EARTH CONTENT OF FOSSIL CORALS

| Species | Where collected | Geological age | p.p.m. dry wt. | | | wt./wt. | |
|---------------------------------|------------------|-----------------|----------------|------|------|---------|----------|
| | | | Ca | Sr | Ba | Ca/Sr | Ca/Ba |
| <i>Dendrophyllia elegans</i> | | Oligocene | 361,000 | 8300 | 66 | 44 | 5,500 |
| <i>Balanophyllia calyculata</i> | | Upper chalk | 326,000 | 6850 | 251 | 47 | 1,300 |
| <i>Caryophyllia cylindracea</i> | Wilts | Upper chalk | 335,000 | 640 | <5 | 523 | >67,000 |
| <i>Caryophyllia</i> sp. | | Upper chalk | 345,000 | 526 | 35 | 658 | 10,000 |
| <i>Coelosmilia regularis</i> | Wilts | Upper chalk | 310,000 | 524 | <9 | 591 | >34,000 |
| <i>Holocystis elegans</i> | Isle of Wight | Lower greensand | 83,900 | 278 | <21 | 301 | >4,000 |
| <i>Micrabacia coronula</i> | Yorks | Upper chalk | 270,000 | 273 | 8 | 990 | 34,000 |
| <i>M. fittoni</i> | S. England | Gault | 265,000 | 4230 | 160 | 63 | 1,700 |
| <i>Parastraea stricta</i> | | Cretaceous | 309,000 | 7640 | 18 | 41 | 17,000 |
| <i>Placosmilia rudis</i> | Lérída, Spain | Cretaceous | 312,000 | 1760 | <15 | 177 | >21,000 |
| <i>Trichosmilia granulata</i> | | Cretaceous | 369,000 | 530 | 15 | 695 | 25,000 |
| <i>Chromatoseris porpites</i> | Boulogne, France | Jurassic | 309,000 | 209 | <19 | 1040 | >16,000 |
| <i>Dimorphoseris terquemii</i> | Glos | Jurassic | 384,000 | 295 | <6 | 1300 | >64,000 |
| <i>Goniocera socialis</i> | Wilts | Jurassic | 335,000 | 1860 | <220 | 180 | >1,500 |
| <i>Isastraea explanata</i> | Berks | Jurassic | 391,000 | 1500 | <19 | 260 | >21,000 |
| <i>I. explanata</i> | Berks | Jurassic | 365,000 | 1130 | — | 322 | — |
| <i>I. limitata</i> | Dorset | Jurassic | 337,000 | 730 | <10 | 461 | >34,000 |
| <i>Montlivaltia delabecki</i> | Glos | Jurassic | 313,000 | 538 | <28 | 583 | >11,000 |
| <i>M. dispar</i> | Berks | Jurassic | 259,000 | 1356 | — | 184 | — |
| <i>Oppelismilia mucronata</i> | Leics | Lower Lias | 269,000 | 972 | 20 | 276 | 13,000 |
| <i>O. victoriae</i> | Oxon | Middle Lias | 254,000 | 548 | <66 | 465 | >4,000 |
| <i>Rhabdophyllia phillipsii</i> | Berks | Jurassic | 386,000 | 219 | <4 | 1760 | >100,000 |
| <i>Stylina tubulifera</i> | Wilts | Jurassic | 375,000 | 1540 | <210 | 243 | >1,800 |
| <i>Thamasteria arachnoides</i> | Wilts | Jurassic | 351,000 | 437 | — | 802 | — |
| <i>T. concinna</i> | Berks | Jurassic | 398,000 | 1180 | <2 | 338 | >200,000 |
| <i>T. defranciana</i> | Glos | Jurassic | 330,000 | 575 | <3 | 574 | >110,000 |
| <i>Thamasteria</i> sp. | Berks | Jurassic | 353,000 | 810 | — | 435 | — |
| <i>Theocosmilia annularis</i> | Wilts | Jurassic | 371,000 | 678 | <11 | 549 | >34,000 |
| <i>Dibunophyllum bipartitum</i> | Glos | Carboniferous | 277,000 | 418 | 8 | 661 | 35,000 |
| <i>Lithostrotion decipiens</i> | Glos | Carboniferous | 196,000 | 155 | <31 | 1270 | >6,000 |
| <i>L. martini</i> | Pembs | Carboniferous | 367,000 | 154 | 11 | 2380 | 33,000 |
| <i>L. pauciradiale</i> | Somerset | Carboniferous | 362,000 | 383 | <22 | 944 | >16,000 |
| <i>L. portlocki</i> | Westmorland | Carboniferous | 365,000 | 398 | 4 | 917 | 91,000 |
| <i>Lithostrotion</i> sp. | | Carboniferous | 353,000 | 304 | — | 1160 | — |
| <i>Lonsdaleia floriformis</i> | Glos | Carboniferous | 358,000 | 537 | <27 | 658 | >13,000 |
| <i>Michelimia favosa</i> | Pembs | Carboniferous | 241,000 | <850 | 17 | 233 | 14,000 |
| <i>M. megastoma</i> | Westmorland | Carboniferous | 305,000 | 902 | 5 | 338 | 61,000 |
| <i>Palaeosmilia murchisoni</i> | Glos | Carboniferous | 375,000 | 308 | <6 | 1250 | >62,000 |
| <i>P. regia</i> | Glos | Carboniferous | 356,000 | 733 | <44 | 486 | >8,000 |
| <i>Alveolites billingsi</i> | W. Ontario | Devonian | — | 364 | 6 | — | — |
| <i>A. cervicornis</i> | Devon | Devonian | 389,000 | 157 | 7 | 2480 | 56,000 |
| <i>Cystiphyllum vesiculosum</i> | Devon | Devonian | 113,000 | 489 | 35 | 230 | 3,200 |
| <i>Fasorites goldfussi</i> | Devon | Devonian | 400,000 | 675 | 3 | 592 | 130,000 |
| <i>F. stricklandi</i> | Salop | Silurian | 354,000 | 842 | — | 418 | — |
| <i>Halysites catenularius</i> | Worcs | Silurian | 305,000 | 1780 | <26 | 172 | >12,000 |
| <i>H. catenularius</i> | Salop | Silurian | 327,000 | 973 | 10 | 336 | 33,000 |
| <i>Kodonophyllum truncatum</i> | Salop | Silurian | 340,000 | 828 | 7 | 411 | 50,000 |

DISCUSSION

Our value for the amount of strontium in sea water is 5% higher than recent flame spectrometric determinations by Odum (1951a) and Chow & Thompson (1955), and an activation determination by Hummel & Smales (1956). The discrepancy may arise since our sample was collected near the shoreline whereas the other workers used oceanic water, but it is within the limits of accuracy of both methods. Our value for barium is considerably lower than has been previously reported. Thus Thompson & Robinson (1932) report 200 $\mu\text{g/l.}$, and von Engelhardt (1936) found 54 $\mu\text{g/l.}$ by a spectrometric method. The discrepancy is not surprising in view of

Goldschmidt's remarks (1937); 'In several cases we have found that in traditional methods of analytical determination of minor constituents a higher percentage of, for instance, barium, has been contributed from the reagents than from the specimen'. The mean of the published results for calcium in sea water of 19‰ chlorinity is 403 mg/l. (Harvey, 1955), so we find the Ca/Sr and Ca/Ba ratios in sea water to be 47.4 and 65,000 (wt/wt) respectively.

Relatively little work has been reported on the alkaline earth contents of marine organisms. Forchammer was the first worker to detect strontium (1859) and barium (1884) in the ash of *Fucus vesiculosus*, a species which later work has shown to be an accumulator and a discriminator for both elements. All the later analytical work has been spectrometric in nature. Fox & Ramage (1931) found strontium in nearly all the soft tissues of marine invertebrates they examined, but could not detect barium. Webb (1937) showed that two brown algae, *Fucus serratus* and *Saccorhiza bulbosa*, both discriminate for strontium and barium, while most of the seven molluscs studied discriminated against strontium. The mantle of *Archidoris britannica* is remarkably rich in strontium, which is interesting in view of the recent observations of Fretter (1953) and Rao & Goldberg (1954) that alkaline earths are absorbed largely through the mucus of marine invertebrates. McCance & Masters (1937) also record concentration of strontium by *Archidoris*. Analyses of algae by Borovik-Romanova (1939), Wilson & Fieldes (1941), and Black & Mitchell (1952) are of the same order as those found here. The last authors are responsible for the interesting observation that the strontium-content (p.p.m. dry matter) of all the algae studied diminished by a factor of 3-6 between January and June.

Shells of marine molluscs have been analysed for strontium by Vinogradov (1937) and for barium by Borovik-Romanova (1939) (see also Vinogradov, 1953). Earlier, Thomas, quoted in Thompson & Robinson (1932), stated that the Ca/Sr ratio in shells is roughly equal to the ratio in sea water. Our results do not support this contention, nor do those of Odum (1951*b*) who found a mean Ca/Sr ratio of 174 in a number of recent mollusc shells, in good agreement with our figures. Odum also showed that the shells of brachiopods discriminate against strontium about as much as molluscs: recent corals were found to have a mean Ca/Sr of 43, again in agreement with the present work.

The terms 'accumulation' and 'discrimination' as applied to the uptake of nutrient elements need clear definition, since different authors use these words in different senses. Black & Mitchell (1952) define an 'accumulation factor' which we will call A here, as

$$A = \frac{\text{p.p.m. element in dry organism}}{\text{p.p.m. element in sea water}},$$

while Spooner (1949) uses a more complex definition based on the effective dilution of sea water in the element per g of organism. In this work we shall

define a 'discrimination factor D ' for the uptake of a pair of related elements X and Y as:

$$D = \frac{X/Y \text{ in dry organism}}{X/Y \text{ in sea water}},$$

so that clearly

$$D(X, Y) = A(X)/A(Y).$$

The rather unwieldy data in Tables II-IV can be summarized in terms of mean accumulation and discrimination factors for the different groups (Table VI). Hence we see that all the organisms studied concentrate calcium, strontium and barium. Marked discrimination for strontium and barium occurs in the brown algae; the other algae discriminate for barium but not strontium. Mollusc shells, unlike corals, discriminate against both strontium and barium.

TABLE VI. MEAN ACCUMULATION AND DISCRIMINATION FACTORS FOR MARINE ORGANISMS

| Group | No. studied | A (Ca) | A (Sr) | A (Ba) | D (Sr, Ca) | D (Ba, Ca) |
|----------------------|-------------|--------|--------|--------|------------|------------|
| Brown algae | 8 | 23 | 96 | 1800 | 4.2 | 78 |
| Red algae | 3 | 8.5 | 11 | 450 | 1.3 | 53 |
| Green algae | 4 | 14.5 | 7.3 | — | 0.50 | 16 |
| Chiton shells | 2 | 690 | 560 | 2400 | 0.81 | 3.5 |
| Cephalopod bone | 1 | 600 | 340 | 3200 | 0.57 | 5.3 |
| Other mollusc shells | 11 | 940 | 250 | 650 | 0.27 | 0.7 |
| Corals | 15 | 800 | 1090 | 4400 | 1.4 | 5.5 |

The amount of ^{90}Sr which will ultimately reach the ocean from all atomic explosions to date is estimated to be about 0.8 megaCurie. If this were uniformly mixed into the ocean, which it certainly is not, this would amount to $5 \times 10^{-12} \mu\text{C/ml}$. Since $10^{-1} \mu\text{C}$ is about the smallest amount of β -activity that can be detected experimentally, 1000 kg of sea water would have to be concentrated down to determine this isotope. However, it should be possible to measure ^{90}Sr in kilogram samples of coral, since corals accumulate the element by a factor of 1000. This would constitute a very delicate test for the isotope in any given area of ocean. It might be possible to determine the rate of mixing of the oceans by measuring the ^{90}Sr content of corals from different depths. The hazard from contamination of the ocean by radioactive strontium is negligible at present, in view of the enormous quantities of naturally radioactive substances already existing there, e.g. nearly 500,000 megaCuries of ^{40}K alone.

The mechanism of accumulation of ions is fairly obvious. Large volumes of sea water are strained of their ions by natural ion-exchange systems in animals and sea weeds, and these ions may then be precipitated as insoluble inorganic structures (as is calcium in molluscs and corals) or retained in the ion-exchange systems (as in sea weeds). In this connexion it is interesting to notice that in

order to increase in weight by 1 g., a coral needs to filter all the calcium ions from 800 ml. of sea water. The barium content of the coral shows that it must have taken up all the barium from 4400 ml. of water, so that the efficiency of calcium uptake must be less than or equal to $800/4400$ or 18%. The accumulation factors of calcium and barium for molluscan shells are nearly equal, so that for these organisms the efficiency of calcium uptake may be as high as 100%. It is much more difficult to account for the discrimination between similar ions which we have found here. It is known, however, that ion-exchange resins always discriminate for the rarer of a pair of similar ions, and it is noteworthy that the very scarce ion, barium, is retained more strongly than the more common ion strontium in almost every case.

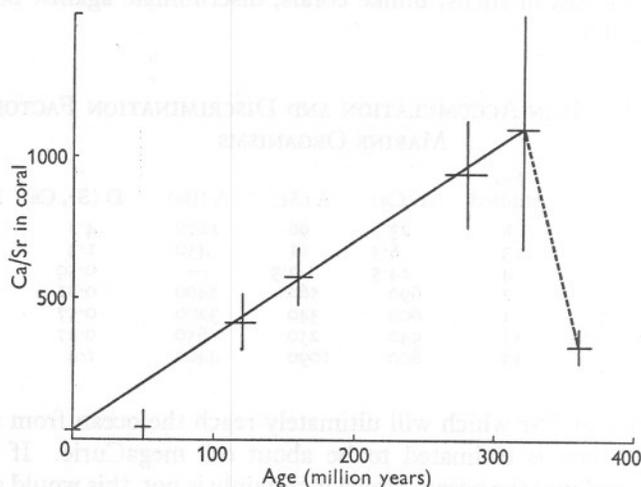


Fig. 1. Apparent Ca/Sr in corals plotted against geological age.

During inorganic precipitations traces of foreign ions are generally left in the mother liquor so that the precipitate is purer than the original solution. Barium and strontium are likewise excluded in the biochemical precipitation of calcium carbonate by molluscs, but not by corals. Some of the molluscs studied were constructed of calcite and others of aragonite, but we could find no consistent difference in strontium and barium content between the two forms. Theoretically one would expect strontium to prefer the aragonite structure to calcite.

The fossil corals were studied in order to check the results of Odum (1951*b*) and Kulp, Turekian & Boyd (1952) regarding the constant level of strontium in the ocean during geological time. These authors analysed a number of recent and fossil molluscs and brachiopods by a spectrometric method and reported that the Ca/Sr ratio remained constant at roughly 175/1 in all the specimens. We have two comments to make on this work.

In the first place molluscs and brachiopods are perhaps not the most suitable organisms for this kind of work since they discriminate against strontium by a factor of four. We have chosen corals since they appear scarcely to distinguish strontium from calcium. Secondly, the present day Ca/Sr ratio in sea water (50/1) is much smaller than in any common igneous or sedimentary rock, where it ranges from 120/1 to 1000/1. This suggests that strontium, like sodium and magnesium, is an element which has accumulated in the sea during the earth's history.

Our results are summarized in Fig. 1. They indicate a progressive increase in the Ca/Sr ratio with geological age, passing backwards in time as far as the Devonian period. The Devonian and Silurian results are of limited value because few samples of this age could be obtained. In addition, it is obvious that in the older samples the Ca/Sr ratios may have been drastically altered from their original values by recrystallization. This may well apply to the four Silurian corals analysed, as there is no reason to suppose a catastrophic change in the Ca/Sr ratio in the ocean between Devonian and Silurian times. Otherwise it appears that strontium has been steadily accumulating in the ocean during geological time.

SUMMARY

Strontium and barium have been determined in sea water. The strontium content of sea water was found to be 8.5 mg/l., in agreement with recent work, but the barium content (6.2 μ g/l.) is lower than previously reported values.

Strontium and barium have also been determined in a number of marine algae, mollusc shells and corals. All the organisms studied concentrate these elements from sea water, but whereas brown algae discriminate markedly for them in preference to calcium, mollusc shells discriminate against them.

The amounts of strontium found in fossil corals are very much smaller than they are in recent corals, and there is an approximately linear relation between the Ca/Sr ratio and geological age as far back as the Devonian period: the Silurian results are anomalous. It is suggested that strontium is an element which accumulates in sea water, though further work is needed to establish the point.

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