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STUDIES ON THE METHOD FOR THE PREPARATION OF STRONTIUM FROM CORALS AND CALCAREOUS ALGAE

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(1) INTRODUCTION

Storntium is a metal important for chemical, medical and other industries. The occurrence of minerals containing strontium, e. g., coelestine and bromlite, is rare in Japan. Hence it is of the utmost importance to develop all possible methods for extracting from sources hitherto unexploited strontium. It has been known that the skeleton of some radiolaria solely consists of strontium sulfate[1]. In order to know, accordingly, whether or not these organisms can be expected to be a good resource for strontium, the auther first made the determination of strontium in the marine calcareous materials, especially in corals and calcareous algae, and has further tried to extract strontium from these organisms.

(2) ESTIMATON OF STRONTIUM IN CORALS AND CALCAREOUS ALGAE.

Determinations have been made of strontium in corals and calcareous algae by the gravimetric method of Rose-Stromeyer-Fresenius[2]; see table I.

It is seen from the table that these calcareous organisms mainly consist of carbonate of calcium, magnesium and strontium. The strontium oxide content is 2.9 per cent in fresh corals, I. 97 per cent in whitened corals, which have remained for a long time on the sea shore, and 0.87 per cent in fresh calcareous algae. As a result of research conducted on molluscs, marine algae, the bone of tunny fish and the other invertebrates[3] it was found

Table 1

	Specimen	Moisture (%)	SiO_2 (%)	CaO (%)	SrO (%)	MgO (%)	Fe_2O_3 (%)	P_2O_5 (%)	SO_3 (%)	Cl (%)	CO_2 (%)	Protein (%)	Fat (%)	Reference
Corals	Stylophora sp., No. 1.	0.80	1.46	50.19	2.00	0.69	0.42	0.004	0.69	0.12	41.4	0	—	whitened
	,, ,, No. 2.	2.16	0.01	50.62	3.94	0.87	0.52	0.005	0.58	0.27	40.0	0.69	0.054	fresh
	Coeloria sp.,	1.04	0.62	52.87	1.38	0.51	0.40	0.004	0.34	0.10	41.5	0.25	—	whitened
	Favia amplior	0.97	0.03	50.52	3.62	0.80	0.30	0.007	0.72	0.60	40.1	1.13	—	fresh
	,, sp.,	0.94	0.98	50.64	2.24	1.12	0.48	0.014	0.46	0.33	39.8	0.69	—	,,
	Favites sp.,	1.35	1.33	51.20	2.00	0.98	0.36	0.012	0.76	0.43	40.2	0.63	0.29	,,
	Goniastraea sp., No. 1.	1.05	1.69	51.80	0.87	0.62	0.36	0.008	0.46	0.16	40.6	0.12	—	whitened
	,, ,, No. 2.	0.98	1.36	50.96	1.25	0.51	0.26	0.005	0.55	0.13	41.2	0	—	,,
	Cyphastraea sp., No. 1.	0.66	1.83	51.96	1.47	1.37	0.34	0.004	0.45	0.16	41.0	0	0.01	,,
	,, ,, No. 2.	1.57	1.53	49.06	1.03	2.06	0.52	0.006	0.31	0.38	40.2	0.25	—	,,
	Phymastraea sp., No. 1.	1.86	0.58	52.34	0.44	0.87	0.30	0.007	0.45	0.11	42.0	0.37	—	,,
	,, ,, No. 2.	0.94	1.49	50.04	2.14	1.02	0.84	0.006	0.41	0.15	40.9	0.31	—	,,
	,, ,, No. 3.	1.22	1.14	52.32	1.02	1.20	0.30	0.008	0.41	0.21	40.4	0.12	—	,,
	Domoseris sp.,	2.79	0.77	47.12	3.38	1.09	0.60	0.008	0.65	0.26	39.6	0.75	—	,,
	Madrepora sp.,	1.95	0.24	51.20	2.36	0.66	0.54	0.006	0.65	0.17	40.2	0.35	0.175	fresh
	Turbinaria foliosa	0.59	0.17	51.74	2.35	0.58	0.42	0.007	0.38	0.18	40.5	0.44	—	,,
	,, elegans No. 1.	0.84	0.09	50.44	2.44	1.88	0.52	0.006	0.69	0.13	41.0	0.44	0.41	,,
	,, ,, No. 2.	0.94	0.	50.88	4.02	0.54	0.36	0.009	0.82	0.24	40.0	0.45	—	whitened
	Seriatopora sp.,	1.54	2.0	47.21	3.15	0.83	0.32	0.011	0.65	0.13	41.0	0.25	—	,,
	Species unknown No. 1.	0.74	2.29	49.99	0.63	2.25	0.36	0.007	0.51	0.13	41.0	0	—	,,
	,, ,, No. 2.	1.15	0.87	48.24	4.86	0.91	0.50	0.006	0.58	0.11	40.7	0.19	—	,,
	,, ,, No. 3.	1.46	0.44	47.26	3.08	3.95	0.80	0.005	0.28	0.08	41.3	0	—	,,
	,, ,, No. 4.	1.03	0.40	52.32	1.35	0.87	0.38	0.009	0.38	0.13	42.2	0	—	,,
	,, ,, No. 5.	1.54	1.50	51.80	0.78	0.80	0.36	0.006	0.55	0.20	41.2	0.19	—	,,
Calcareous algae	Goniolithon frutescens	2.43	—	45.64	1.35	8.69	—	—	0.34	0.25	41.6	—	—	fresh
	Cheirosporum maximum	5.70	—	43.21	0.62	5.73	—	—	—	—	—	—	—	,,

that these values represent the highest degree of strontium content for this variety of marine organisms.

On the other hand, it is well known that coral reefs are generally formed of corals or, in some cases, calcareous algae as Halimeda. Since these organisms are widely distributed over the southern areas of the Pacific ocean, they are worthy of being examined for the value they have as a resource for the preparation of strontium.

(3) Process for the Preparation of Strontium

Corals and calcareous algae are crushed into small particles. By heating in an electric furnace at a temperature of 1200~1300°C for several hours, they are calcinated and changed into inorganic oxide of calcium, magnesium and strontium. These metal oxides are poured into water free from carbon dioxide and hydrolysed to corresponding hydroxides as follows:

$$MeO + H_2O \rightleftarrows Me(OH)_2 \quad \left(\begin{array}{l}\text{Me means metal of}\\ \text{Ca, Mg and Sr.}\end{array}\right)$$

The hydroxides of calcium and magnesium are barely soluble in water whereas strontium is easily soluble as is seen from the following figure.[4]

grams dissolved in 1000 c.c. of water at 20°C	$Ca(OH)_2$	$Mg(OH)_2$	$Sr(OH)_2$
	1.65	0.01	35.64

Thefore, the filtrate contains besides strontium hydroxide the other impurities as alkaline metals and a small amount of hydroxides of calcium and magnesium.

When a solution of sulfuric acid or sulfate is added to the filtrate, a reaction occurs as follows:

$$Sr(OH)_2 + H_2SO_4 \rightleftarrows SrSO_4 + 2H_2O$$

As a result of this reaction, sulfate of calcium, magnesium and the other alkaline metals are easily soluble in water, but strontium sulfate is less soluble. Thus, a pure strontium sulfate can readily be precipitated and separated from the solution. The degree of the insolubilities of these sulfates makes the separation quite feasible as is seen from the following figure.[5]

grams dissolved in 1000 c.c. of water at 10°C	$CaSo_4$	$MgSO_4$	$SrSO_4$
	1.93	107.16	0.99

Strontium sulfate is then collected and dried. It is obtained as a white, pure crystal of rhombic form.

Experiment I.

One kilogram of whitened Madrepolaria is crushed into small particles and heated in the electric furnace at 1200°C for 5 hours. After cooling, 650 grams of the calcinated materials are poured into 3 liters of water, free from carbon dioxide, and allowed to remain for about 3 hours. Then the solution is filtered off, and the precipitates are washed several times with small portions of cold water. The filtrate contains besides strontium hydroxide about 4.5 grams of calcium hydroxide and the other alkaline metals. 15 grams of concentrated sulfuric acid are then added. After allowing to stand for 10 hours, crystals of strontium sulfate separate completely from the solution. They are collected on the filter paper and washed several times with cold water and dried at 100°C for 2 hours.

Strontium sulfate thus obtained was a white, pure crystal, yield of which was 40 grams.

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