Cathodo-luminescence as Applied to the Detection of Rare Earths Contained in Some Natural Calcareous Substances

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Introduction

Crookes detected minute amounts of yttrium and samarium in calcareous portions of some marine organisms. It has been said that this fact led him to a confirmation of the presence of rare earths in sea water.[1] Goldschmidt found rare earths also in the calcium carbonate, which constitutes reef corals.[2] As is well known, some of the rare earths contained in calcium oxide behave as activators in giving the characteristic luminescence under the cathode-ray bombardment, the spectra of which consist of fairly sharp line-like bands. This phenomenon proved already to be an efficacious aid in making some geochemical researches: Rare earths sparingly present in anorthite and

1) Cited in V. M. Goldschmidt, *J. Chem. Soc.*, **1937**, 667.

2) V. M. Goldschmidt, *J. Chem. Soc.*, **1937**, 667.

TABLE I

CATHODO-LUMINESCENCE SPECTRA DUE TO RARE EARTHS CONTAINED IN CONVERTED CALCIUM-OXIDE SAMPLES

Wave-length	Miyako Main Isle		Akiyoshi	Hiroshima
(mμ)	*Acropora*	*Pocillopora*	Stalactite	*Licina*
648.0	w	—	wwb	—
639.5	w	—	wwb	—
633.4	m	w	m	—
626.0	s	w	s	—
620.0	ww	—	w	—
616.0	w	ww	w	—
613.2	w	—	w	—
606.6	ss	m	ss	w
604.6	m	—	s	—
596.5 594.0	ww	—	w	—
590.3	ww	—	—	—
588.0	w	w	w	—
585.2	ss	m	s	w
583.4	w	—	w	—
580.5	w	—	ww	—
578.5	w	—	ww	—
575.9	w	w	w	—
571.3	w	—	w	—
568.3	—	—	ww	—
558.6	—	—	ww	—
555.0 552.1	ww	—	ww w	—
549.2	—	—	w	—
546.3	w	—	ww	—
543.3	—	—	w	—
537.0	—	—	w	—
517.0	—	—	ww	—
500.0 499.0	ww	—	ww	—
494.6	ww	—	ww	—
489.8	w	—	ww	—
486.9	ww	—	w	—
483.8	ww	—	ww	—
481.7	ww	—	ww	—
479.9	w	w	ww	—
477.0	ww	ww	—	—
460.5	—	—	ww	—
457.2	—	—	w	—
454.3	—	—	ww	—
448.5	—	—	ww	—
439.0	—	—	ww	—
436.9	—	—	w	—
421.8	—	—	ww	—
421.0	—	—	ww	—
419.5	—	—	ww	—
418.0	—	—	ww	—
416.0	—	—	ww	—
415.0	—	—	ww	—
413.5	—	—	ww	—
411.8	—	—	ww	—

ordinary augite from Taga volcanoes in Shizuoka Pref. were investigated by means of the cathodo-luminescence spectra, which appeared in one paper[3] entitled "A short note relating to the evolution of magma", and the detection of rare earths was also made by the inspection of cathodo-luminescence spectra, which is seen in another paper[4] entitled "On the crystallisation of fluorites," regarding two kinds of samples of fluorite from Tateiwa village, Fukushima Pref. one is a green octahedral crystal crystallised at an earlier stage and the other a violet cubic one at a later stage.

In the present paper the applicability of the cathodo-luminescence method to the detection of rare earths is revealed on such natural calcareous substances as reef coral, stalactite, molluscan fossil and calc-sinter.

Materials and Experimental Procedures

Seven specimens were used in the experiments; two reef corals, one stalactite, one molluscan fossil, and three calc-sinters. Two kinds of reef corals from Miyako Main Isle, *Pocillopora Sp.* and *Acropora variabilis Verrill* are reproduced in Figs. 1 and 2 respectively. The former is of amber white antler form and the latter has an appearance closely resembling a group of small flower clusters, like those of a cauliflower. It is to be mentioned that the *Acropora* is soluble in hydrochloric acid without any perceptible residues,

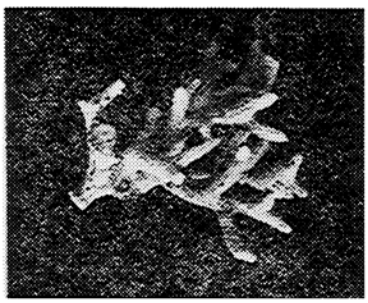

Fig. 1. *Pocillopora sp.*

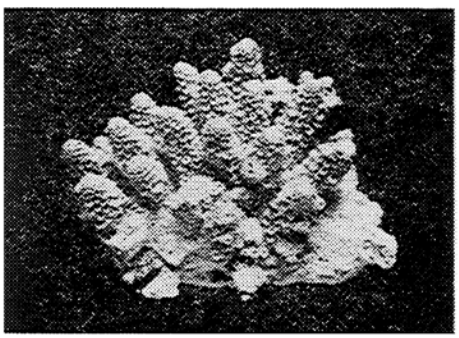

Fig. 2. *Acropora variabilis verrill.*

3) E. Iwase, *J. Chem. Soc. Japan*, **63**, 633 (1941).
4) E. Iwase, *Bull. Inst. Phys. Chem. Researches* (Tokyo), **21**, 61 (1942).

while the *Pocillopora* leaves a thin transparent yellow cuticular sack after the same treatment.

An ochrey stalactite from Akiyoshi in Yamaguchi Pref. shows, when cut crosswise, onyx-like banding near the periphery and radiated structures in the center portion.

A molluscan fossil, *Licina* (*Anodontia*) *Sp.*, which was found at Hiroshima city, is greasy, translucent and stained with reddish brown tint.

Calc-sinters occurring at Senami springs in Niigata Pref., Miné springs is Shizuoka Pref. and Shirahone springs in Nagano Pref. were also delivered to the author.

About 10 g. of each specimen were dissolved in hydrochloric acid, the solution thus produced was made slightly acidic by the controlled addition of ammonia, and then 2 g. of oxalic acid were added. Rare earths, if present in the original specimen, would have been coprecipitated with calcium as oxalates, which would then be converted to the oxide-form by the calcination. The same procedure is repeated once more, the only difference being the application of a much smaller amount of oxalic acid (0.5 g.). In this way the concentration of rare earths in calcium oxide is increased about fifty times, compared with that in the original specimen. The converted calcium oxide thus obtained is subjected to the cathode-ray bombardment in a small Urbain tube and the luminescence brought about is spectrographically investigated by employing a glass-prism spectrograph of Feuss.

Experimental Results and Discussions

The results of cathodo-luminescence spectra given by the converted calcium-oxide samples from reef corals, stalactite and molluscan fossil are summarised in Table I. Relative intensities are estimated visually and indicated by the following symbols: ss(very strong), s(strong), m(medium), w(weak), ww(very weak) and b(broad).

TABLE II
RARE EARTHS DETECTED BY CATHODO-LUMINESCENCE BANDS

Localites	Specimens	Rare earths identified
Miyako Main Isle	*Acropora*	Dy, Pr, (Sm), (Tb)
	Pocillopora	Dy, Pr, (Sm)
Akiyoshi	stalactite	Dy, Pr, Sm, Tb
Hiroshima	*Licina*	Dy, Pr

The presence of dysprosium and praseodymium in these four specimens is confirmed, as illustrated in Table II, by comparing the wave-lengths of the observed luminescence bands with Fagerberg's data[5], which give the precise numerical figures for the wave-lengths of the cathodo-luminescence bands yielded by the calcium oxide containing each individual rare earth element. Furthermore,

5) S. Fagerberg, *Nova Acta Regiae Societatis Scientiarum Upsaliensis*, Ser. IV, Vol. 7, No. 6 (1931).

samarium and terbium are distinctly detected in the stalactite and also perceptible in the *Acropora*, whereas not at all in the molluscan fossil. Under the conditions of the present experimental work, none of the calc-sinters investigated here revealed the presence of rare earths.

To be precise, the concentration of rare earths in the samples of converted calcium oxide has been increased 45 and 67 times for the *Acropora* and the *Pocillopora* respectively. It is a remarkable fact that the luminescence bands due to dysprosium, samarium and terbium have been all distinctly visible in the case of *Acropora variabilis Verrill*, but have been, in the case of *Pocillopora Sp.*, found much weaker in intensity with the complete disappearance of the terbium bands, although the latter specimen has been subjected to a considerably higher concentrating treatment than the former one. These observations may possibly be interpreted by a distinction found between the surface conditions of the two reef corals; *Acropora variabilis Verrill* seems to be naked, while the surface of *Pocillopora Sp.* is covered by a thin superfacial membrane of organic nature, which would be expected to exercise various restricting influences on the assimilation of rare earths from sea water during the natural growing process of the reef corals.

Summary

Specimens of reef corals, stalactite, molluscan fossil and calc-sinters were converted to the form of oxide, in which rare earths, if present in the original specimens, would be concentrated by chemical means. Luminescence spectra given by these samples of calcium oxide were investigated under the cathode-ray bombardment and the presence of minute amounts of rare earths could be confirmed; dysprosium, praseodymium, samarium and terbium in a stalactite from Akiyoshi, dysprosium, praseodymium and presumably samarium in reef corals from Miyako Main Isle, and dysprosium and praseodymium in a molluscan fossil from Hiroshima. Not even slight traces of rare earths were perceived in calc-sinters from several springs, so far as this detecting method was concerned. Two kinds of specimens of reef corals from the same locality gave a remarkable difference in the rare-earth content and this observation may be explained by the different conditions of the surfaces found in these reef corals, during the growth of which the assimilation of the rare earth ions from sea water were possibly much more disturbed by the existence of an organic membrane covering the surface of one specimen as compared with another lacking such a membrane.

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