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# Concentration and State of Cerium in Coastal Waters<sup>1</sup>

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## ABSTRACT

The cerium contents of several coastal water samples were found to be 0.1 to 0.6  $\mu\text{g/l}$ . These are in contrast to the cerium concentrations of 0.004 and 0.014  $\mu\text{g/l}$  observed in samples taken near Bermuda. The edible portions of several marine organisms were analyzed to determine concentration factors. These were observed to be less than 20 for striped bass (*Roccus saxatilis*), less than 100 for oysters (*Crassostrea virginica*), and 1000 for soft clams (*Mya arenaria*).

Radioactive cerium added to coastal waters became associated with the natural solids, particularly material with apparent diameters of 0.02 to 0.1  $\mu$ . Removal of the natural solids permits apparent solubility of several micrograms per liter for added cerium. Fluorometry was used to observe oxidation of +3 cerium added to seawater. The oxidation is pH-dependent, indicating the importance of ceric-hydroxide precipitation and complexing. The oxidation is inhibited by increased phosphate concentrations, suggesting a strong phosphate complex.

*Introduction.* Observations of the cerium content in natural waters are not numerous. At the time that the work described here was undertaken, only a single value, 0.4  $\mu\text{g/l}$ , had been reported by Goldschmidt (1937), and this sample was for an unspecified location. Recently, Goldberg et al. (1963) reported results for most of the rare-earth elements in seawater samples collected near San Diego, California, including a cerium value of 0.0013  $\mu\text{g/l}$  for a surface sample.

Interest in cerium distribution has increased as a result of the introduction of cerium radioisotopes into marine waters. Studies of cerium radioisotopes in the marine environment under field and laboratory conditions have been reviewed by Palumbo (1963). He summarized the physico-chemical properties

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of cerium as being common to the rare-earth group and characterized their occurrence as particulate, with a resulting low level of uptake by marine organisms.

We have measured the cerium content in coastal waters to provide a basis for better understanding of the behavior of natural cerium and radiocerium added to these waters. Measurement of the cerium content of several marine organisms for comparison with the observed uptake of radiocerium was also undertaken.

*Analytical Procedure for Cerium in Water Samples.* The cerium was collected with hydroxide precipitation of ferric chloride added to the sample, after removal of carbon dioxide to avoid precipitation of carbonates. Ion-exchange chromatography was used to isolate the cerium from the collected iron and other elements. Carrier-free  $Ce^{141}$  was added to the original sample to estimate the recovery of cerium throughout the whole of the manipulations. Terminal analysis by ultraviolet spectrophotometry was based on oxidation to the strongly absorbing ceric sulfate complex, followed by reduction with hydrogen peroxide to provide an absorbance difference specific for cerium.

**SAMPLING.** Approximately 200-l samples were collected with a submersible pump and polyethylene hoses directly into polyethylene tanks, except for the ocean samples that were collected with a large-volume sampler (Bodman et al. 1961). Precipitation was carried out in these tanks, except for those samples from which the settleable solids were separated. Loss of added radioactive cerium to the tank walls was found to be less than 3.5%.

**PRECIPITATION.** Distilled hydrochloric acid was added to the sample to bring the pH to about 4.6, air was bubbled through the sample for 3 to 4 hours, and then additional acid was used to lower the pH to 3. A solution containing 4 g ferric chloride and carrier-free  $Ce^{141}$  equivalent to  $2 \times 10^4$  cpm was added and mixed thoroughly. The pH was adjusted to 9 with distilled ammonium hydroxide solution, and the resulting precipitate was allowed to settle for several days. Iron analysis of the supernatant indicated that 95% of the added iron settled out.

The supernatant was drained off slowly until 10 l remained in the tank. The precipitate was resuspended and then collected in a single 200-ml centrifuge bottle by successive aliquot centrifugation at 170 RCF. The collected material was extracted with 40 ml of 0.2 N HCl at 80°C for several hours. Cerium minerals, such as monazite, were probably not decomposed by this treatment. The insoluble residue was washed with 0.1 N HCl and water, and the extracts were combined for centrifugation at  $4 \times 10^4$  RCF for one hour to remove the very small particles that would clog the ion-exchange column. The resulting acid solution (pH approximately 1) was diluted to 100 ml volume, and sufficient 0.1 M  $Na_2EDTA$  was added to complex 90% of the iron present.



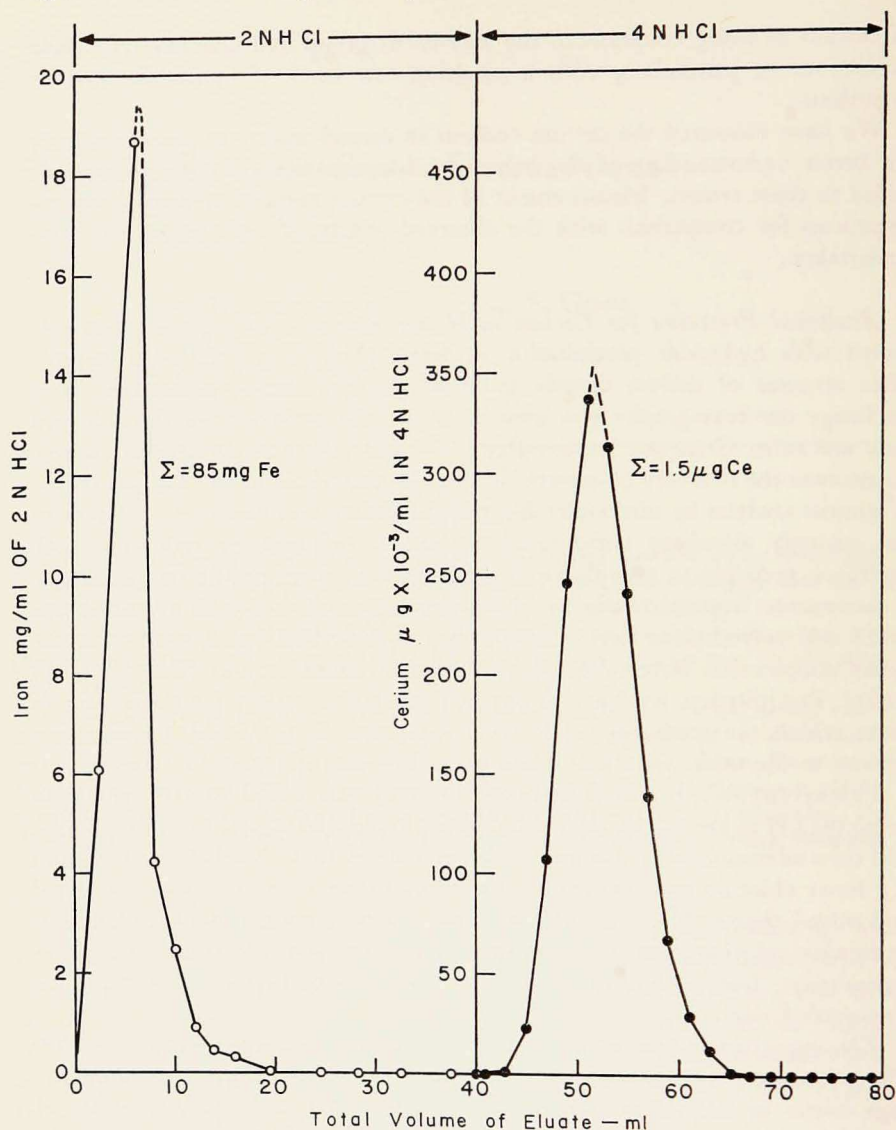


Figure 1. Successive elution of iron and cerium for a synthetic sample from a Dowex 50 ion exchange column.

ION-EXCHANGE. The work of Strelaw (1960) indicated that cerium could be separated from iron and other cations by ion-exchange chromatography. This was confirmed by the results for a synthetic sample as shown in Fig. 1.

The acid solutions from the precipitation sequence were passed through an 8-mm diameter and 8-cm long column of Dowex 50 ( $8 \times 100-200$  mesh).

The iron and other cations were eluted with 40 ml of 2 N HCl, and then the cerium was eluted with 40 ml of 4 N HCl. Following evaporation of the eluate to near dryness, the residue was redissolved in 2 ml of 5 N HCl and diluted to 100 ml with distilled water. The chromatographic separation was repeated. The eluted cerium was treated with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  to remove traces of organic material derived from the ion-exchange resin. The dried residue was dissolved in 10 ml of water, and aliquots were taken for radiation counting and spectrophotometric cerium analyses. Recovery of added cerium tracer ranged from 60% to 75% for the samples. Results for each sample have been corrected for yield.

**SPECTROPHOTOMETRIC CERIUM MEASUREMENT.** The method described by Blatz (1961) was used with slight modifications that gave improved sensitivity and precision. An aliquot containing 1 to 6  $\mu\text{g}$  cerium was placed in a 10-ml Erlenmeyer flask and diluted to 4.0 ml. Following the addition of 0.55 ml 1 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , 0.025 ml 5 mM  $\text{AgNO}_3$ , and 0.1 ml 12 N  $\text{H}_2\text{SO}_4$ , the solution was heated in an 80°C water bath for 30 minutes. The solution was cooled quickly in an ice-water bath and allowed to stand for 24 hours at room temperature.

The oxidized cerium solution was transferred to a 12-cm pathlength cuvette that had a capacity of 5.5 ml, which was used volumetrically. The absorbance spectrum of the solution was measured between 320 and 360  $m\mu$  with a Beckman DK-2 spectrophotometer, using a reagent blank in the reference path. The cerium was reduced with 0.010 ml of 1%  $\text{H}_2\text{O}_2$  solution and the spectrum was measured again. Changes in absorbance at 320, 340, and 360  $m\mu$  were used to calculate cerium concentrations, using calibrations prepared concurrently with known cerium solutions. The replication of the measurement at the several wavelengths gave a precision estimate and also provided evidence for the absence of interfering elements. Additional evidence for the absence of interference was repetition of the chromatography without significant alteration of the photometric results.

*Results of Cerium Analyses on Water Samples.* The data for the samples are shown in Table I. The Bermuda samples had much lower cerium concentrations than those found in the coastal samples. The 900-m and 2000-m depths composite sample had a cerium content that is comparable to that observed by Goldberg et al. (1963) for a seawater sample collected 15 km west of San Diego, California. The surface Bermuda sample concentration was higher, for which we have no explanation.

The cerium concentration of the samples had some covariance with the suspended solids, as shown in Fig. 2. The coastal samples had cerium concentrations corresponding to approximately 55 ppm if all the cerium were associated with the solids. However, for the sample off the entrance to Chesapeake Bay, the settleable solids had a cerium concentration of 48 ppm and the unsetttable

Table I. Cerium concentration in water samples from several localities.

Sample location	Date	Depth	Cl (‰)	Solids* (mg/l)	Cerium ( $\mu$ g/l)
Inlet at Ocean City, Maryland . . .	Oct. 1963	surface	17.2	15	0.85
Atlantic Ocean, 54 km from entrance to Chesapeake Bay	Oct. 1963	surface	18.2	2§	0.18
				1§	0.12
				12§§	0.58
Chesapeake Bay near Annapolis, Md.	Jan. 1964	surface	8.2	4.5	0.18
Atlantic Ocean, 6 km from Cape Kennedy, Florida . . . . .	Mar. 1964	surface	20.0	1.9	0.14
Atlantic Ocean, 23 km from Bermuda . . . . .	June 1964	surface	20.3	0.1	0.014
		900 m and			0.004
		2000 m composite			

\* Insoluble in 0.4 N HCl.

§ Duplicate samples, settled 7 days and liquid decanted, solids remaining and cerium analysis on these supernatant samples.

§§ Composite of settled solids from both samples.

fraction had 90–120 ppm concentration. The surface Bermuda sample had 140 ppm cerium to solids ratio. The less dense or smaller sized materials appear to be richer in cerium than the settleable materials or else an appreciable fraction of the cerium is present in solution.

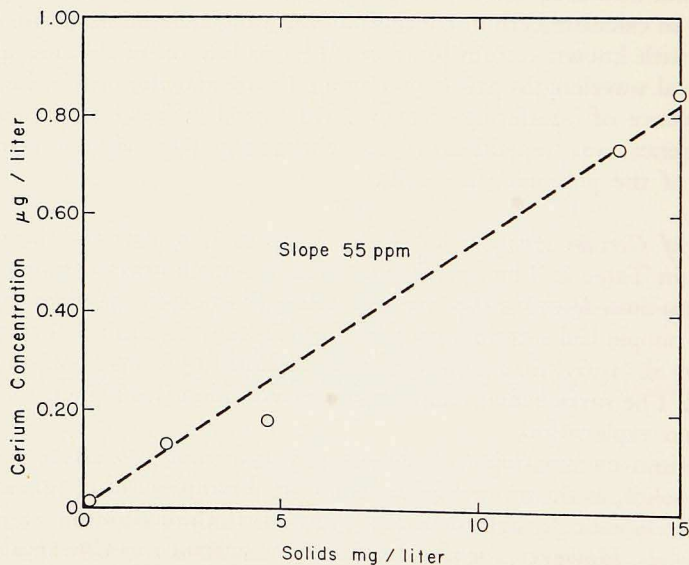


Figure 2. Cerium content versus solids for the samples.



*Cerium Content in Some Marine Organisms.* The edible portions of several marine organisms were analyzed for cerium by the chromatographic separation and photometric measurement procedure described above.

The tissues were homogenized and radioactive cerium was added to provide yield estimates. The tissue was ashed by heating in a muffle furnace and then extracted

with 6 N HCl. Following two successive chromatographic separations, recovery of the added cerium tracer was 75–80%. The results of these analyses are shown in Table II.

Table II. Cerium concentration (wet weight) in the edible portions of some marine organism.

Organism	Ce ( $\mu\text{g}/\text{kg}$ )	Conc. factor
<i>Roccus saxatilis</i> * .....	< 10	< 20
<i>Crassostrea virginica</i> § .....	60	ca. 80
<i>Crassostrea virginica</i> * .....	32	ca. 60
<i>Mya arenaria</i> * .....	520	10 <sup>3</sup>

\* From Chesapeake Bay.

§ From Chincoteague Bay.

*Observations on the Physical Distribution of Added Cerium.* TRACER CONCENTRATIONS ADDED. Solutions of  $\text{Ce}^{141}$  (cerous chloride) in 1 N HCl were added to natural water samples in the proportion of 1 to 1000. Pretreatment of the waters consisted of storage at room temperature for various time periods, during which some of the solids settled out and perhaps aggregation occurred. Several hours after the cerium addition, the samples were filtered or centrifuged as shown in Table III.

The data in Table III show that the fraction of the added cerium tracer that appears as "particulate" depends on the source of the water, and this property may be altered by storage. These observations suggest that the added cerium became associated with a preformed solid phase rather than precipitated from solution as a simple solid phase.

Appreciable fractions of the added cerium became associated with particles having sizes from 0.01  $\mu$  to greater than 1  $\mu$ . Arbitrary definitions of solubility, such as material that passes a 0.45  $\mu$  filter, would be misleading and appear to have only limited usefulness.

CERIUM ADDITIONS TO PRECENTRIFUGED SEAWATER. Seawater samples were centrifuged for five hours at 30,000 RCF to remove natural particles. Known quantities of cerous and ceric solutions tagged with radioactive cerium were added to these precentrifuged solutions. After aging for various time periods, the solutions were again centrifuged for two hours at 30,000 RCF and the radioactivity remaining in the liquid was measured.

The results for the experiments in which trivalent cerium was added are shown in Fig. 3. With added concentrations of 0.01 and 0.1  $\mu\text{g}/\text{l}$ , 10–20% of the cerium was removed by centrifuging. Aging for 16 days did not increase the quantity removable to greater than 20%. With added concentrations of

Table III. Cerium removal with residual particulate phase.

Source Water	Pretreatment	Treatment	% Ce Removed
Ocean City, Md. . . . S = 31 ‰	Settled 3 months	Filtered 0.8 $\mu$ pore	18
			15
		Filtered 0.45 $\mu$ pore	23
	Settled 5 months		30
		Filtered 0.8 $\mu$ pore	9
		Filtered 0.45 $\mu$ pore	18
	Settled 5 months	Filtered 0.1 $\mu$ pore	27
		Centrifuged, RCF, 36,000	
		1 hour	25
		2 hours	28
	Chesapeake Bay . . . . S = 15 ‰	Settled 2 weeks	3 hours
5 hours			41
Settled 2 weeks		Filtered 0.8 $\mu$ pore	28
		Filtered 0.45 $\mu$ pore	54
Settled 2 weeks		Centrifuged, RCF, 10,000	
		2 hours	97
Settled 5 weeks		Centrifuged, RCF, 36,000	
		1 hour	97
Settled 7 weeks		Filtered 0.8 $\mu$ pore	29
		Filtered 0.45 $\mu$ pore	28
		Filtered 0.1 $\mu$ pore	29
Settled 7 weeks	Centrifuged, RCF, 36,000		
	1 hour	80	
	2 hours	86	
		4 hours	90

10 to 50  $\mu\text{g-l}$ , 80–90% of the cerium was centrifugable, and most of this would also settle out in five days, as observed in replicates not centrifuged.

The results for additions of ceric-sulfate solutions were similar to those observed for the cerous additions, except that the cerous additions produced centrifugable particles more readily.

Added cerium might react with the anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{=}$ ,  $\text{Br}^-$ ,  $\text{HCO}_3^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{HPO}_4^-$ ,  $\text{OH}^-$ ) of seawater to produce complexes or insoluble compounds. The published estimates of stability and solubility constants as tabulated by Sillén (1964) suggest that cerous ion would be most strongly affected by phosphate ( $\log K_1 = 18.5$ ,  $\log K_s = -22$ ). The phosphate complex formation constant reported by Mayer and Schwartz (1950) is so large that it must be suspect, but their results clearly demonstrate the formation of either a soluble or colloidal phosphate complex. Ceric ion reacts strongly with hydroxide to form complexes (first hydrolysis constant = 10) and the extremely insoluble hydroxide ( $\log K_s = -50$ ). While ceric phosphate is very insoluble ( $\log K_s = -90$ ), the reported solubility products suggest that ceric phosphate would completely hydrolyze at normal seawater pH.



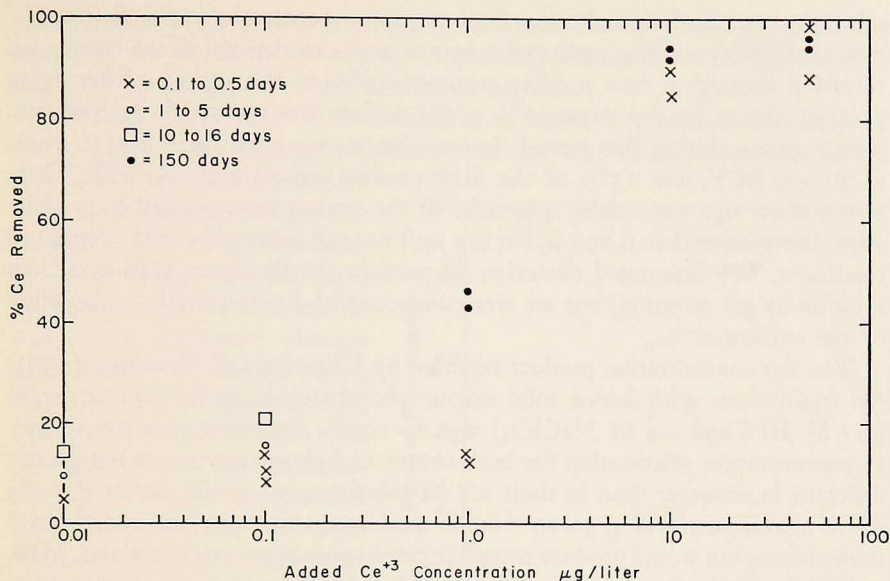


Figure 3. Removal of cerium added as cerous chloride solutions. Seawater precentrifuged, cerium added, solutions aged as indicated, and then centrifuged for two hours at 30,000 RCF.

In planning the cerium addition experiments, we hoped that precipitation would be indicative of cerous oxidation to produce ceric hydroxide. However, the extreme insolubility of cerous phosphate prevents simple interpretation. The phosphate concentration was not controlled, and measurements on the stock seawater bottle showed 0.05 to 0.1  $\mu\text{g-at/l}$  after these experiments were completed. The results with additions of 0.01 to 0.1  $\mu\text{g/l}$  (10–20% centrifugable) are difficult to reconcile with the results for additions of 10 to 50  $\mu\text{g/l}$ . At the high added concentrations, 1 to 5  $\mu\text{g/l}$  remained after centrifuging, suggesting a solubility that would permit complete resistance to centrifuging for the low concentration additions. A possible explanation for the centrifugation losses at low concentration levels is that the precentrifugation did not remove all particles and the added cerium became associated with these particles, so that the post addition centrifuging removed some of these particles and their associated cerium. Sterile techniques were not used, so that cerium association with microorganisms grown during storage and centrifugation is also a possibility.

**MORE RIGOROUS SOLIDS SEPARATION AND HIGHER PHOSPHATE CONCENTRATION.** Another possibility is that the cerium not removed by centrifuging at the higher concentration levels was present in particles of extremely small size (less than approximately 0.02  $\mu$ ). Filtration and extended centrifugation were used to test this possibility. Seawater was filtered through a 0.01  $\mu$  membrane filter, phosphate was added to a level of 0.5  $\mu\text{g-at/l}$ , and cerous sulfate

solution was added to make the final cerium concentration  $10 \mu\text{g/l}$  ( $7 \times 10^{-8}$  molar). Gravity settling produced a loss of 11% at the end of 24 hours, and filtration through a  $0.01 \mu$  filter removed 46% of the cerium. After aging another aliquot for five days, 50% of the cerium was removable by filtration. The cerium solution that passed the membrane was centrifuged for 16 hours at 30,000 RCF, and 15% of the filter-passing cerium was removed. These results show that appreciable quantities of the cerium were present in particles with sizes greater than  $0.005 \mu$ , but  $4.3 \mu\text{g/l}$  was not removable by the combined treatment. We attempted detection of particles in the filter passing cerium solution by gel filtration, but we were unsuccessful due to complete adsorption of the cerium.

The ion concentration product reported by Ul'yanov and Kazakova (1963) for equilibrium with added solid cerous phosphate at 0.5 M ionic strength (0.1 M HCl and 0.4 M  $\text{NaClO}_4$ ) was  $2 \times 10^{-24}$ . Assuming that the activity to concentration relationship for both cerous and phosphate ions is not greatly different in seawater than in their 0.5 M solutions, we would expect that the above mixture containing  $5 \times 10^{-7}$  molar total inorganic phosphate and  $7 \times 10^{-8}$  molar cerous ion would produce complete cerous phosphate precipitation at pH 8.

The dominant form of phosphate at pH 8 is  $\text{HPO}_4^-$  and, assuming  $\log K_1' = 11$ , then the free phosphate ion concentration would be approximately  $5 \times 10^{-10}$  molar in this solution and the equilibrium cerous ion concentration would be  $4 \times 10^{-15}$  molar. These calculations would be more accurate if the thermodynamic (activity) solubility product for cerous phosphate were known and if the activities of cerous and phosphate ions in seawater were measurable. We use the observed ion product at 0.5 M and the measured concentrations as approximations, and an uncertainty approaching two orders of magnitude may be present. The calculated  $4 \times 10^{-15}$  value is so much smaller than the observed  $3 \times 10^{-8}$  solubility that more complex species of cerium and phosphate must be postulated to account for the observations. Kester (1966) found the apparent activity coefficient of phosphate ion in seawater to be 0.004 of its value in 0.68 M NaCl solutions, suggestive of phosphate complexes with magnesium, calcium, or potassium ions. Even taking this reduction in phosphate activity into account, it still appears that a complex form of cerous is present in seawater.

*Oxidation State of Cerium.* Due to the extreme insolubility of both cerous phosphate and ceric hydroxide, the solubility observations are not clearly indicative of the oxidation state of cerium. The strong fluorescence of +3 cerium and the absence of fluorescence by +4 cerium have been used by us to determine the oxidation state of cerium added to seawater. Excitation with  $250 \text{ m}\mu$  light and emission measurement at  $350 \text{ m}\mu$  in a Farrand spectrofluorometer permit a cerous ion detectability of  $1 \mu\text{g/l}$ . A point of uncertainty is the fluorescence efficiency of +3 cerium when it is present in minute particles. However, in a test solution in which only 66% of the



cerium would pass a  $0.01 \mu$  filter, fluorescence intensity was equal to that measured in an acidified control. Apparently diminution of fluorescence is not great in the particle sizes formed in seawater.

The pH dependence of the oxidation of added +3 cerium was observed using settled, aged seawater to which HCl and NaOH solutions were added. The pH of the altered seawater underwent further changes due to loss or gain of carbon dioxide. This change was inhibited by storage in closed volumetric flasks and significant changes did not occur for several hours, but, with several days storage, drift toward equilibrium with the atmosphere was unavoidable. In view of the possible complex formation, we were reluctant to add other buffers to seawater for pH stabilization.

Cerium (+3) was added to settled seawater samples that had an inorganic phosphate content of  $0.1 \mu\text{g-at/l}$  and a chlorinity of  $17\text{‰}$ . Total added cerium was  $28 \mu\text{g/l}$  ( $0.2 \mu\text{g-at/l}$ ). A similar addition was made to a sample after it had been irradiated with far ultraviolet light to oxidize organic matter and release the total phosphorus as inorganic phosphate ( $0.7 \mu\text{g-at/l}$ ). Radioactive cerium was added with the stable cerium, so that loss (precipitation) of cerium could be followed.

The results of fluorescence measurements on these solutions are shown in Fig. 4. The data have been corrected for cerium loss. Rapid loss to the container of 20 to 30% was found in the lower pH solutions but, of the remaining, 66% would pass through a  $0.01 \mu$  filter. Loss from the higher pH solutions was 2 to 5%, but only 2% of the cerium would pass the  $0.01 \mu$  filter. For the irradiated (high phosphate) sample, loss was 41% at the end of three days.

These results show that cerium is rapidly oxidized at pH 8 and greater to the insoluble but colloidal ceric hydroxide. At pH 7 to 7.5 cerium is persistent for at least several days. The irradiated sample should have contained less organic reductants, but the oxidation was inhibited. This could be interpreted as stabilization of the +3 state by the increased phosphate concentration.

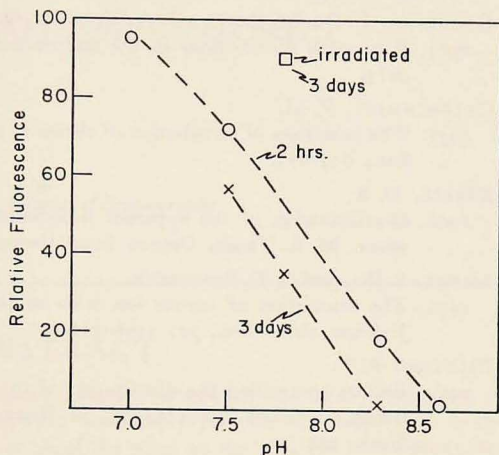


Figure 4. Relative fluorescence of +3 cerium added to seawater solutions. Losses of cerium from samples measured by radioactivity counting and the fluorescence measurements are expressed relative to the maximum fluorescence expected for the cerium remaining in suspension or solution. Time after cerium addition as indicated.



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