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*Original Scientific Paper*

# Precipitation and Hydrolysis of Metallic Ions in Sea Water. II. Precipitation of Some Rare Earths in Sea Water

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The solubility limits of lanthanum, praseodymium, neodymium, samarium, gadolinium, dysprosium, europium, ytterbium, lutetium, and yttrium hydroxides in various concentrations of sea water have been determined by tyndallometric and *p*H measurements. By a simple graphical method the solubility and hydrolysis constants have been evaluated from the solubility limits represented in the general precipitation diagrams, in which the ordinate is *p*H and the abscissa is the logarithm of the metal concentration. The precipitation *p*H values (4.70 to 5.49) and the values of the solubility products ($\log K_{S0} = -28.4$ to $-26.2$) obtained for the rare earths in various concentrations of sea water, indicate that lanthanides in the acid range in sea water, at lanthanide salt concentrations greater than $10^{-4}$ *M*, form compounds other than rare earth hydroxides.

In the same concentration and *p*H range, the predominant soluble species are free or hydrated $Ln^{3+}$ ions in equilibrium with the solid phase so formed. Since any other step of hydrolysis is not evident from the solubility limits, the reaction of the formation of the Ln $(OH)_3$ precipitate may be written as:

$$Ln^{3+} + 3\,OH^- \rightleftarrows Ln\,(OH)_3\,(s)$$

All rare earth elements studied in natural sea water (*p*H ∾ 8) at rare earth salt concentrations less than $10^{-5}$ *M* were dissolved in the form of their unchanged hydrated molecules, the so-called »Hydrated ionic associate« $Ln(OH)_3$ aq., and one may expect a rather effective fixation on other solid particles or surfaces.

The cumulative hydrolytic constants, $\log \beta_3$, for the studied rare earth hydroxides in sea water have values ranging from 21.3 to 23.5.

## INTRODUCTION

The hydrolysis and precipitation of rare earth elements with hydroxides in distilled water have been the subject of many investigations. The *p*H values at which precipitation (precipitation *p*H values) of the rare earth hydroxides begins have, in most cases, been obtained by electrochemical titrations of rare earth salt solutions with hydroxides, by using hydrogen, glass or other electrodes[1].

M. I. Korenman[2] has calculated the solubility products from *p*H data at the instant of precipitation of some rare earth hydroxides.

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* Based on the M. Sc. Thesis of B. Pokrić presented to the Faculty of Science, University of Zagreb, 1966.

The papers treating the problem of rare earth elements in sea water are, in most cases, occupied by the determination of the concentration of rare earths and their distribution in the marine environment[3].

The precipitation *p*H range and the solubility constants of the rare earth hydroxides in sea water presented in this paper were determined by the similar graphical method to that used in previous papers on the hydrolysis of thorium[4], on the precipitation and hydrolysis of yttrium and the rare earths in distilled water[5], and on studies of the ionic states of thorium and zirconium in sea water[6].

In water medium, the soluble rare earth salts hydrolyse and form the consecutive hydrolytic species as follows:

$$Ln^{3+} + OH^- \overset{K_1}{\rightleftarrows} LnOH^{2+} \tag{1}$$

$$LnOH^{2+} + OH^- \overset{K_2}{\rightleftarrows} Ln(OH)^+_2 \tag{2}$$

$$Ln(OH)^+_2 + OH^- \overset{K_3}{\rightleftarrows} Ln(OH)_3 \tag{3}$$

It is possible to calculate the logarithm of the cumulative hydrolytic constant log $\beta_3$ from the same precipitation diagrams and solubility limits from which the solubility constants are determined.

The cumulative hydrolytic constant $\beta_3$ is defined as:

$$\beta_3 = K_1 \cdot K_2 \cdot K_3 \tag{4}$$

$K_1$, $K_2$ and $K_3$ are the consecutive stability constants for the chemical reactions represented by eqs. (1) to (3). A general consecutive stability constant is given by the following expression:

$$K_n = \frac{\left[Ln(OH)_n^{(3-n)+}\right]}{\left[Ln(OH)_{n-1}^{(4-n)+}\right] \cdot [OH^-]} \tag{5}$$

n = 1, 2, and 3

The values obtained for $K_1$, $K_2$ and $K_3$ from eq. (5) are substituted in eq. (4) and the following expression is obtained:

$$\beta_3 = \frac{[Ln(OH)_3]}{[Ln^{3+}]\,[OH^-]^3} \tag{6}$$

$[Ln^{3+}]\,[OH^-]^3$ corresponds to the solubility constant $K_{S_0}$. $[Ln(OH)_3]$ indicates the »solubility of the hydrated ionic associate« ($M_S$) and defined by the metal salt concentration at which the solubility limit has the slope $\infty$.

Since the graphical method[4-6] gives the logarithmic values of the solubility constants ($K_{S_0}$) and the solubilities of the hydrated ionic associates ($M_S$), it is preferable to express the cumulative hydrolytic constant in logarithmic form:

$$\log \beta_3 = \log M_S - \log K_{S_0} \tag{7}$$

## EXPERIMENTAL

The systems for the *p*H and turbidity measurements are prepared in glass tubes by mixing rare earth salt solutions, sea water, and sodium hydroxide or hydrochloric acid solutions[7]. The final volume of the mixed systems is 10 ml., and the concentrations of the components for this volume are always given at room temperature.

Twenty-four hours after mixing the corresponding precipitating components, turbidity measurements were performed by using a *Zeiss* tyndallometer. After the turbidity measurements, the acidity of the systems was determined on a *Pye* *p*H-meter with glass and calomel electrode.

*Materials*

All chemical used were analytically pure and all of the solutions were prepared with double-distilled water.

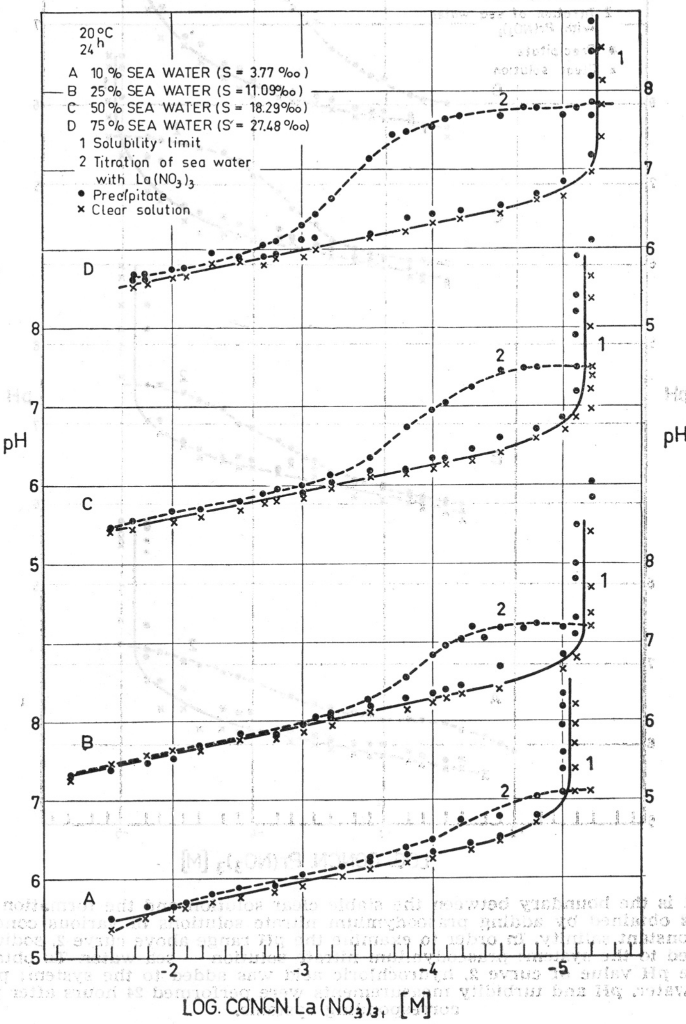

Fig. 1. Curve 1 is the boundary between the stable clear solution and the formation of the precipitate. Curve 2 obtained by adding lanthanum nitrate solutions of various concentrations to sea water of constant salinity. In order to examine the *p*H range above curve 2, sodium hydroxide should be added to the system: lanthanum nitrate solution — sea water. To obtain *p*H values lower than the *p*H value of curve 2, hydrochloric acid was added to the system: lanthanum nitrate — sea water. *p*H and turbidity measurements were performed 24 hours after preparing the corresponding systems.

The standard lanthanum nitrate and yttrium nitrate solutions were prepared by dissolving *C. Merck* salts. Other rare earth nitrates were obtained from the corresponding *Johnson, Matthey Co.* rare earth oxides dissolved in 1 : 1 nitric acid at 60°—70° C[8].

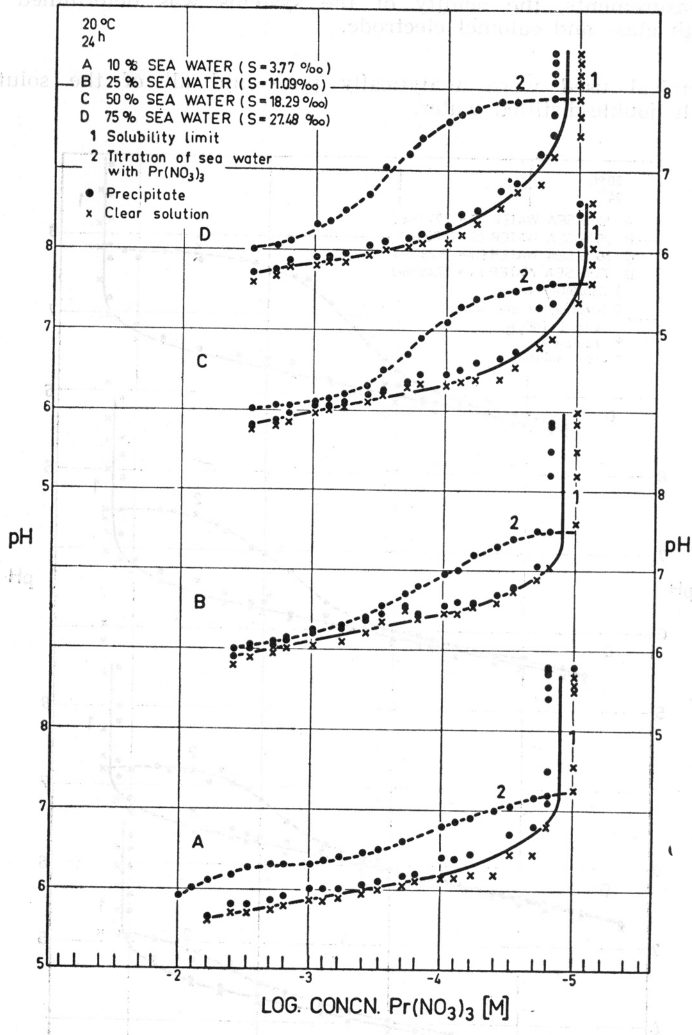

Fig. 2. Curve 1 is the boundary between the stable clear solution and the formation of the precipitate. Curve 2 obtained by adding praseodymium nitrate solutions of various concentrations to sea water of constant salinity. In order to examine the *p*H range above curve 2, sodium hydroxide should be added to the system: praseodymium nitrate solution — sea water. To obtain *p*H values lower than the *p*H value of curve 2, hydrochloric acid was added to the system: praseodymium nitrate — sea water. *p*H and turbidity measurements were performed 24 hours after preparing the corresponding systems.

The salinity (*S*) of sea water used in the experiments was determined by the standard Mohr-Knudsen's method[9] using Knudsen's tables[10]. Prior to the determination of the salinity, the sea water was filtered through a 0.45 μ Millipore filter.

A salinity *S* = 36.45‰, and the *p*H = 7.9, characterized the sea water used in the experiments.

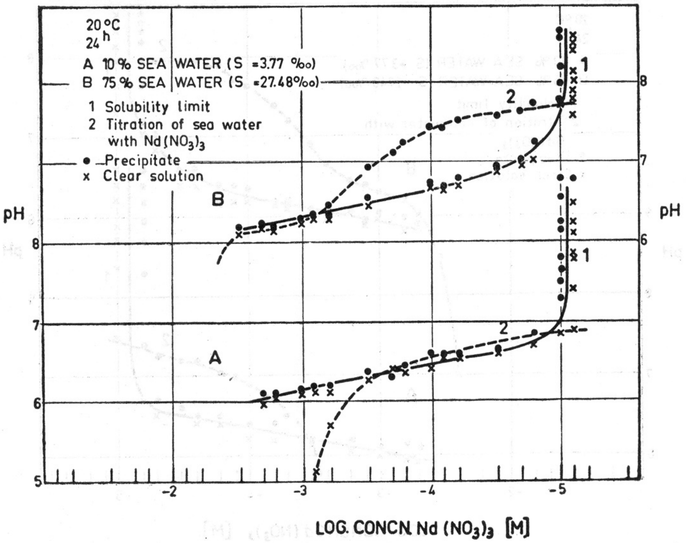

Fig. 3. Curve 1 is the boundary between the stable clear solution and the formation of the precipitate. Curve 2 obtained by adding neodymium nitrate solutions of various concentrations to sea water of constant salinity. In order to examine the *p*H range above curve 2, sodium hydroxide should be added to the system: neodymium nitrate solution — sea water. To obtain *p*H values lower than the *p*H value of curve 2, hydrochloric acid was added to the system: neodymium nitrate — sea water. *p*H and turbidity measurements were performed 24 hours after preparing the corresponding systems.

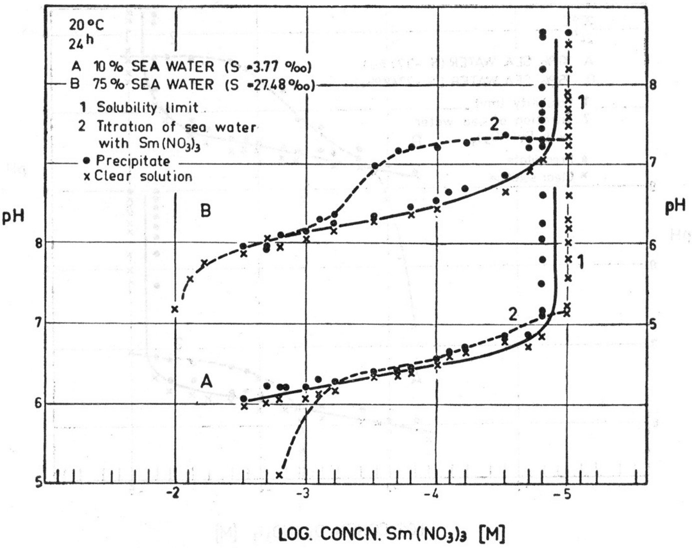

Fig. 4. Curve 1 is the boundary between the stable clear solution and the formation of the precipitate. Curve 2 obtained by adding samarium nitrate solutions of various concentrations to sea water of constant salinity. In order to examine the *p*H range above curve 2, sodium hydroxide should be added to the system: samarium nitrate solution — sea water. To obtain *p*H values lower than the *p*H value of curve 2, hydrochloric acid was added to the system samarium nitrate — sea water. *p*H and turbidity measurements were performed 24 hours after preparing the corresponding systems.

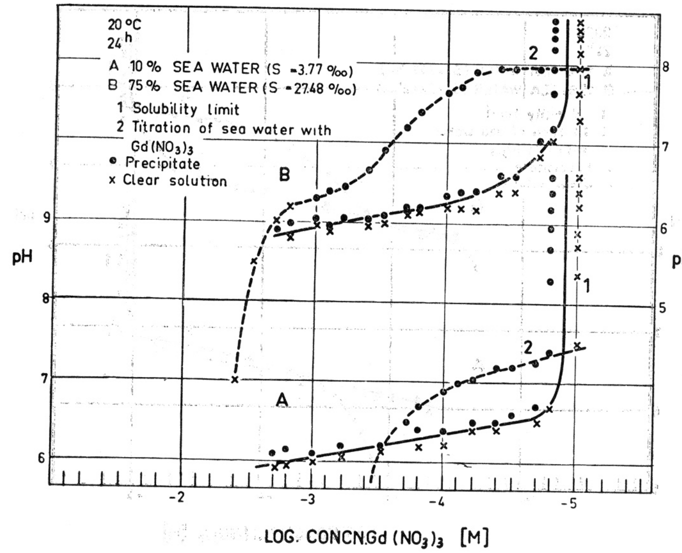

Fig. 5. Curve 1 is the boundary between the stable clear solution and the formation of the precipitate. Curve 2 obtained by adding gadolinium nitrate solutions of various concentrations to sea water of constant salinity. In order to examine the *p*H range above curve 2, sodium hydroxide should be added to the system: gadolinium nitrate solution — sea water. To obtain *p*H values lower than the *p*H value of curve 2, hydrochloric acid was added to the system: gadolinium nitrate — sea water. *p*H and turbidity measurements were performed 24 hours after preparing the corresponding systems.

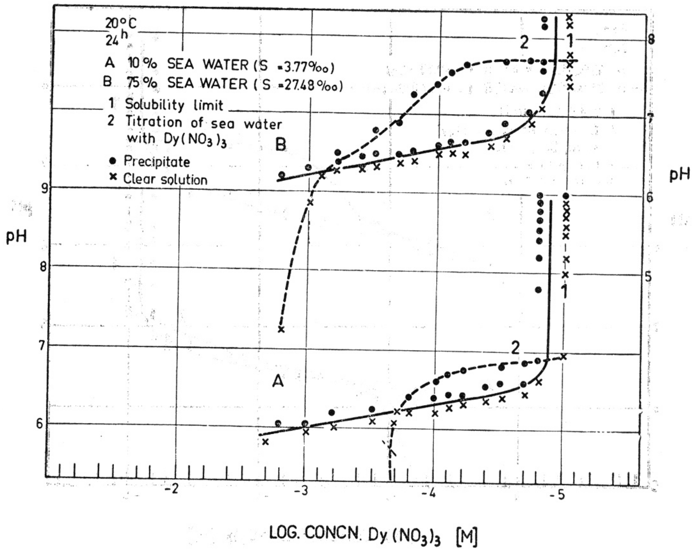

Fig. 6. Curve 1 is the boundary between the stable clear solution and the formation of the precipitate. Curve 2 obtained by adding dysprosium nitrate solutions of various concentrations to sea water of constant salinity. In order to examine the *p*H range above curve 2, sodium hydroxide should be added to the system: dysprosium nitrate solution — sea water. To obtain *p*H values lower than the *p*H value of curve 2, hydrochloric acid was added to the system: dysprosium nitrate — sea water. *p*H and turbidity measurements were performed 24 hours after preparing the corresponding systems.

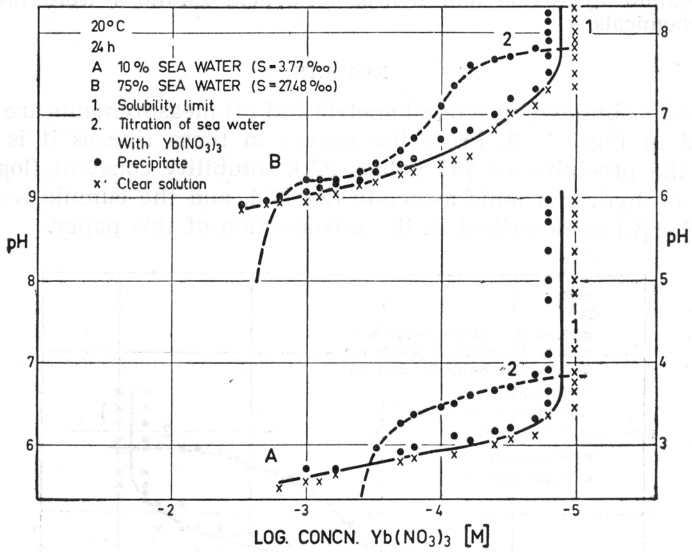

Fig. 7. Curve 1 is the boundary between the stable clear solution and the formation of the precipitate. Curve 2 obtained by adding ytterbium nitrate solutions of various concentrations to sea water of constant salinity. In order to examine the *p*H range above curve 2, sodium hydroxide should be added to the system: ytterbium nitrate solution — sea water. To obtain *p*H values lower than the *p*H values of curve 2, hydrochloric acid was added to the system: ytterbium nitrate — sea water. *p*H and turbidity measurements were performed 24 hours after preparing the corresponding systems.

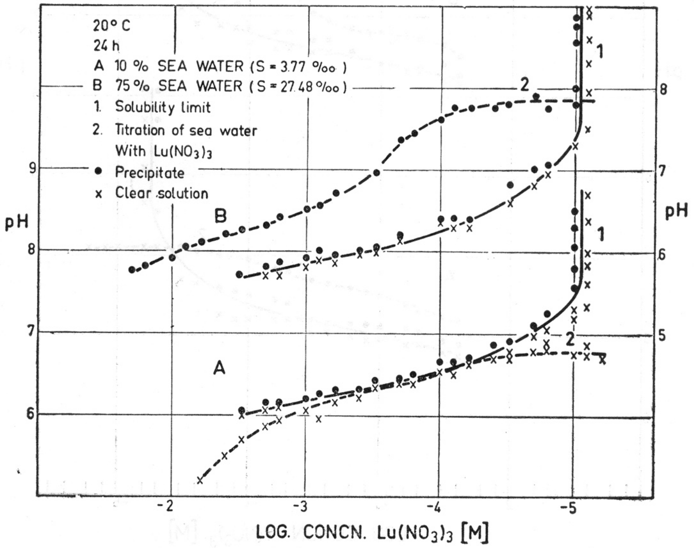

Fig. 8. Curve 1 is the boundary between the stable clear solution and the formation of the precipitate. Curve 2 obtained by adding lutetium nitrate solutions of various concentrations to sea water of constant salinity. In order to examine the *p*H range above curve 2, sodium hydroxide should be added to the system: lutetium nitrate solution — sea water. To obtain *p*H values lower than the *p*H value of curve 2, hydrochloric acid was added to the system: lutetium nitrate — sea water. *p*H and turbidity measurements were performed 24 hours after preparing the corresponding systems.

The sodium hydroxide and hydrochloric acid solutions were prepared from *C. Merck* chemicals.

## RESULTS

The results obtained by tyndallometric and *p*H measurements are graphically represented in Figs. 1—9. From the curves in these figures it is possible to determine the precipitation *p*H values ($C_o$), solubility constant ($\log K_{So}$), solubilities of the hydrated ionic associate ($\log M_S$), and the cumulative hydrolytic constants ($\log \beta_3$) as described in the introduction of this paper.

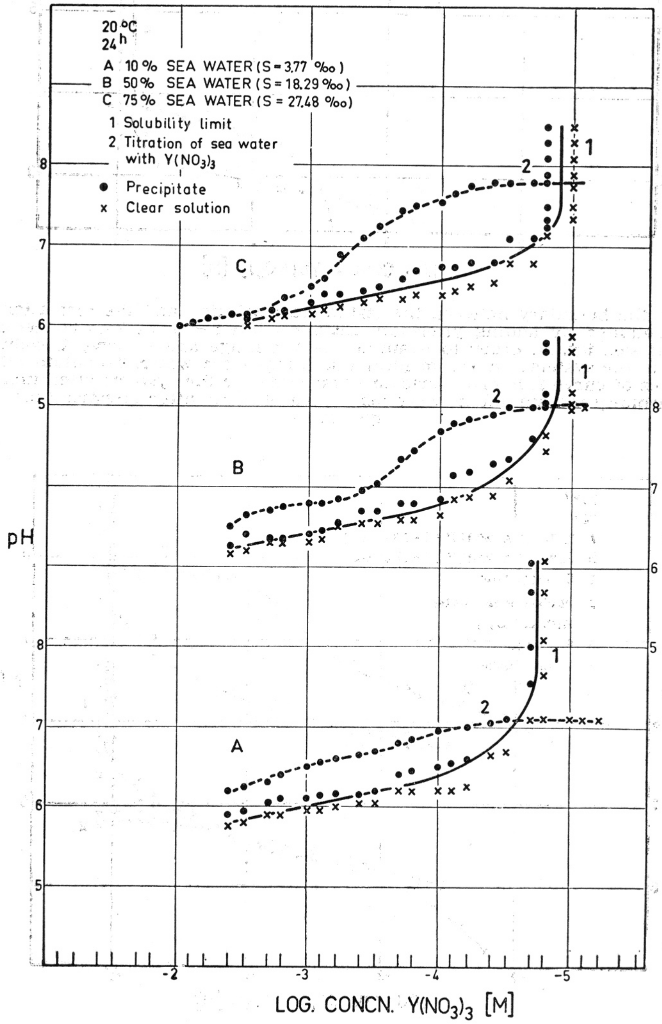

**Fig. 9.** Curve 1 is the boundary between the stable clear solution and the formation of the precipitate. Curve 2 obtained by adding yttrium nitrate solutions of various concentrations to sea water of constant salinity. In order to examine the *p*H range above curve 2, sodium hydroxide should be added to the system: yttrium nitrate solution — sea water. To obtain *p*H values lower than the *p*H value of curve 2, hydrochloric acid was added to the system: yttrium nitrate — sea water. *p*H and turbidity measurements were performed 24 hours after preparing the corresponding systems.

The curves denoted as 1 in Figs. 1—9 indicate the boundaries between the stable clear solution and the turbid system obtained by changing the *p*H values of solutions of lanthanum, praseodymium, neodymium, samarium, dysprosium, ytterbium, lutetium, and yttrium salts in sea water of various concentrations. For salt concentrations higher than $10^{-4}$ *M*, the obtained solubility limits represent straight lines, the slope of which is — 1/3 in each case. At rare earth salt concentrations of about $10^{-5}$ *M* the slope of the solubility limits is changed and its value reaches infinity.

The curves denoted as 2 in Figs. 1—9 were obtained by adding rare earth salt solutions of various concentrations to sea water of constant salinity. These curves may be considered as »the titration curves of sea water with rare earth salts«. When metal salt solutions are added to sea water, the titration curves, which were determined prior to the determination of the solubility curves, indicate either turbid or clear system. In other words, these curves indicate that hydrochloric acid or sodium hydroxide should be added to the system in order to obtain the points of the solubility limits

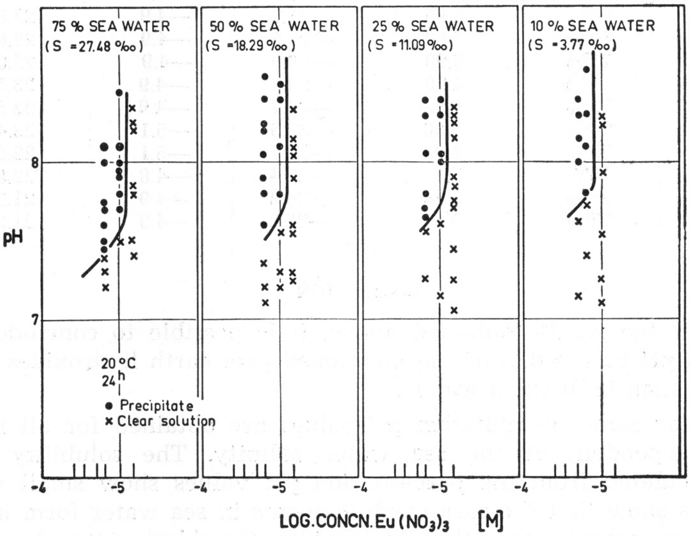

Fig. 10. The boundary between the stable clear solution and the formation of the precipitate in the system: europium nitrate — sea water. The behaviour of europium (III) in sea water was examined for various concentrations of europium nitrate and for constant concentrations of sea water.

The solubility limits of europium in sea water were not determined over such a wide concentration range as for the other rare earth hydroxides, but only in the regions where the slope of the solubility limits was infinity (Fig. 10).

The values obtained for $C_0$, $\log K_{S0}$, $\log M_S$, and $\log \beta_3$ of the examined rare earth hydroxides in sea water are represented in Table I.

TABLE I

*Experimentally obtained precipitation pH-values* ($C_0$) *and values of the solubility of the hydrated ionic associate (log* $M_S$*), the corresponding values of the solubility products (log* $K_{So}$*), and the values of the cumulative hydrolytic constants (log* $\beta_3$*) of some rare earth elements in sea water of various concentrations.*

| $Ln^{3+}$ | Concn. of sea water | $C_0$ | log $K_{So}$ | log $M_S$ | log $\beta_3$ |
|---|---|---|---|---|---|
| $La^{3+}$ | 10% | 4.95 | —27.7 | —5.3 | 22.4 |
| | 25% | 4.95 | —27.7 | —5.2 | 22.5 |
| | 50% | 4.95 | —27.7 | —5.2 | 22.5 |
| | 75% | 4.95 | —27.7 | —5.1 | 22.6 |
| $Pr^{3+}$ | 10% | 4.90 | —27.8 | —4.9 | 22.9 |
| | 25% | 5.10 | —27.2 | —4.9 | 22.3 |
| | 50% | 4.97 | —27.6 | —5.1 | 22.5 |
| | 75% | 4.85 | —28.0 | —4.9 | 23.1 |
| $Nd^{3+}$ | 10% | 5.13 | —27.1 | —5.1 | 22.0 |
| | 75% | 5.30 | —26.5 | —5.1 | 21.4 |
| $Sm^{3+}$ | 10% | 5.15 | —27.1 | —4.9 | 22.2 |
| | 75% | 5.13 | —27.1 | —4.9 | 22.2 |
| $Eu^{3+}$ | 10% | | | —4.9 | |
| | 25% | | | —5.1 | |
| | 50% | | | —5.1 | |
| | 75% | | | —5.1 | |
| $Gd^{3+}$ | 10% | 5.00 | —27.5 | —4.9 | 22.6 |
| | 75% | 4.95 | —27.7 | —4.9 | 22.8 |
| $Dy^{3+}$ | 10% | 5.00 | —27.5 | —4.9 | 22.6 |
| | 75% | 5.20 | —26.9 | —4.9 | 22.0 |
| $Yb^{3+}$ | 10% | 4.70 | —28.4 | —4.9 | 23.5 |
| | 75% | 4.95 | —27.7 | —4.9 | 22.8 |
| $Lu^{3+}$ | 10% | 5.00 | —27.5 | —5.1 | 22.4 |
| | 75% | 4.95 | —27.7 | —5.1 | 22.6 |
| $Y^{3+}$ | 10% | 5.03 | —27.4 | —4.8 | 22.6 |
| | 25% | 5.49 | —26.2 | —4.9 | 21.3 |
| | 75% | 5.23 | —26.8 | —4.9 | 21.9 |

## DISCUSSION

Based on the results obtained above, it is possible to conclude that the precipitation *p*H-values ($C_o$) of the mentioned rare earth hydroxides are lower in sea water than in distilled water[5].

Nearly the same precipitation *p*H-values are obtained for all rare earth elements independent of the sea water salinity. The solubility constants (log $K_{So}$) calculated from the precipitation *p*H values show small variations. These results show that the rare earth elements in sea water form in the acid range some compounds other than hydroxides. Considering the chemical composition of sea water the formation of rare earth chlorides, carbonates, and hydrocarbonates or their mixtures with hydroxides is possible in sea water. The formation of crystals is noticed at the precipitation of lanthanides in sea water in the *p*H range below 7. These crystals, however, appear sometimes in the mixture with colloidal particles.

Similar precipitation *p*H-values, as in sea water, are obtained in distilled water if the rare earths are precipitated with sodium hydroxide in the sodium hydrocarbonate solutions. The precipitation *p*H-values obtained by W. Fischer, J. Müller, and K. E. Neimann[11] for the rare earth hydrocarbonates in distilled water were in the same $pH$ range as those of lanthanides in sea water. From these data one can conclude that rare earths in sea water in the acid range in part form hydrocarbonates.

The influence of the concentration of salts, present in sea water, on the precipitation of rare earth hydroxides[12], can be neglected because the precipitation $pH$ values do not differ appreciably at various concentrations of sea water (Fig. 11).

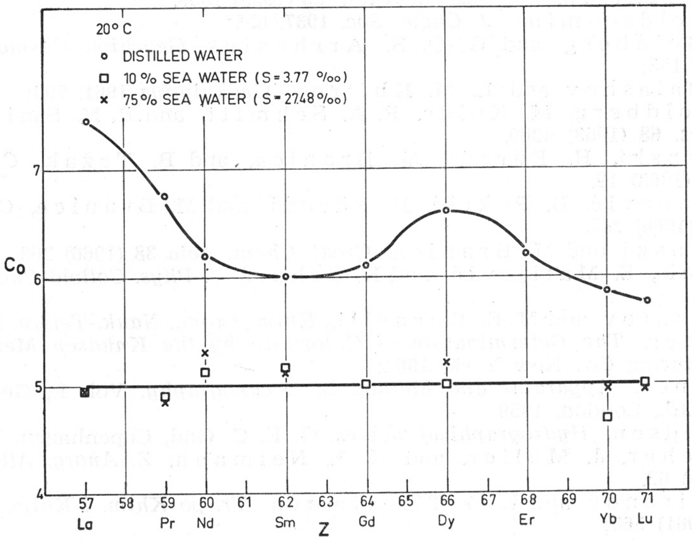

Fig. 11. Graphical representation of the dependence of $C_0$ on the atomic number of rare earth elements. The $C_0$ values are obtained by using the salt solutions of rare earths prepared in distilled water and in sea water of various concentrations.

The formation of rare earth chlorides or hydrochlorides under these conditions is not probable, since such reactions requires higher concentrations of chloride ions than are found in sea water are necessary[13]. Under conditions existing in normal sea water ($pH \sim 8$) at rare earth salt concentrations lower than $10^{-5}$ $M$ the formation of the precipitates was not noticed. Thus, it can be supposed that lanthanides in natural sea water exist in the form of uncharged hydrated molecules whose general formula may be represent by $Ln(OH)_3$ aq. The possibility of the existence of these species of associates is in accordance with the assertion of D. Lal, E. D. Goldberg, and M. Koide[14] that »the dissolved silicon exists nearly entirely as undissociated monomeric silicic acid, $Si(OH)_4$ in both river and marine waters and in an undersaturated state«.

If all the elements studied in natural sea water are dissolved in the form of an uncharged associate, one may expect a very effective sorption on other solid particles or surfaces.

From the results given in this paper it would appear that an increase in the precipitation of the rare earth elements carried by the river can be expected.

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## IZVOD

### Taloženje i hidroliza metalnih iona u morskoj vodi. II. Taloženje nekih rijetkih zemalja u morskoj vodi

*B. Pokrić i M. Branica*

Granice topljivosti lantanum-, praseodinum-, neodinum-, samarium-, europium-, gadolinium-, disposium-, iterbium-, lutecium- i itrium-hidroksida u morskoj vodi različitih koncentracija određene su mjerenjima *p*H i mutnoća. Iz granica topljivosti dobivenih iz taložnih dijagrama kojima je ordinata *p*H a apscisa logaritamska vrijednost koncentracije metalnog iona, određene su konstante topljivosti i konstante hidrolize.

Taložne *p*H vrijednosti (4,70 do 5,49) i vrijednosti dobivene za konstante produkta topljivosti ($\log K_{S0} = -28{,}4$ do $-26{,}2$) ispitivanih rijetkih zemalja u morskoj vodi raznih koncentracija, pokazuju da u kiselom području u morskoj vodi lantanoidi kod koncentracija većih od $10^{-4}$ *M* tvore još neke spojeve osim hidroksida.

U ovom koncentracijskom i *p*H području $Ln^{3+}$ ionske su vrste, koje uglavnom dolaze u otopini u ravnoteži s novo stvorenom krutom fazom. Budući da su nagibi granica topljivosti $—^1/_3$, može se zaključiti da se talozi stvaraju na slijedeći način:

$$Ln^{3+} + 3\,OH^- \rightleftarrows Ln(OH)_3\ (s)$$

Kod koncentracija soli lantanoida manjih od $10^{-5}$ *M* u uvjetima prirodne morske vode (*p*H $\sim$ 8), rijetke zemlje dolaze u obliku nedisociiranih hidratiziranih molekula $Ln(NO)_3$ aq. Taj oblik »hidratiziranog ionskog asocijata« efektivno se fiksira na krute čestice i površine.

Vrijednosti kumulativne hidrolitičke konstante log $\beta_3$ ispitivanih rijetkih zemalja u morskoj vodi kreću se od 21,3 do 23,5.

INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB

**Primljeno 10. studenog, 1966**