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:TITLE: Marine chemistry.
:IMPRINT: [Amsterdam] Elsevier [etc.]
:ARTICLE: Motekaitis, Ramunas, J.; Martell, Arthur/"Speciaiton of metals in the oceans ...."
:VOL: 21 :NO: :DATE: 1987 :PAGES: 101-116
:VERIFIED: OCLC ISSN: 0304-4203 [Format: Serial]
:PATRON: Lee
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Marine Chemistry, 21 (1987) 101–116
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

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SPECIATION OF METALS IN THE OCEANS. I. INORGANIC COMPLEXES IN SEAWATER, AND INFLUENCE OF ADDED CHELATING AGENTS

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(Received April 3, 1986; revision accepted January 29, 1987)

ABSTRACT

Motekaitis, R.J. and Martell, A.E., 1987. Speciation of metals in the oceans. I. Inorganic complexes in seawater, and influence of added chelating agents. Mar. Chem., 21: 101–116.

The speciation of the metal ions in the surface waters of the open ocean has been computed by using critical stability constants describing all of the inorganic complexes that can be formed by the metal ions and inorganic ligands present. The stability constants used were adjusted to change the literature values from 0.10 M ionic strength to the 0.70 M ionic strength of seawater by using a new empirical technique involving experimentally observed variations of stability constants with ionic strength for complexes of similar charge types. For stability constants not listed in Critical Stability Constant compilations, values were estimated by using known trends of stability constants of similar complexes. The speciation determinations made include equilibria with suspended solid phases such as hydroxides, carbonates, and basic carbonates of the metal ions present. Perturbation of metal speciation resulting from the addition of some common chelating agents is determined and the results obtained are discussed in terms of the effects on seawater by the introduction of these chelating agents into the environment. In the 10^{-9} to 10^{-7} range of added chelant, EDTA (ethylenediaminetetraacetate), NTA (nitrilotriacetate), TPP (tripolyphosphate) and CIT (citrate) exist in the ocean primarily as their Ca(II) and Mg(II) chelates. EDTA and NTA are the dominant ligands for Cu(II) and Ni(II), while TPP is extensively complexed to Fe(III). CIT strongly influences Cu(II) speciation, while SSA (sulfosalicylate, a well-known Fe(III) reagent) has no influence on any of these metal ions or their complexes.

INTRODUCTION

The determination of the speciation of metal complexes involves the interaction of several metal ions with a large number of anions, including hydrolysis, and requires computer methods to solve the large number of complex equilibria involved. The problem in a real ocean is exceedingly complex because among other variables a very significant fraction of the total metal content may be attached to particulate matter, through both chemical and physical adsorption (Kremling and Petersen, 1981; Davis, 1984; Gillain and Brihaye, 1985; Mackey,

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1986; Buckely and van den Berg, 1986; Douglas et al., 1986). However, the importance of metal ion speciation is underscored by the increase in recent years of the attention given to this question (Wong et al., 1981; Kramer and Duinker, 1984; Moore and Ramamoorthy, 1984; Berman and Yeats, 1985; Irgolic and Martell, 1985; Haas, 1986; Anderson and Mackas, 1986; Hong and Kester, 1986; Vranken and Heip, 1986) and the appearance of specialized monographs on this subject (Morel, 1983; Pytkowicz, 1983). A complete model would include not only solution and simple equilibria with solid phases, but also would involve the kinetics of these processes together with the kinetics and equilibria of the various particulate adsorption and desorption phenomena. In addition, a complete model would consider the complexities arising from the myriad of organic components (Thurman, 1985), often of ill-defined nature. The scope of the present work is to investigate the effect of added reagents on the natural distribution of metal species within a model environment. A total equilibrium/(necessarily) kinetic description of even a portion of the ocean is beyond the means of present expertise and is expected to remain so for the immediately foreseeable future.

Recently Ahrland (1985) described the major and minor inorganic constituents of the various components of seawater near the surface of the open ocean. With respect to the components present in the absence of organic complexing agents, Ahrland (Table I) listed four major cations, six anionic components and some trace elements. The complex array of elements present at μ (ionic strength) 0.7 M and pH 8.1 in the ocean provides an interesting opportunity to determine the nature of the complexes present by the use of modern computer methods and the critical stability constants (Martell and Smith, 1974, 1977; Smith and Martell, 1975, 1976, 1982) involving the metal ions and ligands present. However, most of the equilibrium constants required have not been measured under seawater conditions (μ = 0.7 M), so that it is necessary to make appropriate adjustments by the use of empirical methods (Smith et al., 1985) using principles described in an earlier paper (Martell et al., 1985a).

TABLE I

Major and some minor constituents of seawater used in this study

Ion	Concentration, M × 10^3	Trace Element	Concentration, M × 10^9
Na^+	479	Mn	4
Mg^{2+}	54.5	Fe	8
Ca^{2+}	10.5	Ni	5
K^+	10.4	Cu	4
Cl^-	559	Zn	5
SO_4^{2-}	28.9	Cd	0.1
HCO_3^-, CO_3^{2-}	2.35	Hg	0.02
Br^-	0.86	Pb	0.05
F^-	0.075	U	14

Ahrland, 1985.

For some of the complexes that may be formed from the components, the required equilibrium data are missing entirely. In such cases appropriate estimates for the equilibrium constants were made using interpolations and correlations recently described (Martell et al., 1985b).

One of the problems encountered in the development of a data base for the calculation of speciation of metal complexes present in the oceans is the inadequacy of the published data on the UO_2 (VI) ion (Smith and Martell, 1976). Although the values of the constants for carbonate complex formation and for hydroxide formation are reasonably reliable, the tendencies of UO_2^{2+} to form basic carbonates and basic chlorides, especially at the high chloride concentration of seawater, have not been completely clarified. This problem, and its possible effect on the speciation calculations, is discussed below.

Calculations of the speciation of naturally occurring inorganic complexes in the oceans were carried out some time ago (Sillen, 1967) although the determinations were hampered by incomplete data and ionic strength problems. Unique features of the present study are the availability of more accurate equilibrium data and the use of the computer methods for the examination of complex multicomponent systems, including determination of the effects of various added commercial chelating agents on metal speciation. These commercial contaminants are generally produced on a large scale and if not properly handled could result in extensive release to the environment. To carry out these calculations, we set up a base line computation for seawater speciation at pH 8.1, and at one pH unit below and one pH unit above, for the complexes present before perturbation by the added chelating agents. The basic inorganic composition of seawater was taken from Ahrland (1985) and is presented in Table I. The unperturbed speciation was then compared with the speciation obtained when various chelating agents are introduced at the $10^{-9} - 10^{-7}$ M range of concentration. In several cases where minor effects needed to be amplified, somewhat higher (up to 10^{-5} M) concentrations of ligand were used. This work addresses a number of principles which had not up to this point been clarified.

Ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are examples of chelating agents which are subject to widespread commercial use and as members of the aminocarboxylic acid family are characterized by strong but poorly-selective chelation tendencies. Citric acid (CIT) is a common carboxylic acid chelator which is used extensively as a cleaning agent. Tripolyphosphate (TPP) is used on a large scale in the U.S.A. as a detergent builder and in water-softening applications. Sulfosalicylic acid (SSA) is an example of a phenolate type ligand with strong binding properties toward trivalent ions such as Fe(III).

Computations

The basic 19 components of the seawater data are considered to have 167 possible complex forming interactions, each of which is described in the form

of stability constants (β-values) for soluble species (Table II) and solubility products for potential solid formation (Table III). Very minor components such as Co^{2+}, or non-complexing species such as borate and selenium were not included. In all, 141 soluble species and 26 solid phases were considered. For example zinc bicarbonate concentration is given by $[ZnHCO_3^+] = \beta[Zn^{2+}]$.

TABLE II

Log overall stability constants for soluble components of seawater (μ = 0.70 M, t = 25.0°C)

Species	Log β	Species	Log β	Species	Log β
$CaCO_3$	2.21	FeH^+_{-2}	−5.88	UO_2SO_4	1.80
$CaHCO_3^+$	9.90	FeH^-_{-4}	−20.76	$UO_2(SO_4)_2^{2-}$	2.50
$CaSO_4$	1.03	$Fe_2H^{4+}_{-2}$	−3.08	UO_2Cl^+	−0.10
CaF^+	0.60	$MnHCO_3^+$	10.00	UO_2F^+	4.4
CaH^+_{-1}	−12.20	$MnSO_4$	0.80	UO_2F_2	8.0
$MgCO_3$	2.05	$MnCl^+$	−0.20	$UO_2F_3^-$	10.55
$MgHCO_2^+$	9.80	$MnCl_2$	−0.3	$UO_2F_4^{2-}$	12.00
$MgSO_4$	0.90	$MnCl_3^-$	−0.50	UO_2Br^+	−0.3
MgF^+	1.30	MnH^+_{-1}	−10.80	$UO_2H^+_{-1}$	−5.8
MgH^+_{-1}	−11.70	MnF^+	0.70	$UO_2(SO_4)_3^{4-}$	3.7
KSO_4^-	0.30	$CuCO_3$	5.60	UO_2CO_3	8.9
$NaCO_3^-$	0.63	$Cu(CO_3)_2^{2-}$	7.90	$(UO_2)_3(CO_3)H^+_{-3}$	−24.94
$NaSO_4^-$	0.33	$CuSO_4$	0.90	$CdCO_3$	2.00
$FeSO_4^+$	2.00	$CuCl^+$	0.10	$CdSO_4$	0.90
$Fe(SO_4)_2^-$	2.00	$CuCl_2$	0.01	$CdCl^+$	1.35
$FeCl^{2+}$	0.64	CuF^+	0.80	$CdCl_2$	1.70
$FeCl_2^+$	0.70	$CuBr^+$	−0.20	$CdCl_3^-$	1.50
$FeCl_3$	−0.70	CuH^+_{-1}	−6.50	CdF^+	0.50
FeF^{2+}	5.20	$Cu_2H^{2+}_{-2}$	−14.80	$CdBr^+$	1.50
FeF_2^+	9.10	$(UO_2)_6H_{-12}(CO_3)_6^{12-}$	−10.46	$CdBr_2$	2.1
FeF_3	12.00	$(UO_2)_2H^{2-}$	−5.90	$CdBr_3^-$	2.5
$FeBr^{2+}$	−0.20	$UO_2(CO_3)_2^{2-}$	15.40	$CdBr_4^{2-}$	2.60
FeH^{2+}_{-1}	−2.76	$UO_2(CO_3)_3^{4-}$	20.3	CdH^+_{-1}	−9.90
CdH^{2-}	−20.0	$HgSO_4$	1.40	$PbCl^+$	0.90
CdH^-_{-3}	−31.0	$Hg(SO_4)_2^{2-}$	2.40	$PbCl_2$	1.30
$ZnSO_4$	0.90	$HgCl^+$	6.73	$PbCl_3^-$	1.4
$ZnCl^+$	0.01	$HgCl_2$	13.23	$PbBr^+$	1.08
$ZnCl_2$	−1.0	$HgCl_3^-$	14.20	$PbBr_2$	1.80
$ZnCl_3^-$	0.0	$HgCl_4^{2-}$	15.20	$PbBr_3^-$	2.10
ZnF^+	0.7	HgF^+	1.00	PbH^+_{-1}	−7.70
$ZnBr^+$	−0.40	$HgCO_3$	10.60	PbH_{-2}	−17.10
ZnH^+_{-1}	−10.20	$HgBr^+$	9.00	PbH^-_{-3}	−27.90
ZnH_{-2}	−19.40	$HgBr_2$	17.10	$Pb_2H^{3+}_{-1}$	−6.30
ZnH^-_{-3}	−27.70	$HgBr_3^-$	19.40	PbF^+	1.40
ZnH^{2-}_{-4}	−37.20	$HgBr_4^{2-}$	21.60	PbF_2	2.50
$ZnHCO_3^+$	10.50	HgH^+_{-1}	−3.70	HCO_3^-	9.54
$NiSO_4$	0.6	HgH_{-2}	−6.30	H_2CO_3	15.54
$NiCl^+$	−0.1	$HgHCO_3^+$	14.90	HSO_4^-	1.2
NiF^+	0.5	$PbCO_3$	6.20	HF	2.95
$NiBr^+$	−0.6	$Pb(CO_3)_2^{2-}$	8.80	H^-_{-1}	−13.76
NiH^+_{-1}	−10.10	$PbSO_4$	1.30		

TABLE III

Log solubility products of solids (μ = 0.70 M; t = 25.0°C)

Phase	Log product	Phase	Log product
MnH_{-2}	14.78	PbF_2	−6.20
$Cu_2CO_3H_{-2}$	−6.00	PbH_{-2}	12.68
CuH_{-2}	9.10	UO_2CO_3	−12.90
$CdCO_3$	−9.60	UO_2H_{-2}	4.10
CdH_{-2}	13.48	$CaCO_3$	−6.60
$ZnCO_3$	−10.80	$CaSO_4$	− 3.00
ZnH_{-2}	12.76	CaF_2	−10.60
$NiCO_3$	−7.00	CaH_{-2}	+22.41
NiH_{-2}	12.38	$MgCO_3$	−3.70
HgH_{-2}	1.58	MgF_2	−6.70
$PbCO_3$	−11.80	MgH_{-2}	16.43
$Pb_3(CO_3)_2H_{-2}$	−19.40	FeH_{-3}	2.77
$PbSO_4$	−6.0	$MnCO_3$	−8.70

$[H^+][CO_3^{2-}]$ ($\beta = [ZnHCO_3^+]/[Zn^{2+}][H^+][CO_3^{2-}]$) where β is the overall stability constant. Similarly the ion concentration product of cadmium hydroxide should not exceed $\beta_{sp} = [Cd][H]^{-2}$, where β_{sp} is the solubility product of $Cd(OH)_2$ divided by the square of the ion product constant of water.

Once these interactions were identified, the required equilibrium constants were obtained from standard sources (Smith and Martell, 1976, 1982) and were corrected to μ = 0.7 M by the use of adjustment factors from Table IV, which were developed by Smith et al. (1985). The subsequent computations of metal complex concentrations were carried out with the aid of the Fortran Program MINEQL (Westall et al., 1976). This program was modified as necessary to run properly within the requirements of a VAX 11/780 computer. Significant optimization was necessary and was achieved through the modification of convergence criteria, since it was found that the same convergence factor could not be universally specified for all the individual species calculations. Thus after 10 iterations, the factor was gradually relaxed to achieve convergence.

Another important and essential modification of the MINEQL program involved the replacement of its non-critical stability constant data base. All of the calculations carried out in this research required the insertion of critical constants from dependable sources (Smith and Martell, 1976, 1982), modified as described above. These are shown in Table V. In the study of the contaminated seawater containing added chelating agents each system consisted of 20 components, with a concomitant increase in the number of soluble species. The general results are summarized in Table VI.

The computations were carried out not only at pH 8.1 but also at somewhat higher and lower pH to determine the resulting effects on coordination tendencies.

TABLE IV

Variation of correction factors for stability constants relative to 0.10 M ionic strength of complexes formed from metal ions and ligands of various charge types

		M^+					M^{2+}					M^{3+}					M^{4+}				
Ionic strength		0.0	0.5	1.0	2.0	3.0	0.0	0.5	1.0	2.0	3.0	0.0	0.5	1.0	2.0	3.0	0.0	0.5	1.0	2.0	3.0
L^-	log K_1	+0.2	−0.1	−0.1	−0.0	+0.2	+0.4	−0.2	−0.2	−0.1	0.0	+0.6	−0.3	−0.3	−0.3	−0.2	[+0.8]	[−0.4]	[−0.4]	[−0.5]	[−0.4]
	log β_2	+0.3	−0.1	0.0	+0.3	+0.6	+0.6	−0.4	−0.4	−0.3	0.0	+1.0	−0.5	−0.5	[−0.4]	[−0.2]	[+1.6]	[−0.6]	[−0.6]	[−0.6]	[−0.5]
L^{2-}	log K_1	+0.4	−0.2	−0.2	−0.1	0.0	+0.8	−0.4	−0.4	−0.4	[−0.3]	+1.2	−0.6	−0.6	[−0.7]	[−0.6]	[+1.6]	[−0.8]	[−0.8]	[−1.0]	[−0.9]
	log β_2	+0.6	−0.4	−0.4	−0.3	0.0	+1.2	−0.8	−0.8	[−0.7]	[−0.5]	+1.8	[−1.0]	[−1.0]	[−1.0]	[−0.9]	[+2.4]	[−1.4]	[−1.4]	[−1.5]	[−1.4]
L^{3-}	log K_1	+0.6	−0.3	−0.3	−0.3	−0.2	+1.2	−0.6	−0.6	[−0.7]	[−0.6]	[+1.8]	[−0.9]	−0.9	[−1.1]	[−1.0]	[+2.4]	[−1.2]	[−1.2]	[−1.5]	[−1.4]
	log β_2	+1.0	−0.5	−0.5	[−0.4]	[−0.2]	+1.8	[−1.0]	[−1.0]	[−1.0]	[−0.9]	[+2.6]	[−1.5]	[−1.5]	[−1.6]	[−1.5]	[+3.4]	[−2.0]	[−2.0]	[−2.2]	[−2.1]

TABLE V

TABLE V

Stability constants of metal complexes of added ligands (expressed as log β values) (μ = 0.70 M; t = 25.0°C)

	EDTA[a]				NTA[b]				CIT[c]				TPP[d]			SSA[e]		
	ML	MHL	$MH_{-1}L$	Other	ML	ML_2	MLH_{-1}	Other	ML	MHL	MLH_{-1}	Other	ML	MHL	MLH_{-1}	ML	ML_2	ML_3
Ca^{2+}	9.60	13.0			5.8	7.8			2.9	7.20		[f]	5.40	11.5				
Mg^{2+}	7.8	11.8			4.9				2.8	6.90			5.82	12.0				
K^+					0.1				0.3				1.39	9.0				
Na^+	1.2				0.9				0.4				1.64	9.38				
Fe^{3+}	23.8	25.1	17.0		15.0	22.0	11.8	[g]	10.3	11.5	8.5	[h]	23.4	26.0		14.4	22.2	30.6
Mn^{2+}	12.8	13.0							3.1	7.1				11.2		4.8		
Cu^{2+}	17.7	20.8	5.8		12.5	16.5	3.9	[i]	5.3	8.8	1.63	[j]	7.1	12.7		8.9	15.9	
Cd^{2+}	15.4	18.4			9.2	13.4			3.2	7.3		[k]	7.1	12.6		4.0		
Zn^{2+}	15.4	18.5			10.1	13.2	0.6		4.3	8.8			7.4	12.7		5.5	9.7	
Ni^{2+}	17.5	20.8			10.9	15.3	0.64		4.7	8.3		[l]	6.9	12.5		5.8	9.2	
Hg^{2+}	20.5	23.7	10.8		13.7		8.0		10.3				10.1	15.0		14.5	18.0	
Pb^{2+}	16.9	19.8			10.7	17.7			4.4	8.2			7.5			5.0		
UO_2^{2+}	9.6	15.6		[m]	8.9				6.8				8.3		−4.9	10.6	18.2	

[a] Log protonation constants EDTA (ethylenediaminetetraacetic acid) 8.78, 15.01, 17.39, 19.39.
[b] Log protonation constants NTA (nitrilotriacetic acid) 8.90, 11.2, 13.1.
[c] Log protonation constants CIT (citric acid) 5.34, 9.45, 12.25.
[d] Log protonation constants TPP (tripolyphosphate) 8.61, 14.30, 16.30.
[e] Log protonation constants SSA (sulfosalicylic acid) 11.40, 13.72.
[f] $\log \beta_{CaCITH_2} = 10.40$.
[g] $\log \beta_{FeNTAH_{-2}} = 4.0$; $\log \beta_{Fe_2(NTA)_2H_{-2}} = 27.60$.
[h] $\log \beta_{Fe_2(CIT)_2H_{-2}} = 21.2$.
[i] $\log \beta_{CuNTAH} = 13.7$.
[j] $\log \beta_{Cu(CIT)H_2} = 12.26$
[k] $\log \beta_{CdCITH_2} = 11.0$.
[l] $\log \beta_{NiCITH_2} = 11.1$.
[m] $\log \beta_{(UO_2)_2EDTA} = 16.5$.

TABLE VI

Components and species present in seawater with and without added chelating agents

Added contaminant	No. components	No. species		
		Soluble	Insoluble	Total
none	19	141	26	167
EDTA	20	174	26	200
NTA	20	175	26	201
CIT	20	175	26	201
TPP	20	168	26	194
SSA	20	162	26	188

EDTA = ethylenediaminetetraacetic acid. NTA = nitrilotriacetic acid. CIT = citric acid. TPP = tripolyphosphate. SSA = sulfosalicylic acid.

RESULTS AND DISCUSSION

In seawater at pH 8.1 the degrees of formation of the principal metal complex species in the absence of added contaminating ligand are given in Table VII. The Ca^{2+} ion is primarily uncomplexed: the sulfato complex is present at < 10%, while an appreciable amount is present as suspended solid carbonate. Most of the Mg^{2+} ion at these levels is uncomplexed with 8.4% as the sulfato complex. The alkali metal ions K^+ and Na^+ have very little tendency to complex to the ligands present. The ions Mn^{2+}, Cd^{2+} and Hg^{2+} show considerable tendency toward chloro complex formation. The ferric ion seems to be 98.3% converted to the colloidal hydroxide, and the Cu^{2+} ion is combined with OH^- as $CuOH^+$. Half of the Zn(II) is in the free form; the remaining species are

TABLE VII

Seawater speciation in the absence of added ligands at pH 8.1. (Numbers give % in terms of metal ion associated with the ligands indicated.)

Metal ion	Cl^-	Br^-	F^-	SO_4^{2-}	$(H)CO_3^a$	OH^-	Uncomplexed	Precipitate	
Ca^{2+}			0.01	9.8	0.54		79.0	10.6	$CaCO_3$
Mg^{2+}			0.07	8.4	0.45	0.02	91.1		
K^+				2.2			97.8		
Na^+				2.4	0.01		97.6		
Mn^{2+}	34.4		0.01	4.4	0.15	0.12	60.9		
Cd^{2+}	96.8	0.08		0.3		0.05	2.9		
Hg^{2+}	99.9	0.05							
Fe^{3+}						1.71		98.3	$Fe(OH)_3$
Cu^{2+}	1.9			0.2	22.4	73.6	1.85		
Zn^{2+}	41.2	0.02		4.86	0.40	0.47	53.0		
Pb^{2+}	22.32	0.02		0.3	71.9	3.9	1.5		
Ni^{2+}	29.6	0.01		3.1		0.67	66.6		
UO_2^{2+}					100.0				

[a] $(H)CO_3$ carbonate and bicarbonate.

distributed between the chloro, sulfato, and small amounts of the hydroxo and carbonato complexes. Lead(II) is about 72% converted to the carbonate, while the remaining fraction in solution consists of the soluble lead chloro and hydroxo complexes. A considerable fraction of the nickel(II) is uncomplexed and 30% is in the form of chloride with smaller amounts of sulfato and soluble hydroxo complexes.

According to the stabilities cited, UO_2^{2+} is quantitatively converted to soluble uranyl carbonates: 0.3% mono-, 29.3% di- and 70.4% tricarbonato complexes. This agrees with Ahrland's (1985) conclusion that $UO_2(CO_3)_3^{4-}$ is the major uranium complex species in the ocean (in the absence of strongly coordinating organic ligands). Under the conditions specified, and in the absence of additional complexing ligand, it appears that the insoluble hydroxide is absent. The possibility of forming insoluble basic chlorides, especially at the high chloride concentration of seawater should be explored further.

The fact that the actual metal species present are varied and are not limited to their aquo ions is of considerable interest and is relevant to the redistribution that occurs when additional chelating ligands are introduced into this seawater model. The form of the metal ion is important since it influences the bioavailability of the metal. Because the presence of unnatural ligands can alter the distribution of complex species, the perturbations that occur may be of considerable importance.

Speciation in the presence of EDTA

Computations were performed at three levels of EDTA contamination: 1.0×10^{-7} M, 1.0×10^{-8} M, 1.0×10^{-9} M. The differences in concentration levels shown in Tables VII and VIII indicate the perturbation in the concentrations of metal complex species when 1.0×10^{-7} M EDTA is added. This level of EDTA has very little effect on speciation of Ca^{2+}, Mg^{2+}, K^+, Na^+, Hg^{2+}, Fe(III) and UO_2^{2+}. However, 88% of the added EDTA is complexed by Ca^{2+} and Mg^{2+}. Solid $CaCO_3$ and $Fe(OH)_3$ are not dissolved by conversion to the respective EDTA complexes. Redistribution of the natural complexes present occurs only for those metal ions that form highly stable EDTA chelates. Ni(II) and Cu(II) are almost completely converted to their EDTA chelates. With respect to the fate of the EDTA at 1.0×10^{-7} M initial concentration, the following are the per cent conversions of EDTA to the corresponding divalent metal chelates, in decreasing order: Ca(II) 79.7%, Mg(II) 7.56%, Ni(II) 4.99%, Cu(II) 3.8%, Zn(II) 3.8%, Mn(II) 0.04%, Pb(II) 0.04% and Cd(II) 0.01%. There is no free EDTA under the conditions that apply to this system.

At 1.0×10^{-8} M, EDTA is overwhelmed by the trace elements present which have relatively high affinity constants. At this level only 30% of the EDTA is tied up with Ca^{2+} and Mg^{2+}. Under these conditions, an entirely different distribution of EDTA in the metal complexes formed occurs, as follows: Ni(II) 47.3%, Ca(II) 27.6%, Cu(II) 17.4%, Zn(II) 5.0%, Mg(II) 2.6%, Pb(II) 0.04%, and Mn(II) 0.01%. With the limited amount of EDTA available, the uptake of Ni(II)

TABLE VIII

Seawater speciation in the presence of 1.0×10^{-7} M added EDTA at pH 8.1. (Numbers give % in terms of metal ion associated with the ligands indicated.)

Metal ion	Cl^-	Br^-	F^-	SO_4^{2-}	$(H)CO_3^a$	OH^-	Uncomplexed	Precipitate		EDTA[b]
Ca^{2+}			0.01	9.8	0.54		79.0	10.6	$CaCO_3$	< 0.01
Mg^{2+}			0.07	8.4	0.45	0.02	91.1			< 0.01
K^+				2.2			97.8			< 0.01
Na^+				2.4	0.01		97.6			< 0.01
Mn^{2+}	34.1		0.01	4.4	0.15	0.12	60.3			0.9
Cd^{2+}	82.4	0.07		0.21		0.04	2.4			14.82
Hg^{2+}	99.9	0.05								< 0.01
Fe^{3+}						1.71		98.2	$Fe(OH)_3$	0.1
Cu^{2+}	0.09				0.95	3.2	0.08			95.7
Zn^{2+}	9.8			1.2	0.1	0.1	12.6			76.3
Pb^{2+}	5.8			0.09	18.73	1.0	0.4			74.0
Ni^{2+}	0.06						0.13			99.8
UO_2^{2+}					100.0					< 0.01

[a] $(H)CO_3$ carbonate and bicarbonate.
[b] % of EDTA complexed: Ca^{2+} 79.7; Mg^{2+} 7.56; Mn^{2+} 0.04; Cd^{2+} 0.01; Cu^{2+} 3.83; Zn^{2+} 3.81; Pb^{2+} 0.04; Ni^{2+} 4.99.

as the EDTA complex is still very high amounting to 94.6% of the total Ni(II) present. For copper(II) this percentage is 43.6, half of the concentration at the higher (1.0×10^{-7} M) EDTA level. Both zinc(II) and lead(II) are about 10% complexed by EDTA, and only traces of the remaining metals are bound.

At 1.0×10^{-9} M EDTA, the EDTA present is complexed almost exclusively by Ni(II) (91.5%), but this represents only 18.3% of the Ni^{2+} present. The remaining percentages are 3.9% by Cu^{2+}, 3.5% by Ca^{2+}, 0.71% by Zn^{2+} and 0.33% by Mg^{2+}. The three ions Pb^{2+}, Cu^{2+}, and Zn^{2+}, are complexed by EDTA at levels of < 1%.

The effects observed for the 1.0×10^{-5} M EDTA system with regard to pH dependence (increase) are not large but the Cd^{2+} complexed to EDTA, perhaps not surprisingly, increases a few percent. The degree of Cu(II), Pb(II) and Fe(III) complexation decreases with an increase in pH while the remaining ions remain substantially the same. The most important cause for these decreases is the formation of soluble $Cu(OH)^+$, $Pb(OH)^+$ and soluble and insoluble Fe(III) hydroxides which release EDTA for more complete Cd(II) chelate formation.

Addition of NTA

With 1.0×10^{-7} M added NTA (pH = 8.1) the results indicate that calcium(II) and magnesium(II) tie up 96% of the NTA, with Ca(II)-NTA accounting for 54.7% and Mg(II)-NTA for 41.2% of the NTA species. There is only about 0.08% free NTA with the remainder (< 2%) distributed between several trace metals. Unlike the results with EDTA, only 1.2% of the NTA binds to Ni(II), and an equivalent amount is coordinated to Cu(II). Zinc(II) accounts for 0.34% of the

bound NTA while Na(I) is also complexed to the extent of about 0.04% of the bound NTA.

Although Ca^{2+} and Mg^{2+} bind most of the NTA present, because of their relatively high concentrations, the actual amount of these metals bound to NTA is < 0.1%. Nevertheless the NTA binds 44.6% of the available copper(II) and 35.8% of the nickel(II). A considerably lesser degree of complexation occurs for zinc(II) (6.8%) and almost negligible amounts of Cd(II) (0.05%) and Pb(II) (0.77%) are bound. The UO_2^{2+} ion is solubilized in this model due to the strong binding by the ubiquitous CO_3^{2-}.

If, on the other hand, NTA is added at the 1.0×10^{-8} M level, the change of the distribution of complex species is minimal. Ca(II) and Mg(II) still have the majority of bound NTA (94%), and the 6% remaining goes to copper(II) and nickel(II). The only significant degree of complexation to trace metal ions occurs via conversion of 7.3% of Cu(II) and 5.2% of Ni(II) to the NTA chelates. The only two other metal ions that form NTA complexes to any extent are Pb(II) and Zn(II), with less than 1% each. At one order of magnitude lower, with 1.0 nM NTA, the distribution of NTA among the metal ions is virtually the same, but with a lesser degree of binding to the trace metal ions.

Addition of TPP

The tripolyphosphate anion exists mainly in the monoprotonated form $HP_3O_{10}^{4-}$ at pH 8.1, and its affinity for metal ions is to a large extent due to the high negative charge of the anion, $P_3O_{10}^{5-}$. Since the ligand contains only oxygen donors, its affinity for some of the less basic metal ions in seawater, such as Zn(II), Pb(II) and Cd(II), is relatively low.

At 1.0×10^{-7} M the TPP present at pH 8.1 is mainly coordinated by Mg(II) and Ca(II). This creates a several-orders of magnitude lower effective concentration for the available TPP compared with that actually present. The degree of complexing of TPP with all other metal ions is considerably less than 1%. Because of the high concentrations of Ca(II) and Mg(II) in seawater, the fractional amounts of Ca^{2+} and Mg^{2+} complexed (< 0.01% total) represent 99.7% of the TPP present. Furthermore, since the stability constant of the Mg(II) complex of TPP is higher than that of Ca(II), the Mg(II) chelate predominates at lower pH. But when pH is increased, the decrease in solubility of the $Mg(OH)_2$ with the second power of the hydroxide ion concentration results in the displacement of the Mg(II) from TPP, and the latter then combines more completely with Ca(II). Although the solid $CaCO_3$ phase also appears, its degree of formation is proportional to only the first power of $[OH^-]$ at these pH values.

At a somewhat higher level of TPP concentration (1.0×10^{-6} M) the distributions of TPP species are very close to those described above for the 1.0×10^{-7} M systems. In addition to the small amounts of Ni(II) and Zn(II) complexes formed (< 0.05%), quite significantly 26.4% of the available iron(III) is converted to the TPP chelate. Thus TPP is the most potent solubilizing agent for Fe(III) in this study. The other complexes of TPP are rather

insignificant and the distribution of metal complex species are for the most part similar to the distributions indicated in Table VII for pure seawater.

The dilute (1.0×10^{-8} M) TPP at pH 8.1 calculations show that about 99.7% of the TPP is distributed between Ca(II) and Mg(II) while 0.2% of the TPP reacts with the Fe(III) ion converting 0.26% of the latter to the corresponding TPP complex. Formation of complexes with other metal ions present is negligible.

Addition of citrate

Citric acid is interesting for several reasons. It is a natural product, is used industrially in large quantities as a cleaning agent, is effective at low pH and is capable of deprotonation at the hydroxyl groups when coordinated with ions such as those of Cu(II) and Fe(III). Table IX shows the metal complex distributions in the presence of a total analytical concentration of CIT of 1.0×10^{-7} M at pH 8.1. As the only trace-metal ion that forms an appreciable amount of citrate complex, 19.7% of the copper becomes bound under seawater conditions, representing 0.79% of the total citrate present. All other complexes, except those of Ca(II) and Mg(II), are present in negligible concentrations. Because of the large concentrations of Ca(II) and Mg(II), and their moderate affinity for citrate ion, only 2.5% of the citrate is left unbound. The affinity of citrate for copper(II) is greatly increased at pH 8.1 by the dissociation of the hydroxyl group of the citrate, a process that allows a five-membered chelate ring to form (Warner and Weber, 1953) and converts a weakly-coordinating

TABLE IX

Seawater speciation in the presence of 1.0×10^{-7} M added CIT as a function of pH

Metal ion	pH = 7.1		pH = 8.1		pH = 9.1	
	M^{n+} [a]	CIT[b]	M^{n+} [a]	CIT[b]	M^{n+} [a]	CIT[b]
Ca^{2+}		17.9		16.3		30.7
Mg^{2+}		76.2		77.5		56.2
K^{+}		0.05		0.05		0.1
Na^{+}		2.8		2.9		6.1
Mn^{2+}						0.02
Cd^{2+}						
Hg^{2+}						
Cu^{2+}	12.8	0.51	19.7	0.79	40.5	1.6
Zn^{2+}						
Pb^{2+}						
Ni^{2+}						
Fe^{3+}					0.02	
Free Citrate		2.47		2.47		5.2

[a] % M^{n+} as citrate.
[b] % citrate complexed to metal ion.

hydroxyl group to a strong alkoxide donor, resulting in the formation of an exceedingly stable complex. The other divalent metal ions do not react with citrate in this manner. As a consequence Cu(II) is the only trace metal bound to any significant degree. Calculations at lower pH (e.g. p[H] 4.1 and 5.1) show that in acid solution a considerable fraction of the citrate is bound to Fe(III). On the other hand, citrate does not effectively compete for Fe(III) at higher p[H].

It can be seen from the effect of pH on the percentages of metal and ligand chelated that if the pH of seawater were a little higher, a significantly higher fraction of the Cu(II) would be converted to the citrate. The insolubility of $Mg(OH)_2$ is responsible for the reversal in the trend of the relative percentages of Ca(II) and Mg(II) complexed as a function of pH. At pH 9.1 less of the citrate would be complexed by Mg(II), because $Mg(OH)_2$ is precipitated to a greater extent under these conditions. Because of the release of CIT from Mg^{2+}, one sees the appearance of 0.02% Ni^{2+}-CIT at pH 9.1. Apart from this, and the strong binding of Cu(II), citrate has very little effect on the redistribution of the trace metal complexes in seawater.

If the concentration of CIT is decreased one order of magnitude to 1×10^{-8} M, the fraction of Cu(II) complexed is also decreased by about one order of magnitude. Further reduction of CIT to 1.0×10^{-9} M would further decrease the degree of Cu(II) complexation by an order of magnitude to 0.15%, but the degree of complexation of CIT would be about the same, 0.59%. The availability of CIT is largely determined by the large excess of the two alkaline earth ions present.

Addition of SSA

The ligand 5-sulfosalicylic acid (SSA) may be considered a model compound for humic acid in view of the presence of phenolate and carboxylate donor groups in the latter. However, because SSA is only bidentate, it is not very effective at very low concentrations. Indeed at 1.0×10^{-7} M the only complex formed in seawater was found to be the 1:1 Cu(II) chelate at 0.05% of the total Cu(II) available, which accounts for $< 0.01\%$ of the available SSA. At pH 8.1, the relative amount of free (uncomplexed), SSA is $> 99.99\%$.

However, an additional computation at 1.0×10^{-5} M SSA was carried out to determine if this higher concentration would have any influence on metal speciation. At this level the SSA combines with Mn(II) 0.02%, Cu(II) 7.3%, Zn(II) 0.08%, and Ni(II) 0.21%. Although it has been considered an effective ligand for Fe(III), no discernable amount reacts with the iron present at these concentrations.

CONCLUSIONS

Although the ocean is a complex mixture of components, valuable information may be gained by the analysis of its constituents by the use of reliable,

known and estimated stability constants which describe the formation of both soluble and insoluble complexes. The resulting distribution may be considered a base that may be used for the calculation of modifications in distribution resulting from changing conditions of temperature and pressure, and from the addition of various inorganic or organic ligands to take into account the effects of naturally-occurring chelating agents such as humic acid, or those that may be added through environmental pollution.

In the model chosen, it was found that seawater is saturated with respect to Ca(II) carbonate, Fe(III) hydroxide and nearly saturated relative to $Mg(OH)_2$. Thus the availability of each trace metal ion considered is based not only on stabilities of the complexes in solution, but also on the solubility products of the various solid constituents. The added ligands, as outlined above, exert their influence through complexation of the dissolved ions. Only negligible dissolution of precipitates was found to occur at the levels of added ligands used in this study. In this multiphase multicomponent competition, the calculations are feasible only if valid equilibrium constants are known. In this work, these constants were selected, individually studied, and adjusted to seawater conditions using empirical relationships developed for the variation of the stability constants with ionic strength and ionic charge, relative to the conditions of 0.10 M ionic strength (Martell, et al., 1985; Smith et al., 1985). Most of the experimental stability constant data found in the literature are reported for 0.10 M ionic strength, which has become a standard in the field.

While the results of this study provide indications of how metal speciation in the oceans is influenced by the addition of chelating agents, the conclusions are limited by the fact that at this stage the effects of naturally-occurring organic ligands have not been considered. While these ligands are very important, the concentration levels at which they exist vary considerably in various regions and at various depths of the ocean. The next stage in this research program will consist in the evaluation of the redistributions of metal complex species that result from the complexing action of these organic oceanic constituents, at the various concentrations at which they have been found to be present. Since the necessary constants and identities of a majority of these constituents are uncertain, this will be a formidable task which will be approached in a systematic manner.

ACKNOWLEDGMENT

This research was supported by a grant, ESO2971, from the National Institute of Environmental Health Sciences, U.S. Public Health Service.

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