The speciation of cobalt in seawater and fresh waters at 25°C

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Cobalt(II) speciation in seawater and fresh waters was calculated using recent spectrophotometricaly determined stability data for cobalt(II) chloride and bromide complexes in aqueous solutions, and a theoretically estimated stability constant for the cobalt(II) bicarbonate complex. Calculations for seawater suggest that 56.25% of total dissolved cobalt(II) occurs as the free ion, Co^{2+} , 39.53% as CoCl^+ , 2.76% as CoCl_2^0 , 1.02% as CoSO_4^0 , and less than 1.0% as CoNH_3^{2+} , CoCO_3^0 , CoHCO_3^+ , CoCl_3^- , CoF^+ and CoBr^+ . In neutral to acidic fresh waters, 90% or more of the dissolved cobalt(II) occurs as the free ion. CoCO_3^0 becomes important in basic fresh waters ($\text{pH} > 8.5$), and predominant in very basic fresh waters ($\text{pH} > 9.5$). Co(II) organic complexes are not included in the calculations, discussions suggest that they are unlikely to be abundant in seawater. Co(II) organic complexes may, however, be important in fresh waters, and future work should investigate this possibility.

INTRODUCTION

The speciation of a metal in natural waters is of primary significance, because it is the species of a metal which determine its chemical activity and toxicity. Although the concentration of cobalt in natural waters is very low (in seawater, about $1 \times 10^{-10} \text{ m}$, Ahrlund, 1985; $6.87 \times 10^{-9} \text{ m}$, Goldberg, 1980), as the principal constituent of Vitamin B₁₂ and methymalonyl GA mutase in livers, cobalt is one of the essential trace elements for man and animals (Brooks, 1977). It is therefore important to understand the behavior of cobalt in the environment, especially in natural waters. Unfortunately, controversy exists over cobalt speciation in seawater. Horne (1965) suggests that the free ion, Co^{2+} and CoSO_4^0 are the principal dissolved species of cobalt in seawater. The model of Turner *et al.* (1981) suggests that 88% of cobalt in seawater is present as Co^{2+} and CoCl^+ (see Table 1). Stumm and Brauner (1975) and Stumm and Morgan (1981) state that the principal cobalt species in seawater are the free ion, Co^{2+} , and possibly,

CoCO_3^0 . Ahrlund (1985) and Byrne *et al.* (1988) made similar, but more complete inference for cobalt speciation in seawater (Table 1). Most of the above authors indicate that Co(II) is a fairly "hard" acceptor in the Pearson (1963) sense. Complexes of cobalt(II) with oxy-anions will be much more stable than with halides (excluding F^-). Because sufficiently reliable stability constants were not available at the time of these early studies, calculations of cobalt speciation in seawater were based mainly on theoretical estimation. Because stability constants for Co(II) bicarbonate complexes are still not available, all the above speciation schemes of Co(II) in seawater do not take the bicarbonate complexes into account.

Millero's (1974) review of trace elements such as Cu, Zn, Cd, Hg and Pb, which have been studied in more detail, indicates a few general points of agreement among authors: 1) only a small portion of trace metals exists in seawater as the free ion; 2) with few exceptions, chloride complexes are the dominant complexed species; 3) F^- , Br^- and SO_4^{2-} are not important complex-

Table 1. Calculated cobalt species distribution in seawater

Species	<i>m</i> (This work)	%			
		This work	(1)	(2)	(3)
Co ²⁺	3.87×10^{-9}	56.25	42.	58.	65.
CoCl ⁺	2.72×10^{-9}	39.53	24.	30.	14.
CoCl ₂ ⁰	1.9×10^{-10}	2.76			
CoCl ₃ ⁻	2.0×10^{-12}	0.03			
CoCl ₄ ²⁻	$3. \times 10^{-15}$	<0.01			
CoBr ⁺	9.7×10^{-13}	0.01			
CoBr ₂ ⁰	$3. \times 10^{-17}$	<0.01			
CoBr ₃ ⁻	$2. \times 10^{-22}$	<0.01			
CoBr ₄ ²⁻	$2. \times 10^{-28}$	<0.01			
CoNH ₃ ²⁺	1.25×10^{-11}	0.18			
Co(NH ₃) ₂ ²⁺	$1. \times 10^{-14}$	<0.01			
Co(NH ₃) ₃ ²⁺	$3. \times 10^{-18}$	<0.01			
Co(NH ₃) ₄ ²⁺	4×10^{-22}	<0.01			
CoF ⁻	5.4×10^{-13}	0.01			
CoOH ⁺	$8. \times 10^{-25}$	<0.01	0.4	1.	1.
CoSO ₄ ⁰	7.0×10^{-11}	1.02	5.	5.	5.
CoCO ₃ ⁰	7.2×10^{-12}	0.10	28.	6.	14.
CoHCO ₃ ⁺	5.5×10^{-12}	0.08			
CoH ₂ PO ₄ ⁺	$3. \times 10^{-13}$	<0.01			
Co(IO ₃) ₂ ⁰	$2. \times 10^{-21}$	<0.01			
CoH ₂ S	$<1 \times 10^{-99}$	<0.01			
Total	6.87×10^{-9}	99.97	99.4	100.	99

References: (1) Ahrlund (1985); (2) Turner *et al.* (1981); (3) Byrne *et al.* (1988).

ing ligands; and 4) CO₃²⁻ may be an important complexing ligand only for Pb. A recent study by Byrne *et al.* (1988) confirmed these observations, with the exception of Zn, which was calculated to occur mostly as the free ion in seawater. Because Cu, Zn, Cd, Hg and Pb are also fairly "hard", the above observations cast doubt upon the previously proposed cobalt speciation schemes in seawater (Table 1). A recent contribution on Co(II) halide complexes by Pan and Susak (1989) have made it necessary and possible to reexamine Co(II) speciation in seawater.

MODELLING

Figure 1 is an Eh-pH diagram for the Co-H₂O system. Since Co³⁺ is stable only at very oxidized conditions, which is unlikely in natural waters, attention will be focused on Co²⁺.

Because seawater has a near-constant composition throughout the world oceans, and a

Fig. 1. Eh-pH diagram for the Co-H₂O system at 25°C. Data from Karapet'yants and Karapet'yants (1970).

large portion of the thermodynamic data at 25°C in the literature were determined in solutions of a constant ionic strength of seawater, it is convenient to define our standard state solution to be at 298.15 K and 1 bar, and with an ionic strength of seawater (0.714). By definition,

$$\beta = \frac{\prod a_i^{\nu_i}}{\prod a_j^{\nu_j}} = \frac{\prod m_i^{\nu_i}}{\prod m_j^{\nu_j}} \cdot \frac{\prod \gamma_i^{\nu_i}}{\prod \gamma_j^{\nu_j}} \quad (1)$$

where β is the stability constant with the conventional standard state; a is the chemical activity of reactant species, j , or product species, i ; ν is the stoichiometric coefficient; m is the molality; γ is the activity coefficient. The stability constant with our defined standard state, β' is given by

(↗)

$$\beta' = \frac{\prod m_i^{\nu_i}}{\prod m_j^{\nu_j}} = \beta \frac{\prod \gamma_j^{\nu_j}}{\prod \gamma_i^{\nu_i}} \quad (2)$$

With the standard state defined above, the concentration of water can be taken as unity, and the molality of a species equals its activity. For simplicity, all bound waters will be dropped from the formulas of the complexes. Based on previous studies (Millero, 1974; Turner *et al.*, 1981; Ahrlund, 1985; Byrne *et al.*, 1988), it is expected that the dominant cobalt(II) species in seawater are the free ion, and the chloride, carbonate and sulfate complexes. In our model, in addition to the free ion, Co^{2+} , we consider the following 20 complexes:

We cannot include all possible Co(II) species in seawater in the list, due to the lack of appropriate thermodynamic data. However, the Co(II) hydroxide, sulfate and fluoride complexes are adequately represented by their first step complexes, as the first step complexes are usually the strongest. When ligand concentrations are very low, as in the present calculations, the concentrations of the first step complexes are usually much higher than those of complexes with higher coordination numbers (Appendix I). The Co(II) phosphate, iodate and bisulfide complexes are represented by $\text{CoH}_2\text{PO}_4^+$, $\text{Co}(\text{IO}_3)_2^0$ and $\text{CoH}_2\text{S}^{2+}$ respectively (data for only these complexes are available), which may not be the most abundant Co(II) bisulfide, phosphate and iodate complexes, but should be close enough to evaluate such terms. When the total concentrations of these complexes are very low (as demonstrated below), it is probably sufficient to know their relative orders of magnitude for the purpose of comparison.

For the i th complex,

$$[C_i] = \beta'_i [\text{Co}^{2+}] [L_i]^{\nu_i} \quad (3)$$

where C_i and β'_i ($i = 1 \cdots 20$) are the i th cobalt(II) complex and its stability constant, respectively, and L_i and ν_i are the i th ligand and its stoichiometric coefficient. Note that the concentrations of both cobalt and the ligand in equation (3) are those of the free ions (equilibrium concentrations), not the total ones. Taking total cobalt concentration in seawater to be $6.87 \times 10^{-9} m$ (Goldberg, 1980), then

$$\begin{aligned} & [\text{Co}^{2+}] + [\text{CoF}^-] + \sum_{n=1}^4 [\text{CoCl}_n^{2-n}] + \sum_{n=1}^4 [\text{CoBr}_n^{2-n}] + \sum_{n=1}^4 [\text{Co}(\text{NH}_3)_n^{2+}] + [\text{CoOH}^+] \\ & + [\text{CoH}_2\text{S}^{2+}] + [\text{Co}(\text{IO}_3)_2^0] + [\text{CoSO}_4^0] + [\text{CoCO}_3^0] + [\text{CoHCO}_3^+] \\ & + [\text{CoH}_2\text{PO}_4^+] = 6.87 \times 10^{-9} \end{aligned} \quad (4)$$

By substituting equation (3) into equation (4), the latter equation can be solved when all the necessary β 's and free ligand concentrations, $[L_i]$, are known.

STABILITY CONSTANTS AND FREE LIGAND CONCENTRATIONS

The discrepancies in cobalt speciation schemes for seawater are primarily a result of the different stability constants of cobalt(II) complexes (or ion-pairs) used by different authors. The stability constants of cobalt(II) chloride complexes in the literature are highly variable (discussed in Pan, 1989; Pan and Susak, 1989). Therefore, a demonstrably valid set of data is required to calculate Co(II) speciation in seawater. Besides, in seawater (pH=8.2), more than 99% of total dissolved carbon occurs as bicarbonate ion in solution. Thus, the cobalt(II) bicarbonate complex has to be considered in order to calculate a complete speciation scheme for Co(II) in seawater.

In a spectrophotometric study of Co(II)-chloride and -bromide complexes, Pan and Susak (1989) obtained the stability constants of all complexes using a combination of graphical and numerical methods. With the distinction between octahedral (6-fold) and tetrahedral (4-fold) complexes and the correction to activities,

we believe that the stability constants reported in Pan and Susak (1989) are better estimates than previously reported ones. All β 's for octahedral chloro- and bromo-cobalt (II) complexes at 25°C and $I=0.714$ (formal ionic strength of seawater, Ahrlund, 1985) were calculated using the data of Pan and Susak (1989), and listed in Table 2.

No stability data for Co (II) bicarbonate complexes are available in the literature. Nevertheless, numerous studies (Hancock *et al.*, 1977; Chen *et al.*, 1984; Elliott, 1988; Mountain and Wood, 1988) suggest that linear free energy relations hold for many metals and ligands. Figure 2 shows such a linear free energy relationship, i.e. $\log \beta'(\text{MHCO}_3^+)$ against $\log \beta'(\text{MCO}_3^0)$, for Fe^{2+} , Cu^{2+} , Ca^{2+} and Mg^{2+} . A regression line was obtained with a correlation coefficient 0.97. From this regression equation, we calculated that $\log \beta'$ for equation (5) below is 0.819, given that $\log \beta'$ for equation (6) is 3.01 (Byrne *et al.*, 1988).

The apparent stability constant of the Cobalt(II) sulfate complex in Table 2 was calculated from the value at infinite dilution (Izatt *et al.*, 1969). The data of Izatt *et al.* (1969) was used, because it was determined using a

Table 2. Data used in cobalt speciation calculations in seawater

	$-\log(m)$	$\log \beta'_1$	$\log \beta'_2$	$\log \beta'_3$	$\log \beta'_4$
Cl^-	0.253 ^a	0.100 ^b	-0.816 ^b	-2.54 ^b	-5.11 ^b
Br^-	3.07 ^a	-0.538 ^b	-2.00 ^b	-4.10 ^b	-7.02 ^b
OH^-	5.8 ^c	-9.9 ^c			
F^-	4.5 ^c	0.64 ^d			
IO_3^-	6.3 ^e		0.15 ^f		
NH_3	4.5 ^e	2.01 ^f	3.52 ^f	4.43 ^f	5.06 ^f
SO_4^{2-}	2.0 ^g	1.36 ^g			
CO_3^{2-}	5.74 ^k	3.01 ^c			
HCO_3^-	3.67 ^k	0.819 ^h			
$[\text{H}_2\text{PO}_4^-]_{\text{T}}$	5.70 ^c	1.6 ⁱ			
$[\text{H}_2\text{S}]_{\text{T}}$	>99	21.3 ^j			

All β 's are stability constants of a ligand with Co(II), with a standard state solution defined as: 298.15 K, 1 bar, at a seawater ionic strength ($I=0.714$). a, Ahrlund (1985); b, calculated from Pan and Susak (1989); c, Byrne *et al.* (1988); d, Kulvinova *et al.* (1976); e, Quinby-Hunt and Turekian (1983); f, Wagman *et al.* (1982); g, calculated from Izatt *et al.* (1969); h, calculated in this work; i, Hogfeldt (1982); j, Smith and Martell (1976); k, calculated from Byrne *et al.* (1988).

Fig. 2. Linear free energy relationship for bicarbonate, carbonate metal complexes ($MHCO_3^+$ and MCO_3^0). Sources of data as follows: for Mg^{2+} , $\log \beta'$ (MCO_3^0) from Dyrssen and Hanson (1972), $\log \beta'$ ($MHCO_3^+$) from Sieber and Hostettler (1977); for Ca^{2+} , $\log \beta'$ (MCO_3^0) from Pytkowicz and Hawley (1974), $\log \beta'$ ($MHCO_3^+$) from Cobble *et al.* (1982); for Cu^{2+} , $\log \beta'$ (MCO_3^0) from Stiff (1971), $\log \beta'$ ($MHCO_3^+$) from Cobble *et al.* (1982); for Fe^{2+} , $\log \beta'$ (MCO_3^0) from Singer and Stumm (1970), $\log \beta'$ ($MHCO_3^+$) from Cobble *et al.* (1982); for Co^{2+} , $\log \beta'$ (MCO_3^0) from Byrne *et al.* (1988).

calorimetric method which is generally considered more reliable over others.

The concentrations of F^- , Cl^- , Br^- and IO_3^- are practically pH independent in natural waters. However, the concentrations of other ligands (CO_3^{2-} , SO_4^{2-} , HCO_3^- , $H_2PO_4^-$, etc.) in natural waters are, to various degrees, pH dependent. At a pH of 8.2, the concentrations of these ligands as free ions are either measured or calculated, as listed in Table 2, for calculating Co(II) speciation in seawater.

The composition of fresh waters varies according to bedrock lithology, latitude and season (cf. Stumm and Morgan, 1981, Table 8.6). In fresh waters, the pH, the concentrations of ligands (e.g. CO_3^{2-} , HCO_3^- , OH^- , SO_4^{2-} , Cl^- , and organic ligands) and the ionic electrolyte concentrations may vary over a wide range. Precise calculations are possible only for specific waterbodies. The equations together with the relevant chemical reactions are given in Appendix II, which may be used to calculate the concentra-

tions of free ligands in fresh waters when the total ligand concentrations are known. Using these equations, it is possible to calculate Co(II) speciation schemes in fresh waters as a function of pH.

RESULTS AND DISCUSSION

(1) In Seawater

Our calculated Co(II) speciation scheme in seawater (Table 1) resembles that of Turner *et al.* (1981), with the major differences in calculated Co(II) carbonate, sulfate and hydroxide complex concentrations. Our calculations show that the principal Co(II) complexes in seawater are $CoCl^+$, $CoCl_2^0$ and $CoSO_4^0$, in decreasing order of abundance. This is in disagreement with Ahrland (1985), Byrne *et al.* (1988), and to a lesser degree, with Turner *et al.* (1981). The cobalt speciation scheme is in general agreement with most of the other trace metal speciation schemes in seawater summarized by Millero (1974).

It should be noted that, because the concentrations of Br^- and F^- in seawater are so low, a change up to two orders of magnitude in the stability constants of the Co(II) bromide and fluoride complexes will not noticeably change the calculated Co(II) speciation scheme (less than 1%). The same situation is more pronounced for complexes of Co(II) iodate, hydroxide, phosphate and bisulfide. However, the calculated Co(II) speciation scheme is sensitive to the stability constants of Co(II) chloride, sulfate and carbonate complexes, as these ligands exist in seawater at significantly higher concentrations. Byrne *et al.* (1988) used a stability constant about 0.5 log units less than ours for $CoCl^+$, and consequently underestimated the concentration of Co(II) chloride in seawater by more than 20% relative to our model. Our value for the concentration of Co(II) carbonate complex differs from values estimated by other models, which did not make allowance for the bicarbonate complex.

Byrne *et al.* (1988) classified all elements in seawater into five groups according to their com-

plexing nature, with cobalt assessed as a weakly complexed metal. However, our results suggest that cobalt is a transitional weakly-complexed to mainly chloride-complexed metal. Such metals are little influenced by changes in temperature and pH (Byrne *et al.*, 1988). Our calculations show that a pH change from 8.2 to 7.8 causes concentration changes of less than 0.03% for the most important complexes. Therefore, our calculated cobalt speciation scheme in seawater is generally applicable to most oceanic water masses, regardless of locality or water depth.

Although only small amounts of organic matter (mainly humic acids) are present in seawater (about $340 \mu\text{g C litre}^{-1}$, Stumm and Morgan, 1981), the presence of organics can cause metal ions to depart from their known inorganic chemistry. However, as pointed out by Stumm and Morgan (1981), the ratio of inorganic to organic constituents is very high in seawater, and Ca^{2+} and Mg^{2+} are present at concentrations many orders of magnitude greater than that of trace element ions such as Co^{2+} . Thus, the competition by Ca^{2+} and Mg^{2+} organic complexes (removal of organic ligands) and by trace metal inorganic complexes (removal of trace metals) will drastically depress the formation of any trace metal organic complexes. Maljkovic and Branica (1971) found that the degree of Cd^{2+} complexing with EDTA is diminished by the competition between Ca^{2+} and Cd^{2+} for EDTA and by the formation of CdCl^+ . Huljev's (1986) experiments show that an increase of NaCl concentration and pH in aqueous solutions will decrease the fixation of Ru, Zn, Co and Hg by humic acids. Huljev (1986) pointed out that in the estuarine environment, Zn and Co may be rapidly released from humic acids due to the change of NaCl concentration (Hg is very slowly released). Turner *et al.* (1981) suggest that, in seawater at a pH of 8.2 only Cu^{2+} is significantly complexed by humic acid, with the Co(II) humic acid complex forming about 0.01% of total Co(II) concentration. Although organic cobalt(II) complexes in seawater can not be ruled out entirely at this stage, it seems that they are less abundant than the free ion and inorganic

complexes.

(2) In Fresh waters

Fresh waters have very low chloride concentrations relative to seawater. Because the total concentration of free anions is much lower in fresh waters, as is the ratio of Cl^- to other anions, it is likely that dissolved cobalt in fresh waters exists predominantly as the free ion. Using the relations outlined in the preceding sections and equations in Appendix II, Co(II) speciation schemes in two specific fresh water-bodies were calculated as a function of pH (Fig. 3). At the specific pH's of the two fresh waters, Co(II) speciations are also listed in Table 3. The same standard state is retained, but for approximation, no effort were made to correct the effect of ionic strength on the stability constants in fresh waters. According to Fig. 3, in acidic to slightly basic fresh waters, nearly 90% or more of dissolved Co(II) is present as the free ion; the remaining 10% exists as the complexes CoCO_3^0 , CoSO_4^0 and CoHCO_3^+ . However, the abundance of CoCO_3^0 increases with pH and becomes a

Table 3. Ligand concentrations and Co(II) speciations in two fresh waters

Ligand	-log m	
	Wind River Formation ¹	Milk River ²
Cl^-	3.85	3.55
Br^-	—	—
OH^-	6.27	6.35
F^-	4.83	5.05
IO_3^-	—	—
NH_3	—	—
TC	2.48	2.14
TS	2.85	2.48
TP	5.92	6.70
Species	%	
Co^{2+}	93.77	87.20
CoCO_3^0	1.14	2.18
CoHCO_3^+	1.97	4.15
CoSO_4^0	3.19	6.52

1. Ground water from the Wind River Formation in the Shirley Basin area (Harshman, 1972), averaged values (pH=7.78). 2. Surface water from the Milk River, at the eastern crossing of the Canada/US boundary, Alberta, average pH=7.65. Sample was taken at 9:00, January 26, 1982 (Environment Canada, 1985). —, not determined.

Fig. 3. The speciation of Co(II) as a function of pH. (a) Ground water (average pH=7.73) from the Wind River Formation in the Shirley Basin area (Harschman, 1972). (b) Surface water (average pH=7.65) from the Milk River, at the eastern crossing of Canada/US boundary, Alberta. Data to construct these diagrams are listed in Table 3.

significant minor species above a pH of 8.5 and the dominant Co^{2+} species above a pH of 9.5.

In fresh waters, inorganic electrolytes are commonly low in concentration, whereas organic ligands may be relatively concentrated. In such waters, cobalt(II) organic complexes should play a greater role than in seawater, and in some cases may bind a significant amount of cobalt. However, a complete and quantitative assessment of Co(II) organic complexes in both seawater and fresh waters cannot be accomplished without much further work.

CONCLUSIONS

A simple equilibrium complexing model together with recent experimental data and theoretically estimated data on stabilities of Co(II) chloride, bromide and bicarbonate complexes indicates that about 56% of the dissolved cobalt in seawater exists as the free ion, Co^{2+} , and another 44% as complexes of CoCl^+ , CoCl_2^0 and CoSO_4^0 (in decreasing order of abundance). In fresh waters, cobalt exists mainly as the free ion (90% or higher), with the cobalt(II) carbonate, sulfate and bicarbonate complexes as the main complexed forms. The organic complexes of Co^{2+} are most likely less important, relative to the inorganic complexes in seawater; however may at least be locally important in fresh waters. But for both seawater and fresh waters, an appropriate assessment of cobalt organic complexes is not possible at present, more work on this subject is needed.

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APPENDIX I

From the Van Pantheleon Van Eck equation
 (Van Pantheleon Van Eck, 1953),

$$\log K_n = \log K_1 - 2\lambda(n-1)$$

Where, K_1 and K_n are the stepwise formation constants for the first and nth complex respectively, of a metal M with a ligand L , λ is an empirical constant for each specific system, and n is the ligation number. Because

$$\log \beta_n = \sum_{i=1}^n \log K_i$$

we can show that:

$$\log \beta_n = n[\log \beta_1 + (1-n)\lambda]$$

or:

$$\log \frac{\beta_n}{\beta_1^n} = n(1-n)\lambda$$

We know by definition that $n \geq 1$. For most known aqueous systems (Van Pantheleon Van Eck, 1953; Pan, 1989), $\lambda > 0$, then

$$\log \frac{\beta_n}{\beta_1^n} \leq 0$$

or

$$\beta_n \leq \beta_1^n$$

by definition

$$\beta_n = \frac{[ML_n]}{[M][L]^n}$$

then

$$\frac{[ML_n]}{[M][L]^n} \leq \frac{[ML]}{[M][L]}$$

or

$$\frac{[ML_n]}{[ML]} \leq [L]^{n-1}$$

Therefore, for diluted solutions, $[L] < 1$ m, $[ML_n] < [ML]$.

APPENDIX II Equations for free ligand concentration calculations

TC, total carbon; TP, total phosphorus; TS, total sulfur. All equilibrium constants except K_{S1} and K_{S2} are from "CRC Handbook of Chemistry and Physics", 63 Ed. (1982-1983). K_{S1} and K_{S2} were calculated using data in Murray and Cubicciotti (1983).