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Organic Speciation of Silver in Marine Waters

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The potential for silver to be strongly bound by organic ligands in marine waters has been examined using a new competitive equilibration/solvent extraction technique. The method is based upon establishing a competition for silver between ligands already present in the sample and added diethyldithiocarbamate in chloroform. The final distribution of the metal is measured by graphite furnace atomic absorption spectroscopy. Analyses of samples from the Weddell Sea and the San Francisco Bay gave no evidence of any significant silver–organic complexation, indicating that the chemical speciation of silver in seawater is dominated by inorganic chloride complexes.

Recent identification of severe silver contamination in some estuaries and coastal waters has generated concern for the health of ecological communities in these areas. In open ocean waters, dissolved silver typically exists at extremely low concentrations, 1–20 pM (*1*), due mainly to its high particle reactivity and low crustal abundance (*2*). In contrast, studies in the San Francisco Bay (*3*) and Southern California Bight (*4*) have revealed elevated dissolved silver at concentrations higher than 100 pM in some cases. Sañudo-Wilhelmy and Flegal (*4*) showed that anomalously high silver concentrations are strong indicators of sewage contamination and can be used as tracers of point-source wastewater discharges. In addition, silver appears to be most available to marine organisms in the dissolved form and at these elevated concentrations has the potential to influence the composition of planktonic communities and other trophic levels (*5*).

There is some preliminary evidence that complexation of silver with natural organic ligands may reduce its toxicity (*6*). If this is true, silver in highly contaminated waters that are also high in dissolved organic matter may not be biologically available to the extent laboratory studies on silver toxicity have indicated (*5*). Studies on copper in marine waters have shown that organic complexation often overwhelmingly dominates the metal speciation (*i.e.*, refs 7–10), but such information is not available for silver.

The neighboring group in the periodic table, including zinc, cadmium, and mercury, has been studied extensively, and the behavior of those metals may provide some insight into the likelihood of significant organic complexation of silver in marine waters. In both estuarine (*11*) and open ocean waters (*12–14*), zinc(II) has been found to be more than 95% bound by strong organic ligands existing at very low concentrations (<20 nM). Speciation of the soft mercury(II) ion, on the other hand, appears to be dominated by chloro complexes in marine waters, with no evidence of organic complexation (*15*). In a single study of North Pacific surface waters, cadmium(II) was about 70% bound by organics (*16*), falling between zinc and mercury in the extent of complexation. Corresponding to the decrease in organic complexation down the group from Zn^{2+} to Hg^{2+}, chloride complexes increasingly out-compete all other inorganic species (*17*).

Since the Ag(I) ion is softer than either Cd(II) or Hg(II) (*18*), we would expect chloride complexes to overwhelmingly dominate silver speciation in marine waters. However, the extent of inorganic silver complexation by chloride in seawater falls between that of mercury and cadmium (*17*), indicating that the importance of organic complexes cannot be ruled out *a priori*.

In order to provide direct evidence of whether or not organic complexation can be important in the marine geochemistry of silver, we have developed an analytical technique to measure any strong silver complexation that might exist in natural waters. Using this new technique, we have analyzed samples from the Weddell Sea, in the Antarctic, and the highly contaminated South San Francisco Bay, representing end-member marine environments with and without elevated silver concentrations.

Competitive Ligand Equilibration/Solvent Extraction Approach To Determining Trace Metal Speciation. To determine the extent of silver complexation with natural organic ligands, we developed a method similar to one originally developed for and applied to studies of copper speciation (*19, 20*). In the silver technique, diethyldithiocarbamate (DDC^-) and chloroform are added to the sample (in contrast to acetylacetonate and toluene for copper speciation analyses) in quantities selected to establish a competition for silver with the natural ligands. After allowing the sample to reach a new equilibrium, the chloroform fraction containing silver–DDC complexes is separated from the seawater phase. Ultimately, the amount of silver removed from the aqueous phase into the chloroform is analyzed by graphite furnace atomic absorption spectrometry. Equilibrium silver speciation in the aqueous phase can be calculated from the total silver concentration, $[Ag_T]$ (analyzed independently), and the silver extracted into the chloroform, $[Ag_{chl}]$, using the equations in Table 1.

Equilibrated extractions are conducted on sample aliquots spiked with increasing amounts of the metal to generate a titration curve (*22*) of the silver concentration removed from the aqueous phase, $[Ag^*]$, against total silver, $[Ag_T]$. Use of the quantity $[Ag^*]$ normalizes $[Ag_{chl}]$ to the volume of the actual sample aliquot, allowing direct comparison to the total concentration. The resulting titration plot is curved, concave upward, if a strong (relative to the added ligand, DDC^-) natural ligand is present (*20*). However, in the absence of such a strong ligand, the plot will be linear, essentially just a standard additions calibra-

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TABLE 1

Equations Required To Calculate Equilibrium Silver Speciation in the Presence of DDC^- [a]

(1)	$[Ag^*] = [Ag_{chl}]V_{chl}/V_{sw}$
(2)	$[AgDDC] = [Ag_{chl}]/K_{d(Ag)}$
(3)	$[Ag^+] = [AgDDC]/(K_1[DDC^-])$
(4)	$[AgX_i] = \alpha'_{Ag}[Ag^+]$
(5)	$[AgL_i] = [Ag_T] - \{[Ag^+] + [AgX_i] + [AgDDC] + [Ag^*]\}$

[a] $[Ag^*]$ ≡ quantity of silver removed from the aqueous phase into the organic phase. Subscripts chl and sw indicate chloroform and seawater phases, respectively. $[Ag_{chl}]$ ≡ total concentration of silver determined in the organic phase. V_x ≡ volume of the phase x. $K_{d(Ag)} = [AgDDC_{chl}]/[AgDDC]$, distribution coefficient of AgDDC between chloroform and water. K_1 ≡ formation constant for AgDDC. AgX_i ≡ inorganic silver complexes. α'_{Ag} ≡ inorganic side reaction coefficient for silver in seawater (*21*). $[Ag_T]$ is from an independent analysis. Assuming that no preexisting silver forms extract into chloroform, $[Ag_{chl}] = [AgDDC_{chl}]$. At the pH of our samples, there are no significant side reactions with major cations for DDC; therefore, total $[DDC_T] = [DDC^-]$.)

tion curve for a method of total metal analysis. Curved titration data can be linearized (*20*, *22*, *23*) to get the total concentration of the natural ligands, [L], and the conditional stability constants of their silver complexes, K'_{AgL}, with respect to Ag^+ and the quantity of the ligand not bound with silver. This information allows calculation of the original, unperturbed speciation in the sample.

This kind of competitive equilibration approach should identify all forms of strong metal complexation, whether with organics, inorganic ligands (such as sulfide), or colloids, so clarification of what we mean by "strong" complexation is in order. Competitive equilibration speciation techniques are most effective when the strength of the competition (α_{AgDDC}) matches the natural extent of binding (α_{AgL}). These parameters are defined by

$$\alpha_{AgDDC} = \sum[AgDDC]/[Ag^+] = ([AgDDC_{chl}] + [AgDDC])/[Ag^+] \quad (1)$$

and

$$\alpha_{AgL} = [AgL]/[Ag^+] = K'_{AgL}[L'] \quad (2)$$

where AgL is the naturally occurring silver complex, and [L'] is the concentration of the natural ligand not bound to Ag^+. As a general rule of thumb, L can be characterized as long as α_{AgDDC} is within 1 order of magnitude to either side of α_{AgL}. However, even if the natural ligand strongly outcompetes the added one (that is, $\alpha_{AgL} \gg \alpha_{AgDDC}$), it still may be possible to recognize the existence of a natural ligand and estimate its concentration, although no information would be available on K'_{AgL}, beyond an estimate of its lower limit (*8*).

Successful use of this technique also requires that the naturally occurring silver complexes are relatively hydrophilic and do not extract into the organic phase. This appears to be the case for most organic–metal complexes that have been identified in marine waters (*24*, *20*), but there have been some instances where more lipophilic metal complexes seem to persist in aqueous solution (*e.g.*, ref 25). If a small fraction of the metal extracts when no DDC^- is present, the data can be corrected (*20*), but the hydrophobic metal complexes cannot be characterized. Therefore, it is necessary to extract each sample with chloroform and without DDC^- to confirm that any silver complexes originally present are not transferred to the organic phase.

An additional limitation to competitive ligand equilibration techniques, in general, is that they require an assumption that the *in situ* metal speciation is at equilibrium and can be characterized by thermodynamic parameters. Geochemically significant pseudoequilibria adequately satisfy this assumption as long as the time scale is longer than that of the analytical measurement (*20*). This means that even if the environmental water body is not at true equilibrium because it is an open system, it may be possible (and perhaps even more useful) to describe it geochemically with a transient "equilibrium" that persists for days to weeks. If this is the case, and the sample rapidly returns to an analogous pseudoequilibrium after addition of the competing ligand, the thermodynamic parameters ([L] and K'_{AgL}) determined for the natural ligands may still be useful in understanding the behavior of the system. Thus, it is important to conduct extractions with varying equilibration times to assure that the kinetics of exchange between the natural and added ligands are rapid.

Well-characterized model ligands in appropriate media are often used to confirm that strong metal-complexing ligands can indeed be identified by speciation techniques. We chose to use glutathione (GSH) as a model ligand, based on the hydrophilic nature of its dominant silver complex (AgHGSH) and its relative binding strength ($\log K' = 33.15$ at an ionic strength of 0.5) (*26*). Despite this strong complexation of Ag(I), large concentrations of glutathione are required to have a significant influence on silver speciation in seawater, because the ligand's effective strength is dramatically reduced by competing interactions with the major cations of seawater. Therefore, it is not practical to conduct a complete titration of GSH with the metal. However, the reliability of the technique still can be established by examining how a large concentration of the model ligand affects the analytical signal (*14*).

TABLE 2

Samples Examined for Silver Complexation

sample	location	date	$[Ag_T]$ (pM) (±5)
	Weddell Sea		
WS1	64°18′ S, 46°57′ W	11/15/92	8
WS2	63°17′ S, 52°24′ W	11/26/92	5
	San Francisco Bay		
SFB1	Dumbarton Bridge	10/31/93	95
SFB2	Coyote Point	1/18/94	75

Analytical Section

Samples. Southern Ocean samples (WS1 and WS2) were collected in the Weddell Sea during November 1992. Sampling was conducted off the stern of the ship at 30 m using an acid-cleaned GO-Flow bottle and clean sampling techniques (27). Within 10 h, the samples were filtered by pressurizing the GO-Flow with particle-free N_2, forcing the sample through acid-cleaned 0.2-μm Nuclepore polycarbonate filters. The samples were stored frozen for 1 year before analysis at UCSC. Table 2 gives the date, sampling location, and total Ag concentrations for each sample.

Sample 1 from the South San Francisco Bay (SFB1) was collected just below the surface from a small boat at the Dumbarton Bridge. It was filtered during sampling with

an in-line 0.2-μm filter cartridge and taken back to UCSC for analysis. That same sample was also used in a study of estuarine colloids (*28*). The sample was divided into two equal portions, and one fraction was ultrafiltered to remove any colloids present. Both fractions were acidified before total silver analysis, which gave identical metal concentrations in each. After 2 months of storage at room temperature in the dark, the remaining portions of the aqueous ultrafiltered and nonultrafiltered fractions were recombined (because of the large seawater volumes required for these complexation determinations), and the pH was brought back up to 7.7 before speciation analysis. The second San Francisco Bay sample, SFB2, was from just below the surface at the Coyote Point Marina, just south of the San Francisco airport, and carried back to UCSC before filtration through another clean 0.2-μm filter cartridge. Analysis of SFB2 was completed within 1 week after collection. Although salinity was not measured on these samples, during the season when they were taken the practical salinity in this area is about 30.5 (*3*). These two samples are also summarized in Table 2.

Experimental. All analyses were performed in class 100 clean work areas. Before use, FEP reagent bottles and separatory funnels were extensively acid-cleaned (*27*). Water, chloroform, and nitric acid were all purified by distillation in quartz. Organic-free artificial seawater (ASW) was made according to the Aquil recipe, using only the major salts (*29*), and passed through a Chelex-100 column to remove contaminating trace metals. Diethyldithiocarbamate solutions were prepared by dissolving the diethylammonium salt (DDDC, Tokyo Kasei, Inc., stored below 0 °C) in quartz-distilled water (Q-H_2O). A slightly basic solution of this ligand is stable and need be prepared only once a day. Silver standards were prepared in Q-H_2O by diluting a 1000 ppm atomic absorption standard (Fisher), which had been stored refrigerated to discourage oxidation. The glutathione solution was made from a previously unopened bottle of the solid compound (Sigma), again in Q-H_2O. HEPES buffers for experiments with varying DDC^- concentrations were made by dissolving the buffer reagent (Aldrich) in Q-H_2O and adding NH_4OH to bring the pH to about 7.

For each titration point, an aliquot of the sample was transferred into a 500-mL separatory funnel, either by volume or by weight. The buffer, if needed, was added first, followed by the DDDC and silver standard solutions and the chloroform. In experiments using glutathione as a model ligand, it was added before the silver, after which the DDC^- was included. Ligands were added before the silver as a precaution against precipitation of silver oxides that may have been slow to dissolve. Once all the reagents had been added, the sample was shaken vigorously for 1–2 min and allowed to sit for the chosen equilibration time, with occasional shaking. The phases were allowed to separate, and the organic fraction was drained into a 125-mL separatory funnel and washed briefly with Q-H_2O to dilute the salts from any aqueous contamination in the phase separation. The organic fraction was drained into a 20-mL quartz beaker, covered with concentrated quartz-distilled nitric acid (Q-HNO_3), and evaporated down to dryness on a hot plate. The residue in the beaker was further oxidized with three sequential 100-μL aliquots of concentrated Q-HNO_3 with evaporation back to dryness between each addition. The sample was finally redissolved in approximately 1.5 mL of 1 **N** Q-HNO_3 before analysis by GFAAS. Table 3 is a summary of the conditions used for each analysis. The final silver determinations were conducted on a Perkin Elmer 5000 atomic absorption spectrophotometer fit with an HGA 500 graphite furnace and an AS 20 autosampler, using pyrocoated graphite tubes with L'vov platforms, manufacturer recommended programs, and the method of standard additions.

TABLE 3
Experimental Conditions for Analyses

sample	V_{sw} (mL)	V_{chl} (mL)	$[DDC_T]$ (μM)	final $[Ag_T]$ (pM)
ASW[a]	250	10	95	100
WS1	250	10	130	200
WS2	250	10	50	50
SFB1	100	10	100	1000
SFB2	250	10	90	600

[a] ASW ≡ organic-free artificial seawater.

The overall procedural detection limit was 6 pM Ag (based on three times the standard deviation of blank analyses), and the blanks averaged 4 pM. The large volume of water required for a complete speciation determination precluded replicate analyses, but the precision of each titration can be estimated from the 95% confidence intervals for the linear regressions.

Total silver analyses were performed using the standard APDC/DDDC extraction method (*1*, *27*), with the exception that the pH of the ammonium acetate solution was lowered for unacidified samples. For these analyses, the detection limit was 5 pM, and the blanks averaged 7 pM.

Results

Both fundamental requirements for use of the CLE/SE method, rapid kinetics and non-extractability of natural complexes, were satisfied. Silver was undetectable in extractions of each sample without added DDC^-, even when silver was added at high levels corresponding to the final titration points, indicating that any organic material present and capable of binding silver did not form extractable complexes. In addition, Figure 1 indicates that equilibrium with the added ligand was established relatively rapidly. Based on this information, each extraction in the sample titrations was allowed to equilibrate for at least 1 h.

To confirm that the technique can identify the presence of a strong silver-binding organic ligand, we extracted artificial seawater with and without glutathione at varying concentrations of DDC^-. The results of this experiment are shown in Figure 2. The lower degree of silver extraction in the presence of glutathione (filled symbols) indicates that GSH is competing with diethyldithiocarbamate for the silver, thereby reducing the analytical signal. Regrettably, neither glutathione nor any other ligand that could be used as a model of natural silver-binding ligands has been characterized fully enough to confirm the ability of this method to quantify such ligands (*30*). Because this method determines the conditional stability constants of the natural ligands, with respect to *total* (not the free) ligand concentration, such confirmation would require knowledge of all the interactions between the ligand and the major cations in seawater, particularly protons, Ca^{2+}, and Mg^{2+}. Therefore, at this stage, we can only confidently claim that this is a qualitative method that also has the potential for providing quantitative information about the thermodynamics of the silver speciation in a sample.

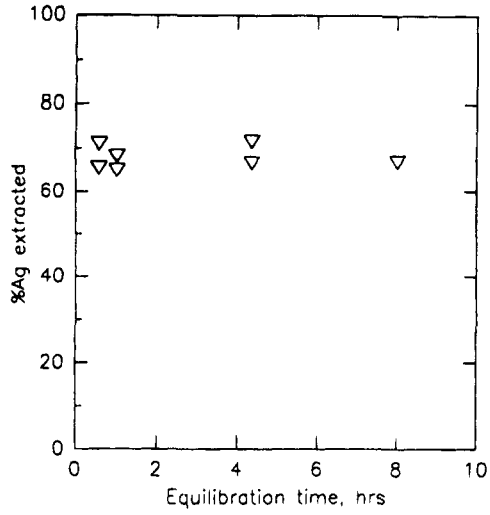

FIGURE 1. Molar percentage of silver in Weddell Sea sample 2 (WS2) extracted into chloroform as a function of equilibration time. [Ag_T] = 54 pM (sum of added metal and that originally present); [DDC_T] = 100 μM; average extracted silver, [Ag*] = 37 ± 1 pM.

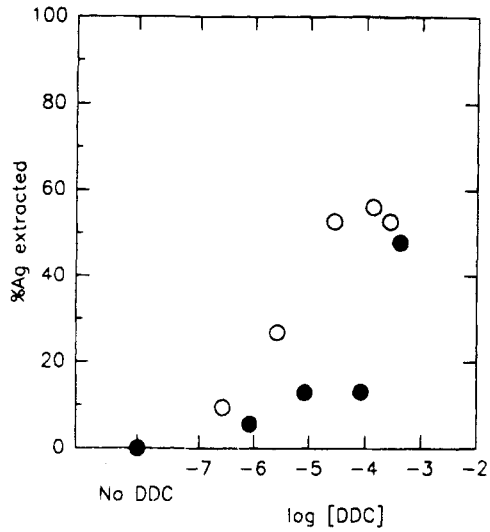

FIGURE 2. Molar percentage of silver in artificial seawater extracted into chloroform as a function of diethyldithiocarbamate concentration. Total silver ≈ 100 pM. Open circles, no glutathione present; filled circles, 1 μM glutathione.

Representative speciation titrations from the Weddell Sea and the San Francisco Bay as well as of organic-free artificial seawater are shown in Figure 3, and the results of all five titrations are summarized in Table 4. Table 5 gives the original titration data. The slope of the titration in ASW provides an external calibration of the ideal sensitivity of the method (Figure 3a). For all four of the natural samples we examined, no definite curvature can be identified in the titration curves (the analytical signal has a linear response to the total silver concentration), the slopes match that of the ASW titration (in which no organic material was present), and the lines pass through the origin (the x-intercept gives a rough estimate of the natural ligand concentration, [L] (*20*)), within the experimental scatter of the data. Therefore, these samples exhibit no evidence for strong organic silver complexation.

For the analyses of WS2 and SFB2, the total DDC^- concentration and solvent ratio were chosen so that the competition strength matched that of inorganic silver complexation, $\alpha_{AgDDC} \approx \alpha'_{Ag} \approx 10^5$ (*30–32*). Any ligands able to out-compete chloride in these samples would have

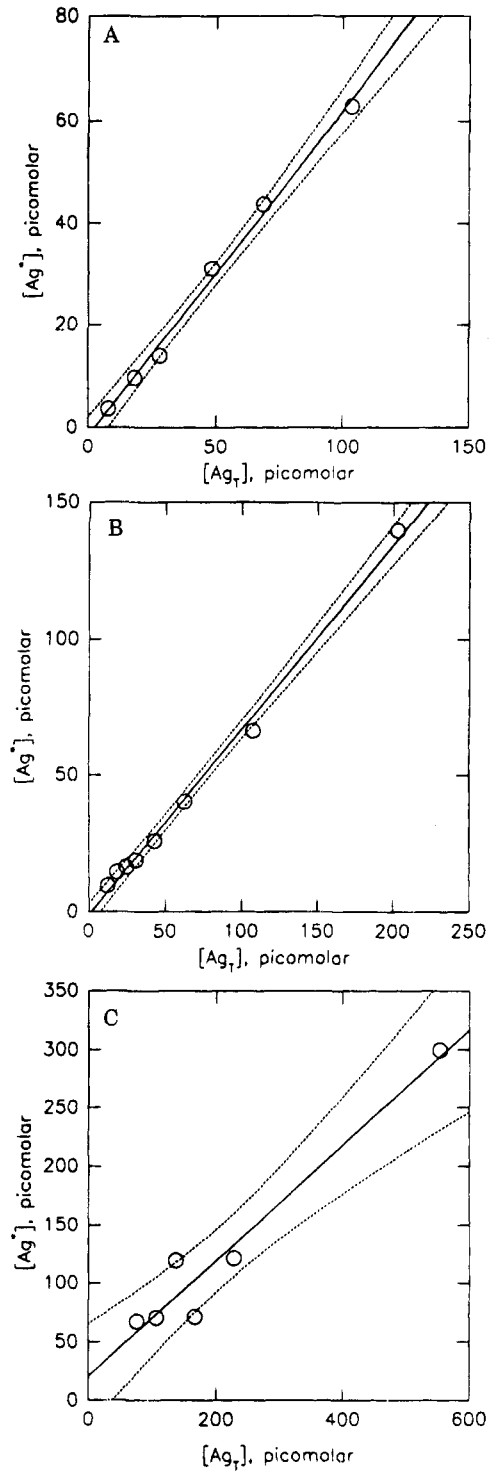

FIGURE 3. Representative titrations of water samples with silver: extracted silver as a function of total silver concentration. See Table 3 for experimental conditions, Table 4 for regression parameters, and Table 5 for original titration data. Dotted lines represent 95% confidence intervals for the linear regressions. (A) artificial seawater (ASW); (B) Weddell Sea sample 1 (WS1); (C) San Francisco Bay sample 2 (SFB2).

given linear titration curves with positive x-intercepts (*8*). The lack of any clear offset from the origin in these two samples indicates that $AgCl_n$ complexes do dominate silver speciation in these waters.

Discussion

From what is known about silver chemistry, it is not particularly surprising that strong complexation was not

TABLE 4

Regression Parameters of Speciation Titrations

sample	slope	*x*-intercept	R^2
ASW	0.64 ± 0.08	3 ± 4	0.994
WS1	0.68 ± 0.06	2 ± 6	0.995
WS2	0.7 ± 0.4	5 ± 8	0.915
SFB1	0.6 ± 0.2	40 ± 80	0.953
SFB2	0.5 ± 0.2	−40 ± 80	0.943

TABLE 5

Titration Data[a]

$[Ag_T]$ (pM)[b]	$[Ag_{chl}]$ (nM)	[Ag*] pM
	ASW	
8	0.1	4
18	0.24	9.6
28	0.35	14
48	0.78	31
69	1.10	43.8
104	1.6	63
	WS1	
12	0.24	9.6
18	0.38	15
25	0.410	16.4
31	0.48	19
43	0.650	26.0
63	1.0	40
108	1.6	66
203	3.5	140
	WS2	
8.8	0.088	3.5
10.9	0.12	4.7
17.1	0.1	5
25.4	0.418	16.7
33.6	0.38	15
46.1	0.75	30
	SFB1	
99.8	0.65	65
131.8	0.81	81
163.3	0.973	97.3
193.0	0.98	98
253.2	0.936	93.6
341.6	1.2	120
590.4	2.51	251
1059.2	6.101	610.1
	SFB2	
77	1.6	67
108	1.8	71
137	2.995	119.8
167	1.79	71.5
228	3.043	121.7
553	7.49	300

[a] Significant figures reflect reproducibility of the GFAAS analysis. [b] Total Ag concentration is the sum of silver originally in the sample, the experimental blank, and the silver added in the titration.

evident in the samples we examined. Like lead and mercury, the silver(I) ion binds preferentially with soft anions and ligand donor atoms such as chloride and sulfur (*30*). Stability constants for silver complexes with ligands like EDTA, which have oxygen and nitrogen donor atoms, are relatively small, and as a result, such ligands are unable to effectively compete with chloride for Ag^+ in marine waters. In fresh waters, on the other hand, with not only less chloride but also fewer hard cations such as calcium and magnesium to bind the oxygen-donor ligands, organic complexation may be able to play a greater role in silver cycling.

In addition, the ligands most likely to overcome the strong affinity silver has for chloride are thiols and sulfide itself (which should be observable using this method), but these species are unstable in oxygenated waters. Therefore, ligands strong enough to out-compete chloride could be more important for silver speciation in suboxic and anoxic waters than we have observed in our samples. Countering this possibility is the fact that at equilibrium, silver(I) should be reduced to the metallic form under anoxic conditions ($[Ag^+] = 10^{-18}$, at pe = −4.5, as in ref 33). However, dissolved silver is enriched in hydrothermal vent solutions (*34*, *35*), indicating that complexation with sulfide or reduced thiols may be able to dominate over reduction of the metal.

Although we did not examine fresh or anoxic waters, the analytical technique developed here should also be applicable to these environments, perhaps even with fewer complications. A particular advantage to the silver–DDC technique is that the diethyldithiocarbamate ligand is also required for the most popular technique currently in use for total trace silver analyses (ref 1, based on ref 27). Therefore, many labs working on silver geochemistry already have the clean reagent readily available. In fact, the solvent extraction procedure for Ag speciation is very similar to that for total silver (except that pH is not adjusted), significantly reducing the additional equipment and experience required to implement the new analyses.

Regardless of the potential for other types of environments, our results indicating that organic speciation is relatively unimportant for silver in the south San Francisco Bay have significant implications for silver cycling and availablity, both here and in other estuaries. Unlike copper, where organic complexation can dramatically reduce adverse biological effects from contamination, we apparently do not have this particular safety net for silver. There may be other as yet unidentified mechanisms by which contaminated ecosystems can ameliorate silver toxicity, but our study warrants further caution and encourages efforts to reclaim silver from wastewater streams.

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