

Sources, Fluxes, and Biogeochemical Cycling of Silver in the Oceans

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1 Introduction

This brief review of silver in the oceans was catalyzed by our observation that there was a relative paucity of published data on the topic. A few authors have reported silver concentrations in the North Pacific (Martin et al. 1983; Zhang et al. 2001, 2004; Ranville and Flegal 2005; Kramer et al. 2011), South Pacific (Murozumi 1981; Zhang et al. 2004), North Atlantic (Flegal et al. 1995; Rivera-Duarte et al. 1999; Ndung'u et al. 2001), South Atlantic (Flegal et al. 1995; Ndung'u et al. 2001), and Southern Oceans (Miller and Bruland 1995; Sañudo-Wilhelmy et al. 2002), as well as in the Bering (Zhang et al. 2004) and Baltic (Ndung'u 2011) Seas. We are not aware, however, of any published data on silver concentrations in the Indian Ocean, and there are only a few reports on silver concentrations in marine sediments.

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That scarcity of data on silver concentrations in the oceans raises the question: Who cares? Silver was not included in the original list of elements for GEOTRACES, “an international programme which aims to improve the understanding of biogeochemical cycles and large-scale distribution of trace elements and their isotopes in the marine environment” (GEOTRACES 2006), because it is neither a nutrient nor a commonly used tracer in sea water. However, silver is extremely toxic to marine phytoplankton and invertebrates, and its increasing use as a biocide has raised concerns about its potential as an environmental pollutant (Purcell and Peters 1998).

Silver has been extracted from geological deposits since 300 BC (Nriagu 1996). It has been mined directly, as well as extracted as a bi-product of gold, copper, lead and zinc deposits. Ancient Greeks and Romans extracted considerable amounts of silver for the production of silver bullion, and it has been used widely throughout history for the production of currencies, ornaments and utensils. Technological innovations since the 1800s have led to new uses of silver. In particular, its photochemical properties were the basis for the development of photography.

However, environmental releases of industrial silver from industrial and municipal wastewater outfalls, and from mining, smelting, and manufacturing operations have adversely impacted the environment (Purcell and Peters 1998), primarily because of silver’s toxicity to invertebrates (Luoma et al. 1995). For example, wastewater discharges of silver from a photography plant into San Francisco Bay measurably decreased the fecundity of benthic invertebrates in the effluent plume (Flegal et al. 2007). Although such discharges have substantially decreased in the United States since the 1970s, industrial silver emissions are likely to have increased in rapidly developing countries that possess limited silver recovery and treatment facilities (Ranville and Flegal 2005).

Moreover, concerns with silver toxicity in aquatic environments have markedly increased with the rapidly growing use of silver nanoparticles (AgNPs) as antimicrobial agents in a wide variety of consumer products (Blaser et al. 2008; Luoma 2008; Bradford et al. 2009; Fabrega et al. 2011). As a result, there have recently been a series of studies on AgNP’s stability (e.g., Benn and Westerhoff 2008; Liu and Hurt 2010; Liu et al. 2010; Levard et al. 2012; Unrine et al. 2012; He et al. 2013; Chambers et al. 2014), bioavailability to aquatic organisms (e.g., Li et al. 2013; Wang and Wang 2014), and toxicity to those organisms (e.g., Navarro et al. 2008; Bone et al. 2012; Turner et al. 2012; He et al. 2013; Chambers et al. 2014). These studies build on previous reports that addressed the bioaccumulation of silver in marine food chains (e.g., Ettajani et al. 1992; Fisher et al. 1995; Fisher and Wang 1998; Xu and Wang 2004; Yoo et al. 2004; Long and Wang 2005; Ng and Wang 2007). Those and other reports are summarized in Eisler’s (2010) recent compendium on silver concentrations in marine organisms. Ratte (1999) and Bianchini et al. (2005) also provided earlier reviews on the bioaccumulation and toxicity of silver in marine organisms, and there have been several complementary reports since then (e.g., Bianchini et al. 2005; Pedroso et al. 2007).

Silver, in its ionic form, is extremely toxic to some aquatic organisms, second to only mercury (Luoma et al. 1995). As such it is listed by the U.S. Environmental Protection Agency (USEPA) as a priority pollutant in natural waters. But, in marine

waters, most silver is associated with chloro-complexes and very little free ion is present (Miller and Bruland 1995). Notwithstanding, silver is rapidly bioaccumulated from solution by some marine invertebrates to potentially toxic levels (Engel et al. 1981; Luoma et al. 1995; Wang 2001).

The nature of silver's biogeochemical cycle in the oceans is still poorly understood. Its vertical concentration profiles in the oceans exhibit typical nutrient-like behavior with similarities to that of silicate, suggesting that their biogeochemical cycles are linked (Martin et al. 1983; Flegal et al. 1995; Ndung'u et al. 2001). However, there are pronounced deviations between the profiles of silver and silicate, which renders them less analogous (Zhang et al. 2004; Ranville and Flegal 2005; Kramer et al. 2011). Moreover, recent studies indicate that the anthropogenic inputs of silver to the oceans may be relatively substantial, compared to natural inputs, and in contrast to those of silicate, which are dominated by natural sources. Consequently, it has been proposed that spatial and temporal gradients of silver concentrations in marine aerosols and surface waters may be used to distinguish between natural and industrial inputs of silver and associated industrial contaminants (e.g., selenium) to the oceans (Ranville et al. 2010).

2 Oceanic Silver: Data and Data Gaps

Although data on the content in seawater of most trace metals (e.g., Cd, Cu, Fe, Hg, Ni, Pb, Zn) are limited (GEOTRACES 2006), there are even fewer measurements of silver in the open ocean (see Table 1 and Fig. 1). As previously noted, we found only a handful of peer-reviewed reports of silver in the oceans, and no reports of silver in the Indian Ocean. Similarly, we found very few peer-reviewed reports on silver in marine sediments (Table 2).

Some data on silver in oceanic hydrothermal plumes have been published, including one in the Mid-Atlantic Ridge (Douville et al. 2002). Concentrations of silver, copper and silicate found in those plumes are summarized in Table 3. This table shows anomalously higher concentrations of silver in sulfidic waters (4–51 nmol/kg) than in other oceanic waters (0.2–87.7 pmol/kg). From this disparity, we believe hydrothermal inputs may be relatively important sources in the budget and cycling of silver within the oceans.

In contrast to the paucity of data for dissolved silver concentrations in oceanic waters, there is a relative wealth of data on silver in estuarine waters—at least in San Francisco Bay (Sañudo-Wilhelmy et al. 2004). There, silver concentrations in total dissolved (<0.45 m) and total (unfiltered) surface waters and sediments have been systematically measured for more than three decades (Flegal and Sañudo-Wilhelmy 1993; Smith and Flegal 1993; Sañudo-Wilhelmy et al. 1996; Rivera-Duarte and Flegal 1997; Spinelli et al. 2002; Squire et al. 2002; Flegal et al. 2007; Huerta-Diaz et al. 2007). In addition, a few other measures of silver in other estuarine and coastal waters exist (Sañudo-Wilhelmy and Flegal 1992; Wen et al. 1997; Buck et al. 2005; Clark et al. 2006; Beck and Sañudo-Wilhelmy 2007; Cozic et al. 2008; Godfrey et al. 2008; Zhang et al. 2008; Tappin et al. 2010) (Table 4).

Table 1 Reported range of silver concentrations (pmol/kg) in oceanic waters

Sample site	Sampling date	[Ag] range	Fraction	Filter size	UV	Chemistry	Analytical method	Reference
Baltic Sea	2005–2008	<1–9.4 (surface)	Filtered	0.4 µm	Yes	Chelating resin extraction	ICP-MS	Ndung'u et al. (2011)
	1990	0.3–7.2	Total	–	No	Solvent extraction	GFAAS	Flegal et al. (1995)
North Atlantic	1993	0.7–6.9	Total	–	No	Solvent extraction	GFAAS	Rivera-Duarte et al. (1999)
South Atlantic	1996	1.7–10.7	Filtered	0.22 µm	No	Solvent extraction	ICP-MS	Ndung'u et al. (2001)
	1990	0.2–9.6	Total		No	Solvent extraction	GFAAS	Flegal et al. (1995)
Southern Ocean	1996	1.2–31.7	Filtered	0.22 µm	No	Solvent extraction	ICP-MS	Ndung'u et al. (2001)
	1991	8.9–22.4 (surface)	Filtered	0.45 µm	No	Solvent extraction	GFAAS	Saúdo-Wilhelmy et al. (2002)
Indian Ocean	1992	5–8 (30 m)	Filtered	0.2 µm	No	Solvent extraction	GFAAS	Miller and Bruland (1995)
	–	–	–	–	–	–	–	–
South Pacific	–	1.0–32.0	Filtered	–	No	Solvent extraction	ID-TIMS	Murozumi (1981)
	2001	9–11.4	Filtered/total	0.2 µm	No	Solvent extraction	ID-ICPMS	Zhang et al. (2004)
North Pacific	1981	0.4–25.0	Filtered	0.4 µm	No	Solvent extraction	GFAAS	Martin et al. (1983)
	1998	4.2–46.8	Filtered	0.45–0.04 µm	No	Solvent extraction	ID-ICPMS	Zhang et al. (2001)
	2000–2001	1.5–66.2	Filtered	0.04–0.2 µm	No	Solvent extraction	ID-ICPMS	Zhang et al. (2004)
	2002	1.0–87.7	Total	–	Yes	Chelating resin extraction	ICP-MS	Ranville and Flegal (2005)
	2009	6.2–72.9	Total	–	Yes	Chelating resin extraction	ICP-MS	GEOTRACES IC cruise
	2005	6.0–71.6	Total/filtered	–	No	Solvent extraction	ID-ICPMS	Kramer et al. (2011)
Bering Sea	1999	2.7–104.5	Filtered	0.04 µm	No	Solvent extraction	ID-ICPMS	Zhang et al. (2004)

GFAAS graphite furnace atomic absorption spectrometry, *ICP-MS* inductively coupled plasma—mass spectrometry, *ID-TIMS* isotope dilution—thermal ionization mass spectrometry, *ID-ICPMS* isotope dilution—inductively coupled plasma—mass spectrometry

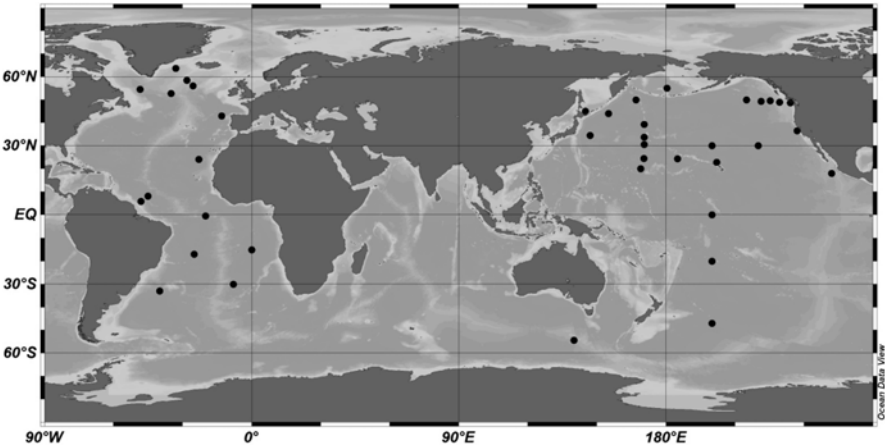


Fig. 1 Locations of reported depths profiles of silver concentrations

Table 2 Silver Concentrations (nmol/kg) in marine sediments

Location	[Ag] range		Reference
	Solid phase	Porewaters	
Coastal zones across the globe	12–2,201		Koide et al. (1986)
Puget Sound, Washington, USA	140–6,560		Bloom and Crecelius (1987)
Massachusetts and Cape Cod bays, Massachusetts, USA	280–8,250		Ravizza and Bothner (1996)
Madeira Abyssal Plain, eastern Mediterranean basin, northeast Atlantic ^a	~0–140		Crusius and Thomson (2003)
Namibian diatom belt	19± 10		Borchers et al. (2005)
Peru OMZ ^b	3–1,305		Böning et al. (2004)
Chile OMZ ^b	8–46		Böning et al. (2005, 2009)
Coastal Massachusetts	6,000–24,000		Kalnejais et al. (2007)
Western Canadian, Mexican, Peruvian and Chilean continental margins	740–13,750		McKay and Pedersen (2008)
Washington/Oregon states, USA	190–6,300	0.03–25	Morford et al. (2008)
Boston Harbor, Massachusetts, USA		0.03–0.17	Kalnejais et al. (2010)

^aExtrapolated from graph

^bOxygen Minimum Zone

Those estuarine data documented that marked anthropogenic perturbations of the biogeochemical cycling of silver occurred in estuarine and neritic waters from surface runoff and point source discharges. The source of much of that discharged silver occurred after use in X-ray and photographic processing, solders, electronics, and as a bactericide and algacide. Most of that silver is rapidly scavenged and deposited in benthic sediments (Benoit et al. 2010), but it may subsequently be

Table 3 Reported range of silver (nmol/kg), copper (μmol/kg), and silicate (μmol/kg) concentrations in Mid-Atlantic Ridge hydrothermal plumes (from Douville et al. 2002)

System name	Location	Collection date	[Ag]	[Cu]	[Si]
Menez Gwen	37°50'N	1994	4.3	<2	8.2
		1997	17	<2	11.2
Lucky Strike	37°17'N	1994, 1997	4.7–25	<2–30	8.2–16
Rainbow	36°14'N	1997	47	140	6.9
Broken Spur ^a	29°N	1993	–	43	–
TAG	23°N	1996	51	130	20
Snakepit	23°N	1996	31	35	20
Logatev	34°45'N	1996	11	27	8.2

^aFrom James et al. (1995)

Table 4 Dissolved silver concentrations (pmol/kg) in coastal and estuarine waters

Location		[Ag] Range	Reference
North America			
	San Francisco Bay	<1–244	Squire et al. (2002)
	San Diego Bay	66–307	Sañudo-Wilhelmy and Flegal (1992)
	Hudson River	<–102	Godfrey et al. (2008)
	Long Island Sound	3–353	Buck et al. (2005)
	Great South Bay	<1–73	Clark et al. (2006)
	Jamaica Bay	2–452	Beck and Sañudo-Wilhelmy (2007)
	Trinity River estuary	4–59	Wen et al. (1997)
Europe			
	Restranguet Creek	25–190	Barriada et al. (2007)
	Adriatic Sea	14–28	“
	Seine Estuary	ND–60	Cozic et al. (2008)
	Gulma Fjord	53–12	Tappin et al. (2010)
	Adriatic Sea	12–33	“
	Tamar Estuary	ND–17	“
	Fal Estuary	14–34	“
	Restranguet Creek	32–181	“
	River Mero Estuary	2–40	“
	A Coruña Bay	23–115	“
Asia			
	Tokyo Bay	Jun–15	Zhang et al. (2008)

ND=Non Detect

remobilized by natural diagenetic and/anthropogenic processes, which also recycle legacy inputs of industrial silver from acid mine drainage and other historic inputs (Smith and Flegal 1993; Rivera-Duarte and Flegal 1997; Tappin et al. 2010). Fortunately, the advent of digital photography has markedly decreased discharges of silver from photographic processing, and that has resulted in recent reductions of industrial silver inputs to the environment (Squire et al. 2002; Flegal et al. 2007).

But as previously noted, environmental inputs of silver nanoparticles have been increasing exponentially, and the bioavailability and toxicity of those materials are poorly understood.

Silver in estuarine waters generally exhibits a non-conservative behavior, with dissolved silver concentrations decreasing with salinity (Smith and Flegal 1993; Wen et al. 1997; Zhang et al. 2008). This pattern has been attributed to silver's high affinity for suspended particulates, as demonstrated by its relatively high partition coefficient ($K_d \sim 10^5$) (Sañudo-Wilhelmy et al. 1996; Wen et al. 1997; Zhang et al. 2008; Tappin et al. 2010). At low salinities, silver is strongly associated with iron and manganese oxyhydroxide/sulfide phases, organic macromolecules, and colloids (Wen et al. 1997; Reinfeldt and Chang 1999). In more saline waters, the macromolecular fraction decreases and dissolved silver chloro-complexes become more important (Turner et al. 1981; Miller and Bruland 1995). However, some "dissolved" ($<0.45 \mu\text{m}$) silver remains tightly bound to refractory organics in estuarine and marine waters (Ndung'u et al. 2006).

Silver may also be present as a soluble sulfide in fresh and estuarine waters, as reported by Rozan and Luther (2009). They proposed this was due to the high association constant of silver sulfides ($\text{p}K$ 12-30) for multi-nuclear metal clusters with stoichiometries of 2:1 and 3:3. The presence of those silver sulfides was associated with anoxic (sulfidic) sediments and wastewater discharges, which would not be a factor in most oceanic waters. However, those complexes could be important in marine hydrothermal plumes.

3 Measurements of Silver in the Oceans

3.1 Waters

Silver concentrations observed in oceanic waters display marked spatial differences (Fig. 2). Recorded silver concentrations show a systematic increase along the oceanic conveyor belt circulation, whereas the nutrient-type vertical profile of silver is retained (Bruland and Lohan 2004). As previously noted, silver's nutrient-type distribution is evidenced by its covariance with the distribution of silicate, which is illustrated in Fig. 3, suggesting that both geochemical cycles are linked (Martin et al. 1983; Flegal et al. 1995; Ndung'u et al. 2001).

Silver is hypothesized to be sequestered within a refractory organic phase that is associated with biogenic silica, and to follow a parallel biological scavenging and subsequent remineralization (Ndung'u et al. 2006). However, departures from the linear correlation between the two elements emphasize that the exact mechanisms of the silver marine cycle are still poorly understood (Zhang et al. 2004; Ranville and Flegal 2005; Kramer et al. 2011). Silver levels exceed those of silica when silver concentrations are $\geq 20 \text{ pmol/kg}$, suggesting that silver may be relatively enriched from aeolian deposition and/or is more slowly remineralized than silica. There may also be a relatively greater diagenetic remobilization of silver from bottom sediments,

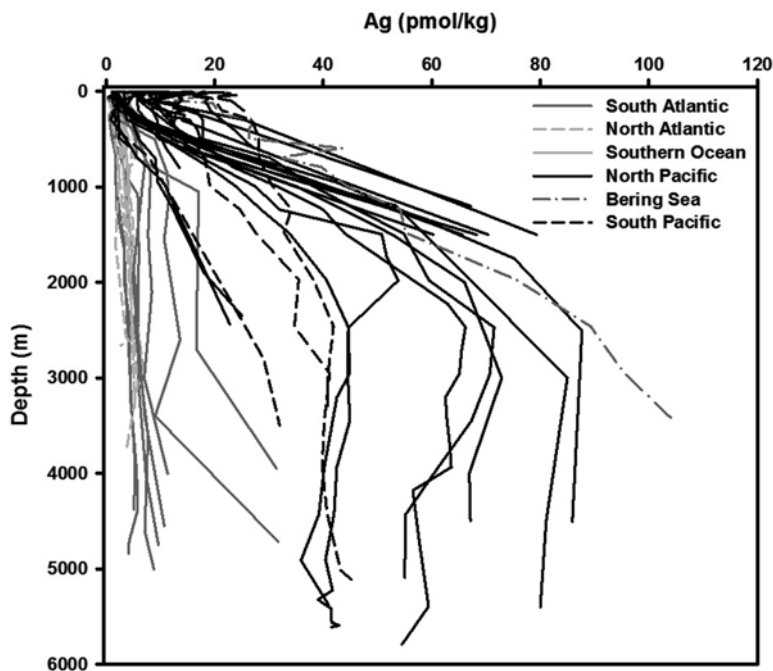


Fig. 2 Vertical profiles of silver concentrations (pmol/kg) in the oceans. Data from Murozumi (1981), Martin et al. (1983), Flegal et al. (1995), Rivera-Duarte et al. (1999), Ndung'u et al. (2001), Sañudo-Wilhelmy et al. (2002), Zhang et al. (2001, 2004), Ranville and Flegal (2005), and Kramer et al. (2011). Also included are previously unpublished data from our laboratory

a more efficient transfer of silver out of surface waters in sinking particle aggregates, and/or a relatively greater input (e.g., hydrothermal vents) of silver in deep oceanic waters.

In addition to silica, silver concentrations in seawater profiles also correlate with those of copper (Fig. 4). The position of silver immediately under copper in the Periodic Table attests to its role as a biogeochemical analog of copper, an essential trace element. This similarity also accounts for some of silver's toxicity to many marine invertebrates, whose respiratory pigment is the copper-based hemocyanin (Burmester 2002). However, as with silica, silver concentrations deviate from a true linear correlation with those of copper, especially at higher concentrations—again attesting to dissimilarities in the biogeochemical cycles of the two elements.

Those differences are illustrated in Table 3, which lists concentrations of silver, silicate and copper that are present in hydrothermal plumes. Based on the sea water concentrations of silver (0.023 nmol/kg) and copper (0.0033 $\mu\text{mol/kg}$), as given in the original compilation by Douville et al. (2002), the atomic ratio of silver to copper in the plumes ($3.4\text{--}8.9 \times 10^{-4}$) is one order of magnitude lower than it is in sea water. Consequently, the relative excess of silver compared to copper in deep ocean water is not due to a simple enrichment from hydrothermal inputs. But differences

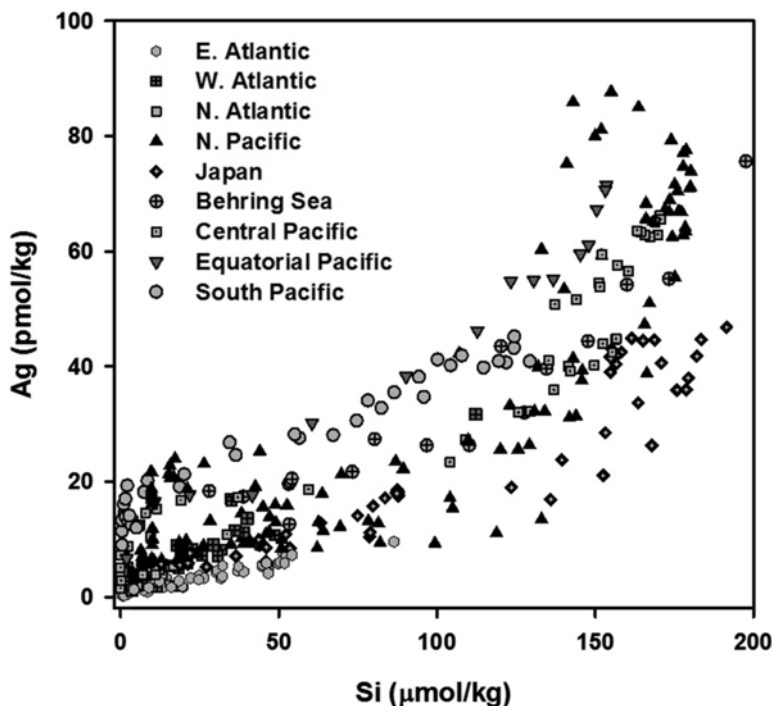


Fig. 3 Plot of silver (pmol/kg) vs. silicate ($\mu\text{mol/kg}$) in oceanic waters. Data from Flegal et al. (1995), Rivera-Duarte et al. (1999), Ndung'u et al. (2001), Zhang et al. (2001, 2004), Ranville and Flegal (2005), and Kramer et al. (2011)

in the solubility, speciation, and dispersion of silver and copper could subsequently enrich silver, compared to copper in those plumes, and that enrichment could extend well beyond the hydrothermal sources, as determined for other trace elements (e.g., manganese).

The most recent silver data in seawater have been mostly derived from the North Pacific Ocean, and have prompted alternate and contrasting hypotheses on the origins and cycling of silver in oceanic waters. Figure 5 synthesizes all of the reported silver vertical concentration profiles in the North Pacific (Murozumi 1981; Martin et al. 1983; Zhang et al. 2001, 2004; Ranville and Flegal 2005; Kramer et al. 2011), excluding those from northeast Pacific coastal and estuarine waters (Bloom and Crecelius 1984; Flegal and Sañudo-Wilhelmy 1993; Smith and Flegal 1993; Rivera-Duarte and Flegal 1997; Squire et al. 2002; Flegal et al. 2007). These data show that recent silver concentrations in water samples collected at intermediate depth (2,400–2,500 m) (Zhang et al. 2001, 2004; Ranville and Flegal 2005; Kramer et al. 2011) are up to four-fold greater than those previously measured in eastern North Pacific waters (Martin et al. 1983). The disparity may, in part, result from differences in sampling protocols (e.g., filtered versus unfiltered samples) and/or analytical protocols (e.g., UV versus non UV), as mentioned below.

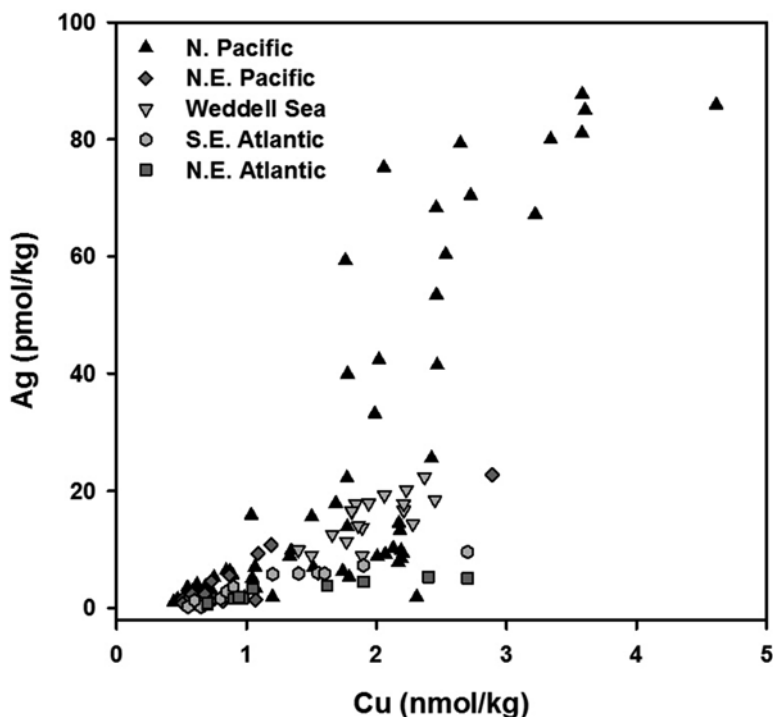


Fig. 4 Plot of silver (pmol/kg) vs. dissolved copper (nmol/kg) in oceanic waters. Data from Martin et al. (1983), Flegal et al. (1995), Sañudo-Wilhelmy et al. (2002), and Ranville and Flegal (2005)

Other factors have been advanced to explain the spatial variation of silver vertical concentration profiles in the North Pacific and the observed departures from the linear correlation between silver and silica. Ranville and Flegal (2005) proposed that the discrepancies observed between measurements in waters collected in 2001 in the western North Pacific and those previously measured in the eastern North Pacific could be explained by the incorporation into intermediate waters in the Sea of Okhotsk of surface waters enriched by atmospheric inputs of contaminant silver aerosols. Silver concentrations in surface waters collected near the Asian mainland during the same cruise had values as high as 12 pmol/kg, higher than any previously reported value for the open ocean (Fig. 5). Concentrations then steadily decreased eastward to levels of 1–2 pmol/kg near the central part of the North Pacific Gyre (Fig. 6). Since this eastward decrease corresponds with the prevailing westerly wind flow from the Asian mainland, it was suggested that atmospheric transport of mineral and industrial aerosols over the North Pacific is responsible for elevated silver concentrations in these surface waters.

The enrichment of silver over aluminum and the lack of correlation between the two elements in surface waters suggested a dominance of atmospheric fluxes of industrial emissions rather than natural processes—with the qualification that the biogeochemical processes governing the residence times of silver and aluminum in oceanic

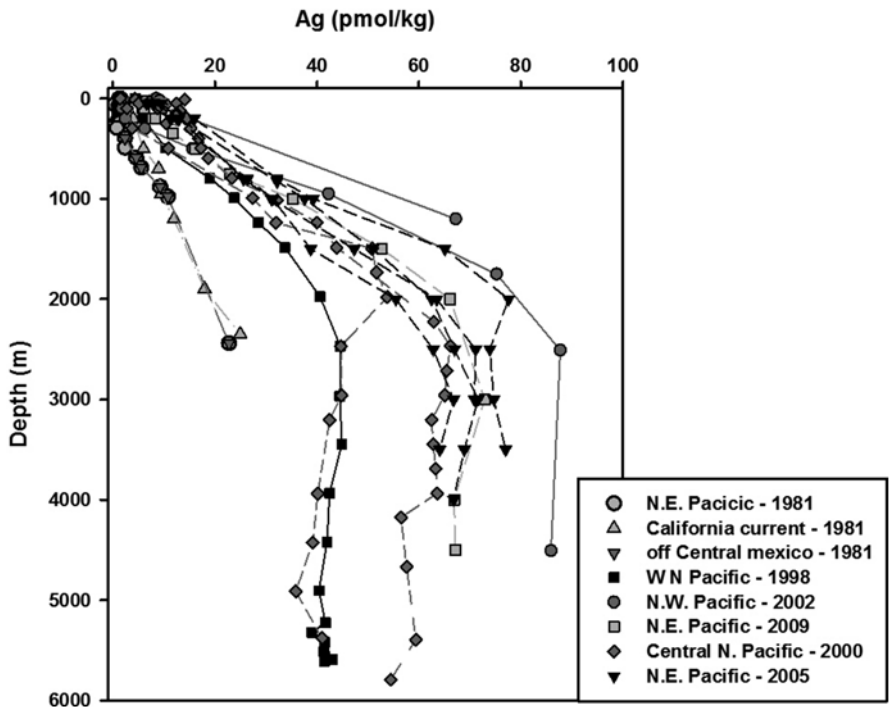


Fig. 5 Temporal variations of silver concentrations (pmol/kg) measured in waters collected in the North Pacific between 1981 and 2009. Data from Martin et al. (1983), Zhang et al. (2001, 2004), Ranville and Flegal (2005), and Kramer et al. (2011). Also included are previously unpublished data from our laboratory

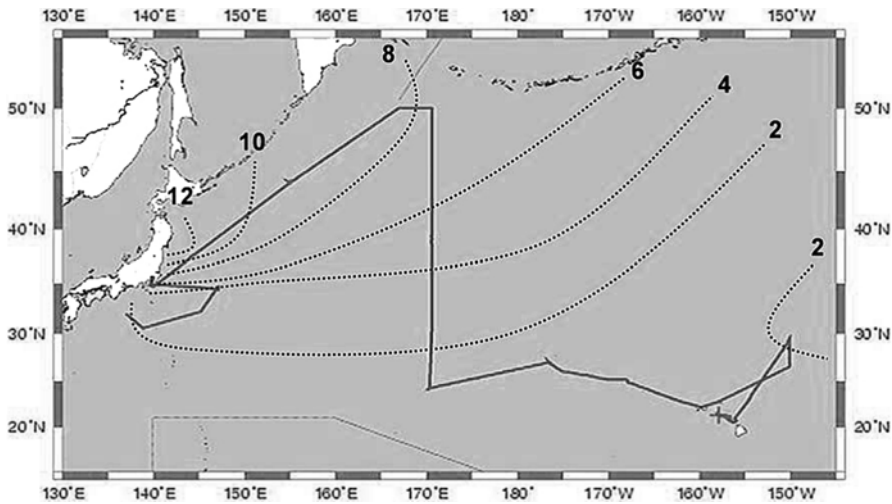


Fig. 6 Oceanic enrichment of silver. Contour plot of surface water silver concentrations (pmol/kg) in the North Pacific Ocean. The solid line indicates the ship's cruise track; contours are extrapolated from data collected along the cruise track (from Ranville and Flegal 2005)

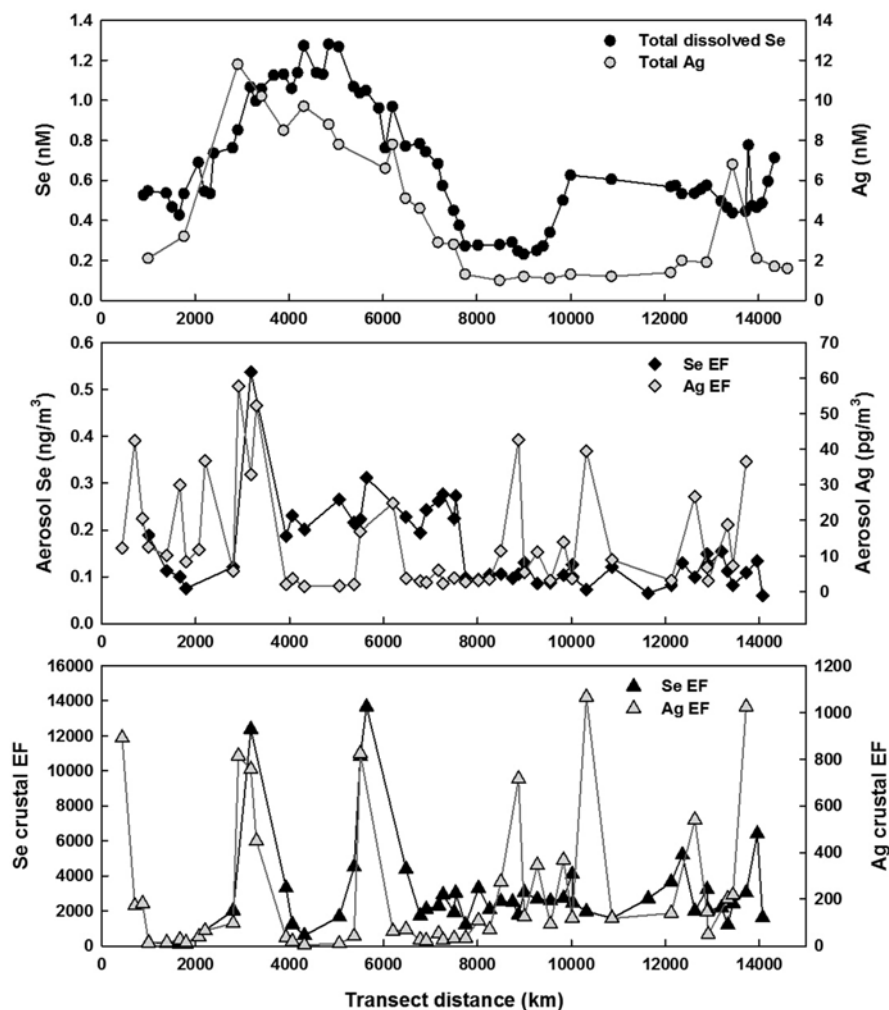


Fig. 7 Covariance of silver and selenium concentrations in surface waters and aerosols, along with their corresponding enrichment factors (EF), in the North Pacific Ocean (from Ranville et al. 2010)

surface waters are quite dissimilar. A similar gradient was also observed in lead concentrations and isotopic compositions in surface waters from the same cruise, and these were traced to Asian industrial emissions (Gallon et al. 2011). That spatial gradient of silver was comparable to the gradient observed in the North Atlantic by Rivera-Duarte et al. (1999), who also hypothesized that relatively elevated silver concentrations in those surface waters were from external inputs, although it was unclear whether this elevation results from atmospheric or terrestrial inputs.

Silver concentrations in North Pacific surface waters were also found to parallel those of selenium, which is both an essential trace element and a contaminant resulting from coal combustion (Ranville et al. 2010), as illustrated in Fig. 7. This similarity

further suggested the predominance of aeolian fluxes of silver from Asian industrial emissions to the North Pacific—again with the qualification that the biogeochemical processes governing the residence times of silver and selenium in oceanic surface waters are also quite dissimilar. Because natural emissions measurably contribute to the aeolian fluxes of selenium—but are presumably negligible for silver—in the North Pacific, variations in the $[Ag]:[Se]$ ratios may be used to distinguish between natural and industrial fluxes of selenium to those oceanic waters.

However, Zhang et al. (2004) proposed that different, natural processes accounted for the distribution of silver in the northwest Pacific. They observed that silver concentrations increased with latitude in the surface waters of the Bering Sea, the central North and South Pacific and the Southern Ocean. They attributed the increased silver in those waters to an upwelling and vertical mixing similar to that of silica. They also attributed elevated Ag/Si ratios in the surface vs. deep waters to differences in biological uptake. Then, they used a scavenging/regeneration model to characterize the $Ag-Si$ relationship.

Finally, Kramer et al. (2011) recently proposed another natural process to account for the distribution of silver in the North Pacific. Their account was based on correlations between low oxygen and silver concentrations in the broad subsurface oxygen minimum zone (OMZ) of the North Pacific, which could produce the spatial variability observed in profiles in the central eastern Pacific. Specifically, they noted that $Ag:Si$ profiles and oxygen profiles present relatively similar shapes, and that the intensity of the subsurface Ag/Si minima follows the same trend as that of the OMZ. In Fig. 8, we show $Ag:Si$ and O_2 profiles in the Pacific Ocean that are available in the literature, as well as a plot of $Ag:Si$ vs. O_2 . These observations were interpreted by Kramer et al. (2011) as an indication that dissolved oxygen content could apply a secondary control on the dissolved silver concentration.

Kramer et al. (2011) also hypothesized that silver may be removed from oxygen-depleted waters by scavenging and/or precipitation of AgS species and subsequent sequestration in the underlying reducing sediments. Such mechanisms could be the result of an exchange of dissolved silver with thermodynamically less stable metal-sulphide nanoclusters (e.g., Cu , Cd , Zn) present in the oxic water column or its complexation with nanomolar concentrations of free sulphide, as described by Rozan and Luther (2009). In addition, silver may be scavenged in the water column and precipitated as Ag_2S in anoxic microenvironments within settling decaying organic matter, as proposed by McKay and Pedersen (2008).

3.2 *Sediments*

Similarly to waters, few researchers have investigated the distribution and biogeochemical cycling of silver in marine sediments. The relative paucity of information is illustrated by the fact that we found only ten peer-reviewed references on silver in marine sediments, which are listed in Table 2. This absence of information is surprising, because there is potential for silver (as a biogeochemical analogue of silicate) to be used as a proxy of past diatom fluxes to the sea floor. But the

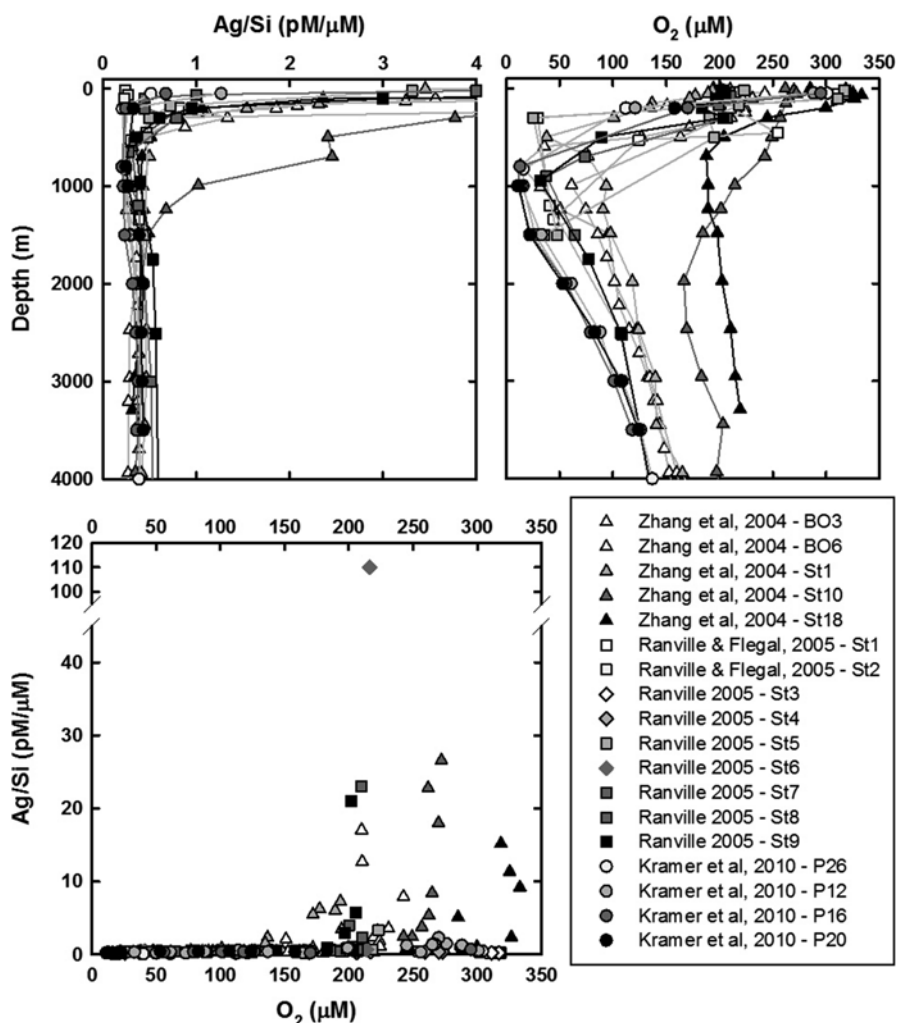


Fig. 8 Dissolved Ag:Si and O₂ profiles and correlations in the Pacific Ocean (Zhang et al. 2004; Ranville and Flegal 2005; Kramer et al. 2011)

deposition silver and its potential for biogenic remobilization in marine sediments is complex, as evidenced in San Francisco Bay (Smith and Flegal 1993; Rivera-Duarte and Flegal 1997).

That complexity is illustrated by studies of silver in marine sediments, which indicate that multiple factors and dynamic processes are involved. Early work by Koide et al. (1986) showed silver enrichment relative to its crustal abundance in coastal anoxic sediments collected around the globe. Later, Borchers et al. (2005) concluded that the enrichment they observed in Namibian upwelling sediments resulted from a biogenic pre-concentration prior to burial. Silver distributions in sediment cores collected within and around the oxygen minimum zone (OMZ) off

Peru could be related to the particle flux of diatomaceous matter to the sediment (Böning et al. 2004). In the suboxic sediment below the OMZ, the observation of 'low-opal sediments' and of a relationship between opal and silver concentrations was attributed to particle dissolution as they settle in the deep water column and the subsequent remineralization of opal and silver in equal proportions. 'High-opal sediments' were observed in anoxic sediments within and in the upper edge of the OMZ. Consequently, silver distributions there were likely related to an early diagenetic fixation with Total Organic Carbon (TOC) or Total Sulfur (TS) during opal dissolution, reflecting a redox-control of silver fixation.

Although organic matter and Ag_2S species seem to play a role in silver fixation, Crusius and Thomson (2003) suggested that it may also be sequestered by precipitation of silver selenide species (AgSe or Ag_2Se) as a result of oxygen exposure of sediments that were initially anoxic. In a subsequent study conducted off Chile, Böning et al. (2005) found that silver content in sediment increased with water depth, which they interpreted as an indication that silver enrichment was controlled by opaline regeneration and/or by a higher availability of silver in seawater. A redox control of silver content was discarded in that case, based on the contrast with Cd and Re contents, which decrease with increasing water depth and reflect decreasing reducing conditions.

The lack of redox influence on silver content was also observed by McKay and Pedersen (2008). They measured concentrations of silver in surface sediments from the Western Canadian, Mexican, Peruvian, and Chilean continental margins, and also observed that concentrations increased with water depth. The lack of correlation observed between the concentrations of silver and redox-sensitive trace metals (Re, Cd, and Mo) led them to conclude that silver accumulation was not controlled by sedimentary redox conditions. Instead, they hypothesized that silver accumulation results from its scavenging decaying organic particles as they settle through the water column. More specifically, they proposed that silver precipitates as Ag_2S within anoxic microenvironments that develop as a result of organic degradation inside sinking organic particles. In addition, McKay and Pedersen (2008) observed a positive correlation between silver and barium in surface and near surface sediments, suggesting similar mechanisms of enrichment. Because barium is commonly used as a tracer of paleoproductivity, these similarities suggest that silver may also be used as a paleoproxy.

Morford et al. (2008) further highlighted the highly dynamic process of silver diagenesis through the analysis of porewater and sediment profiles in the northeast Pacific. They observed background concentrations of silver in oxic sediments associated with high levels in pore waters, indicating a flux of silver from the sediments to the overlying water. In addition, increasing porewater concentrations with water column depth led them to theorize that silver is delivered to the sediments by scavenging—sorbing onto settling particles (a longer path leading to an associated higher content of silver), and subsequently being released to pore waters. Similarly, erosion chamber experiments by Kalnejais et al. (2010) showed that silver can be released from sediments to the dissolved phase during erosion events, and over longer time scales in association with the reaction of suspended particles in the water column.

3.3 *Qualifications*

A major problem in understanding the biogeochemistry of silver in the world oceans, apart from the paucity of data, is the difficulty in comparing the different data sets. The few measurements of truly trace concentrations of silver in the oceans have been conducted by different investigators using different sampling, treatment, and analytical methods (Table 1). For example, onboard collections have been conducted using different sampling systems, and have included—or not—a filtration of the samples on various types and sizes of filters. The disparities extend to the laboratory, wherein two types of methods have primarily been used to separate and pre-concentrate silver: solvent-extraction and chelating resin column partitioning (Table 1). One method, developed in the 1970s (Danielsson et al. 1978, Bruland et al. 1979), uses a combination of 1-pyrrolidinedithiocarbamate and diethyldithiocarbamate (APDC/DDDC) to chelate silver, followed by a double extraction into chloroform, and back-extraction into nitric acid. Another method, developed more recently (Ndung'u et al. 2006), consists of separating silver on a mini-column packed with a strong anion exchange resin (Dowex 1-X8) connected to a flow-injection system that allows on-line determination by high resolution inductively coupled mass spectrometry (HR ICP-MS). Different analytical methods have also been used for the analysis of silver concentrations, including thermal ionization mass spectrometry (TIMS), atomic absorption spectrometry (AAS), and HR ICP-MS.

In addition, the use—or not—of ultraviolet (UV) irradiation prior to the analysis may introduce some disparity among silver measurements. Ndung'u et al. (2006) showed that a digestion with UV radiation is necessary prior to silver analysis with anion exchange resin to liberate any metal bound in refractory organic complexes. Analysis of waters from the San Francisco Bay estuary and the North Pacific Ocean showed a 10–70% increase in silver concentrations measured after exposure to UV radiation. Similarly, comparable measurements on the Safe D2 and GEOTRACES GDI intercalibration samples showed an increase of silver following UV irradiation (unpublished data). Whether such discrepancies apply to the use of APDC/DDDC extraction is not clear.

Comparison of the silver data generated by different laboratories is further complicated by the lack of a certified value for silver in any reference seawater material. The National Research Council of Canada (NRC-CNRC) certified reference material for trace metals in estuarine water (SLEW-3) has an “information” value for silver, but it is not certified. To date, only two laboratories (including ours) have reported silver concentrations in the GEOTRACES North Pacific (SAFe Reference Samples) and North Atlantic (GEOTRACES Reference Samples) intercalibration waters, and these measurements have not been published (Ken Bruland, personal communication). But a few authors have reported numbers for the NRC-CNRC reference materials for trace elements in nearshore seawater (CASS-4) and estuarine water (SLEW-3), which are listed in Table 5.

Finally, there have been a few measurements of silver isotopes in the marine environment, but they have not been substantiated by intercalibration. Folsom et al.

Table 5 Silver concentrations (nmol/kg) reported in National Research Council Canada (NRC-CNRC) reference material for trace metals in nearshore seawater (CASS-4) and estuarine water (SLEW-3)

Reference	Ag (pmol/kg)	
	CASS-4	SLEW-3
Ndung'u et al. (2001)	56.6 ± 8.3	
Yang and Sturgeon (2002)	50.2 ± 0.7	17.9 ± 0.8
Ndung'u et al. (2006)	78.6 ± 18.2	27.5 ± 7.1
Ranville and Flegal (2005)	101 ± 2.6	36.3 ± 0.3
Morford et al. (2008)	53 ± 3; 54 ± 6; 59 ± 10	
Ndung'u (2011)		22.5 ± 1.5

(1970) used ratios of radiosilver ($^{110m}\text{Ag}/^{108m}\text{Ag}$) associated with the 1961–1962 atmospheric nuclear weapons testing period to date marine organisms; then, two of these authors (Hodge and Folsom 1972) used those ratios and $^{90}\text{Sr}/^{110m}\text{Ag}$ ratios in particulate aerosols to independently estimate the global budget of atmospheric “fallout” ^{110m}Ag from that testing period. Murozumi et al. (1981) measured silver concentrations, but not stable silver isotopic compositions in seawater by using isotope dilution TIMS. Recent advances, however, have demonstrated that silver isotopic ratios may be accurately and precisely measured in environmental materials (Schönbächler et al. 2007; Luo et al. 2010). Therefore, we expect that silver isotopic measurements will soon be employed to trace natural and industrial fluxes of silver and its biogeochemical cycling within the oceans.

4 Summary

Despite its relatively high acute toxicity to marine phytoplankton and invertebrates and its increasing use as a biocide, silver measurements in seawaters are still few and far apart. That paucity of data limits our understanding of its global biogeochemical cycle and an assessment of its potential applicability as a tracer of anthropogenic contamination of the oceans. The need for such an assessment has been heightened by the dramatic increase in AgNPs over the past decade.

Available measurements indicate that silver has a nutrient-type behavior in the oceans, and preliminary data indicate that its cycling is being perturbed by aeolian inputs of industrial silver. However the processes governing silver's biogeochemical cycle in the ocean are still subject to debate. For instance, precipitation/scavenging of AgS species in oxygen-depleted waters has been proposed to play a role in silver removal from ocean waters and subsequent accumulation in sediments. This hypothesis could be tested by undertaking additional measurements in waters and sediments in regions impacted by extensive oxygen minimum zones (OMZ). Furthermore, analysis of silver concentrations in waters impacted by hydrothermal plumes could resolve what their potential impact is on silver distribution in deep water masses.

In addition to the relative scarcity of reported silver concentration measurements in the oceans, comparing those few measurements that do exist is hampered by

inadequate application of quality assurance and quality control steps during the original analyses. Future studies need to be calibrated with standard reference materials that have certified values for silver, and intercalibrated with measurements made by other institutions. Those criteria are benchmarks for the international GEOTRACES program, and they certainly apply to future new measurements of silver to be made in the oceans.

Finally, new tools are needed to resolve open questions about silver fluxes and biogeochemical cycling in the oceans. Variations in silver isotopic ratios ($\delta^{107/109}\text{Ag}$) have been reported between standard materials of different environmental media, including sediment, industrial and domestic sludge, and fish liver (Luo et al. 2010). Consequently, variations in that ratio may be used to fingerprint different sources of silver in the environment and study its biogeochemical cycle in the oceans. Similarly, more sophisticated models should be developed and used to assess the validity of the assumed chemical properties and behavior of silver compounds in the water column and sediments, and to improve our understanding of anthropogenic perturbations of its cycle and identify areas for additional measurements. Lastly, we endorse the suggestion by McKay and Pedersen (2008) that the applicability of sedimentary silver as a proxy of paleoproductivity needs to be determined.

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