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The marine biogeochemistry of selenium: A re-evaluation[1]

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Abstract

Vertical and horizontal profiles from the North and South Pacific Oceans demonstrate the existence of three species of dissolved selenium: selenite, selenate, and organic selenide (operationally defined). In surface waters, organic selenide makes up about 80% of the total dissolved selenium, selenite concentrations are uniformly low, and selenate concentrations rise with increased vertical mixing. The organic selenide maximum (thought to consist of seleno-amino acids in peptides) coincides with the maxima of primary productivity, pigments, bioluminescence, and dissolved free amino acids. Deep ocean waters are enriched in selenite and selenate, while organic selenide is nondetectable. In suboxic waters of the tropical northeastern Pacific, organic selenide concentrations rise, while selenite values decrease. The downward flux of particulate selenium generally decreases with depth, and fluxing particulate selenium is found to be primarily in the (−2) oxidation state. These data allow a re-evaluation of the internal biogeochemical cycle of selenium. This cycle includes selective uptake, reductive incorporation, particulate transport, a multistep regeneration, and kinetic stabilization of thermodynamically unstable species.

The marine biogeochemical cycles of many trace elements include the processes of uptake from dissolved to particulate form, particulate transport, and regeneration back to the dissolved state. Uptake can occur passively by adsorption onto particle surfaces and coprecipitation into solid phases, or actively by selective incorporation into biological tissues and skeletal material. The vertical transport of trace elements from the surface zone to the deep sea via detrital matter is a function of the type of carrier and of sinking rates. The regeneration of a particulate-bound trace element to the dissolved state can occur by simple dissolution of the carrier or by the complex microbial process of oxidative degradation. The regeneration of nitrogen provides an example of this latter process; several intermediates (e.g. ammonia, nitrite) occur in the production of nitrate from organic nitrogen. Oxidation-reduction reactions may also be an important process for trace elements such as selenium. Dissolved selenium may exist as selenate (+6), selenite (+4), or several possible forms of selenide (−2).

Previous studies have dealt with different aspects of the marine biogeochemical cycle of selenium. Sugimura et al. (1977) showed both selenite and selenate to be present in oxic seawater, with higher concentrations in deep waters than at the surface. The presence of substantial amounts of selenite throughout the water column was surprising, since thermodynamics would predict that only selenate should be present in oxic seawater. Measures and Burton (1980*a*) and Measures et al. (1980) presented the first oceanographically consistent vertical profiles of selenate and selenite in the Atlantic and Pacific Oceans. They concluded that selenium displays nutrient-type behavior. Multiple correlations with silicate and phosphate were made, and it was suggested that selenium has both deep and shallow regeneration cycles, depending on the particulate phase (i.e. selenite is found with silica phases, while selenate is found in soft tissues as is phosphate). It was pointed out, however, that these conclusions assumed preservation of the original oxidation states. If, on the other hand, selenate was reduced during incorporation, oxidative regeneration could then produce the thermodynamically unstable selenite. The work by Measures et al. (1980) during the GEOSECS-I reoccupation emphasized a model involving particulate transport of selenite and selenate to deep water.

Cutter (1982) found that in Saanich Inlet selenite and selenate concentrations decrease in the suboxic zone and are at the detection limits in anoxic water. The major

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selenium species in the reducing waters was operationally identified as dissolved organic selenide, and most of it was found to be associated with total dissolved amino acids. Thus, dissolved selenide may exist in the form of seleno-amino acids in certain environments. Cutter also presented evidence that selenium undergoes a multistep release from biogenic particles. The first regenerative step is the release of dissolved organic selenide, which oxidizes to selenite, and then to selenate. It was suggested that the extent to which this multistep regeneration is completed can be a function of ambient redox conditions.

In addition to regeneration, the particulate uptake of selenium has also been studied. Wrench and Measures (1982) presented data indicating the preferential uptake of selenite over selenate during seasonal plankton blooms in a Nova Scotian fjord. This observation is in accord with several laboratory studies (Butler and Peterson 1967; Fowler and Benayoun 1976).

It is evident that much work remains to be done in order to clarify the selenium cycle in the ocean. We attempt here to further elucidate the marine chemistry of selenium by examining the vertical and horizontal distributions of selenium species in several ocean regimes. We also determine selenium speciation in fluxing particulate material in order to resolve the question of adsorption vs. active incorporation (uptake).

We thank G. Smith for analyzing the horizontal transect nutrient samples, S. Moore and L. Small for the VERTEX nutrient data, the members of the VERTEX program, and R. Franks for manuscript review. The Center for Marine Studies, UCSC, provided the analytical facilities which made this work possible. We also extend our appreciation to the masters and crews of the RV *T. G. Thompson* and RV *Wecoma.*

Sampling and methodology

Samples for dissolved selenium species were taken by clean sampling techniques (Bruland et al. 1979), including filtration through 0.3-μm Nuclepore membrane filters. Fluxing particles were collected in Soutar-type sediment traps (*see* Dymond et al. 1981) deployed as floating surface arrays at multiple depths. Trap contents were preserved while in the trap cod-ends with a buffered Formalin solution and concentrated after retrieval by centrifugation. The particle mass was corrected for sea salt. Determination of dissolved selenite, selenate, and organic selenide has been described previously (Cutter 1978, 1982, 1983). The technique involves selective hydride generation, liquid nitrogen-cooled trapping, and atomic absorption detection. Selenite is determined directly with samples acidified to 4 M HCl and subsequent sodium borohydride addition. A sulfanilamide solution is used to remove potential interference from nitrite. Selenite+selenate is determined by boiling a 4 M HCl acidified sample for 15 min, and then following the selenite procedure. Selenate is determined by difference. The total dissolved selenium determination entails boiling a 4 M HCl sample, with potassium persulfate addition, for 1 h. The difference between total selenium and selenite+selenate is the concentration of Se(−2+0) in a dissolved sample. As done by Cutter (1982), dissolved organic selenide will be operationally defined as this difference [i.e. Se(0) is not considered]. This definition is examined below.

Particulate selenium determinations were performed on biogenic sediment trap material which had been dried at 40°C and ground in an agate mortar and pestle. A 25-mg sample is placed in a 50-ml beaker with 5 ml of concentrated nitric acid, 0.1 ml of perchloric acid, covered, and refluxed for 3 h. The beaker is uncovered and the acids allowed to evaporate until only a slight amount of moisture remains. The above process is repeated twice. At no time is the sample allowed to go dry or char, since selenium losses may result. The sample is then taken up in 4 M HCl, 1-ml aliquots diluted to 100 ml, and treated as above for selenite+selenate. This procedure was evaluated with standard reference materials (NBS Bovine Liver, Oyster Tissue, and IAEA Copepods) and gave complete recoveries. For determination of the amounts of selenite and selenate which might be adsorbed or associated with biogenic particulate material, 50-mg samples plus 1.5 ml of distilled water are placed in Teflon centrifuge tubes

and sonically disrupted (20 kHz); 1.5 ml of 2 M NaOH is added, and the tubes covered and placed in a sonic bath for 4 h. The samples are then adjusted to pH 1.6–1.8 with HCl, and centrifuged to concentrate the particulate material remaining. The supernatants are collected and the pellets rinsed with 1 ml of pH 1.6 HCl solution and respun. This process is repeated twice. The collected supernatants are passed through Amberlite XAD-8 columns (3 ml) previously rinsed with pH 12 KOH solution and pH 1.6 solution; 4 ml of pH 1.6 solution is passed through each column after the sample. Aliquots of the column flow-through are analyzed for selenite and selenite+selenate as above. With ^{75}Se radiotracer selenite and selenate, the above procedure can quantitatively desorb selenate and selenite from biogenic particulate material without altering the oxidation states. Selenite+selenate bound in carbonate, iron oxide, and manganese oxide phases is quantitatively released by the basic leach (Cutter unpubl. data). The basic leach also releases some organically bound selenium, which the XAD-8 column removes. Particulate organic selenide is operationally defined as the difference between the total particulate selenium and particulate selenite+selenate determinations (similar to the dissolved definition). This fraction could also include elemental selenium. However, Se(0) has only been found associated with microorganisms in the presence of high selenium concentrations (Doran and Alexander 1977). In marine phyto- and zooplankton, selenium is predominantly found in proteins and amino acids; selenium in lipid components is nondetectable (Wrench 1978; Wrench and Campbell 1981; Foda et al. 1983). This particulate selenium is not merely associated with the proteins, but appears to be actually covalently attached to carbon as seleno-amino acids and their derivatives (organic selenide forms). Indeed, the abundance of selenium in proteins is consistent with its proposed biochemistry (Stadtman 1974) which is similar to that of sulfur. Thus, although our definition of particulate organic selenide is operational and potentially subject to change, it is in accord with previous findings.

Nitrate, nitrite, phosphate, and silicate were determined on an AutoAnalyzer using modified procedures of Strickland and Parsons (1972). Particulate carbon and nitrogen were determined on a Perkin-Elmer 240B elemental analyzer.

Results and discussion

Vertical distribution and speciation of dissolved and particulate selenium—In order to examine the vertical distribution of selenium species, we will discuss data from the VERTEX II (V-II) site in the eastern tropical North Pacific Ocean. The V-II site (18°N, 108°W) was occupied in October–November 1981 by the RV *Wecoma*. The water is 3,500 m deep with a surface mixed layer of about 30 m. Chemically, the most significant feature at the site is a suboxic zone from 150 to 600 m in which dissolved oxygen levels are <10 μmol·liter^{-1}. Measurements on board ship (Cutter and Bruland unpubl. data) show that the suboxic region is well defined by a region of almost complete iodate reduction. Nutrient profiles are shown in Fig. 1. Denitrification is apparent in Fig. 1A, with nitrate showing a substantial negative anomaly between 150 and 600 m. This we attribute to microbial organisms using nitrate as a terminal electron acceptor for suboxic respiration; a nitrite maximum resulting from this nitrate reduction can be seen in Fig. 1B.

The data for dissolved selenium species at V-II are given in Table 1 and shown in Fig. 2. Total dissolved selenium (Fig. 2A) ranges from 1 nmol·kg^{-1} in the 30-m mixed layer to concentrations of about 2.3 nmol·kg^{-1} at 3 km. Selenite (Fig. 2B) averages 0.05 nmol·kg^{-1} in the upper 60 m of the water column and increases gradually with depth to values of 0.9 nmol·kg^{-1}. The increase is similar to that of silicate (Fig. 1D), but with a slight negative anomaly in the suboxic zone between 150 and 600 m. Surface selenate values (Fig. 2C) average 0.14 nmol·kg^{-1}. From 30 to 125 m, selenate increases rapidly to 1.16 nmol·kg^{-1}. At depths between 500 and 3,000 m, selenate exhibits a fairly uniform distribution, with concentrations between 1.2 and 1.3 nmol·kg^{-1}.

The operationally defined dissolved organic selenide fraction (Fig. 2D) averages

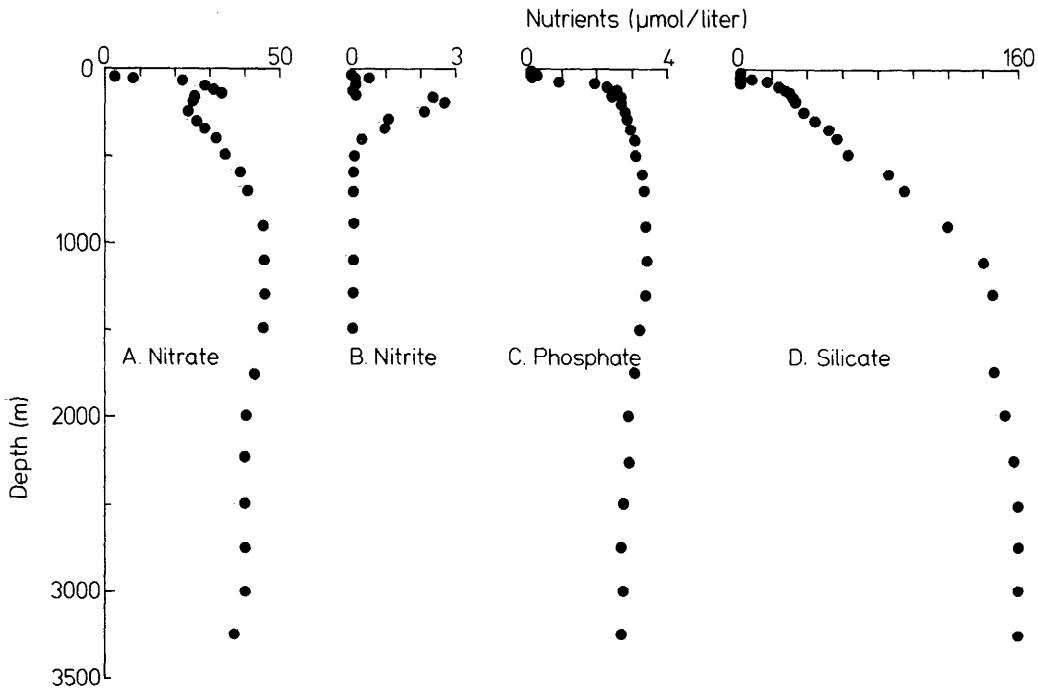

Fig. 1. Vertical profiles of dissolved nitrate, nitrite, phosphate, and silicate at the VERTEX II site.

0.8 nmol·kg^{-1} within the 30-m mixed layer, and increases to a maximum of about 1.0 nmol·kg^{-1} between 45 and 60 m. This organic selenide maximum correlates well with the various indicators of biological activity also measured at the V-II site. Total pigments show a maximum at 50 m (Broenkow and Krenz 1982), bioluminescence at 60 m (Broenkow and Krenz 1982), and primary productivity at 40 m (Knauer unpubl. V-II data). Dissolved organic selenide then decreases to a minimum of 0.14 nmol·kg^{-1} at 150 m, before increasing to a secondary maximum of 0.47 nmol·kg^{-1} centered at 350 m. The dissolved free amino acids profile at V-II (C. Lee unpubl. V-II data) also shows a maximum in the suboxic region at 300 m, as well as a maximum at 100 m. The similarity between depth profiles of dissolved organic selenide and free amino acids is in accord with the finding of Cutter (1982) that the organic selenide was associated with total dissolved amino acids (presumably as seleno-amino acids in dissolved peptides). The Se(−2+0) concentration in a dissolved sample is operationally defined as organic selenide (*see methods*). It should be re-emphasized that the analytical method yielding the concentration of dissolved organic selenide would not distinguish between forms of Se(−2) and Se(0). However, Se(0) is insoluble in seawater and could only exist as a pseudo-dissolved microcolloid. Takayanagi and Wong (1984) have observed colloidal selenium in rivers and estuaries, but none has been detected in coastal seawater. Thus, selenide is the probable dominant form of dissolved selenium in the (−2+0) fraction. The V-II data do not provide an actual characterization of the reduced selenium species [e.g. seleno-amino acids, Se(0), inorganic Se(−2)]. However, these V-II data, together with the results of Cutter (1982), do suggest a strong organic association, while the analytical technique identifies the selenium oxidation state as (−2+0). Therefore, we use the term dissolved organic selenide, but recognize that the definition is operational and subject to change.

Measures et al. (1983) gave a summary of their selenium data for various stations in

Table 1. VERTEX II dissolved selenium data (in nmol·kg^{-1}).

Depth (m)	Total Se	Se(+4)	Se(+6)	Organic Se(−2)
15	0.95	0.07	0.13	0.75
30	1.02	0.05	0.14	0.83
45	1.32	0.07	0.19	1.06
60	1.63	0.02	0.68	0.93
75	1.51	0.15	0.98	0.38
100	1.52	0.26	0.92	0.34
125	1.66	0.28	1.16	0.22
150	1.50	0.26	1.10	0.14
200	1.40	0.23	1.09	0.08
250	1.42	*	*	0.33
350	1.93	0.31	1.15	0.47
400	1.78	0.40	1.13	0.25
500	1.80	0.43	1.28	0.09
600	1.91	0.53	1.26	0.12
700	1.80	0.62	1.33	0.16
900	1.98	0.73	1.26	≤0.01
1,100	2.03	0.77	1.18	0.08
1,300	2.08	0.81	1.16	0.11
1,500	2.10	0.89	1.20	0.01
1,750	2.21	0.94	1.27	0.13
2,000	2.13	0.91	1.22	†
2,250	2.20	0.92	1.28	
2,500	2.17	0.94	1.23	
2,750	2.11	0.91	1.20	
3,000	2.44	1.03	1.31	
3,250	2.40	0.92	1.48	

* Se(+4) not determined, thus no Se(+6) value reported.
† Organic Se(−2) not detected below 1,750 m.

the eastern North Pacific which can be compared with the V-II results. They determined selenite by selective formation of a piazselenol compound and extraction into an organic solvent, followed by gas chromatography with electron capture detection (Measures and Burton 1980*b*). Total dissolved selenium is determined by irradiating samples with UV light for 5 h. Regardless of the initial concentrations of selenate and selenite, 86±6% of the original selenium is converted to selenite due to disproportionation. Selenate is then calculated to be the difference between total selenium and selenite—organic selenide is not considered. Work by Suzuki et al. (1980) and Cutter (1982), as well as the present data, indicates that a portion of total dissolved selenium may be in the form of organic selenide. It is not known whether the UV technique quantitatively oxidizes organic selenide; however, any selenite resulting from the disproportionation of organic selenide would be incorrectly considered selenate.

Plots of deep water selenite/silicate and selenate/phosphate from VERTEX II agree with the Pacific results of Measures et al. (1983). Thus, the V-II deep water selenite and selenate data are in agreement with, and confirm, the results of Measures et al. This is especially relevant since completely different analytical approaches were used. This agreement adds a great deal of confidence to the accuracy of both data sets.

In the surface waters of the Pacific, Measures et al. (1983) reported average selenate concentrations of 0.5 nmol·kg^{-1}, a value considerably greater than that at V-II. However, if the UV technique used for selenate determinations does in fact include organic selenide, the higher values of Measures et al. could result from the summation of selenate and organic selenide. The only other open ocean data for organic selenium in the Pacific are those of Suzuki et al. (1980) from the western North Pacific; they found maximum mixed-layer concentrations of 0.28 nmol·kg^{-1} and agree on the absence of organic selenium from deep waters. Although Suzuki et al. (1980) do not assign an oxidation state to the organic selenium, their profiles are remarkably similar to the VERTEX II profile.

The concentrations and fluxes of particulate selenium, carbon, and nitrogen from V-II sediment trap material are presented in Table 2. The decrease in carbon and nitrogen concentrations and increase in C:N ratios indicate that the fluxing material becomes more refractory with depth as the labile organic material, in particular nitrogen, is selectively removed. At 100 m the atomic C:N ratio is 5.36 while that at 470 m is 8.04, demonstrating the effects of biodegradation and repackaging. The selenium flux generally decreases with depth, in concert with carbon and nitrogen. The selenium speciation in the 50-m trap material shows that only 9.5% of the total selenium flux from the mixed layer is in the form of selenite and selenate. Thus, selenium is being delivered to deeper waters primarily as selenide, not as selenite or selenate. This implies that the uptake process must include reduction, and therefore, the loss of original

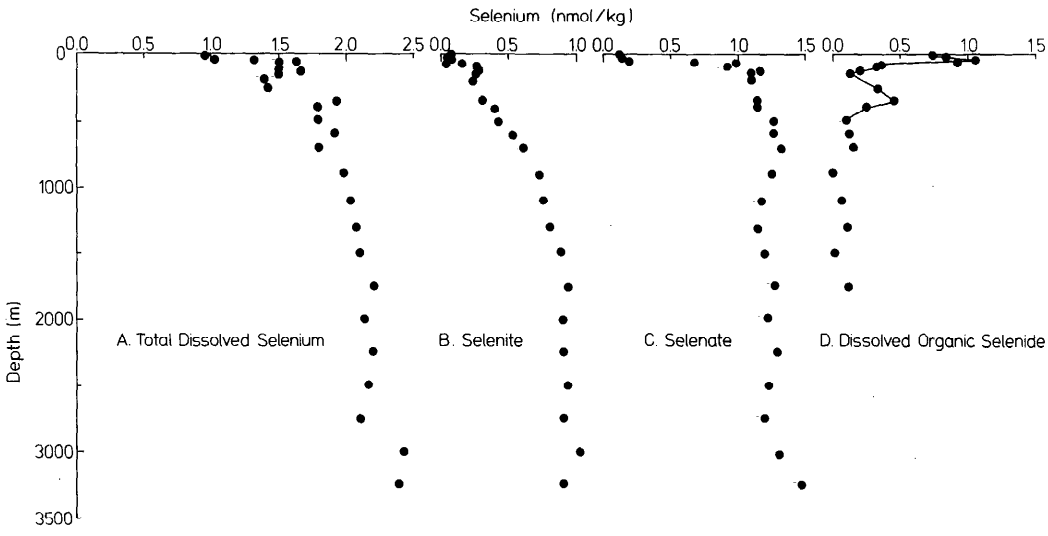

Fig. 2. VERTEX II depth profiles of total dissolved selenium, selenite, selenate, and organic selenide.

oxidation state identity. The predominance of selenide in biogenic particles is consistent with one of the models of Measures and Burton (1980*a*) and the multistep regeneration model suggested by Cutter (1982).

Surface water selenium speciation on a horizontal transect—The uptake of dissolved selenium occurs primarily in the euphotic surface layer. Previous studies (Butler and Peterson 1967; Fowler and Benayoun 1976; Wrench and Measures 1982) indicate that selenite is preferentially removed by biological activity, leading to changes in the relative abundance of selenium species in surface waters. In order to assess the effects of selective uptake on the speciation and residence times of selenium in surface waters, we analyzed samples from the surface mixed layer on a cruise through several oceanic regimes. The cruise track followed the great circle route from Monterey, California, to Hawaii, and from 20°N to 20°S, along 160°W aboard the RV *T. G. Thompson* in September–October 1980 (Table 3).

As seen in the salinity (Fig. 3) and phosphate (Fig. 4) profiles, there are two distinct regimes between Monterey and Hawaii. The California Current is a broad and diffuse low salinity current, loosely defined in Fig. 3 as the low salinity water extending to about station 6 (870 km from Monterey). A transition zone with increasing salinity and temperature separates the California Current from the North Pacific gyre; stations 10–15 can be considered within the gyre. The California Current is meso- and eutrophic due to spring and summer wind-induced upwelling. This is best illustrated in the phosphate profile (Fig. 4) and by nitrate+nitrite concentrations that are elevated within the current but at the analytical detection limits in the gyre.

On the north–south transect, three major regimes are encountered: the North Pacific gyre, the equatorial upwelling region, and the South Pacific gyre. These three areas are clearly seen in the nitrate profile (Fig. 5), which identifies the divergence region from about 4°N to 8°S.

Table 2. VERTEX II sediment trap data for selenium, carbon, and nitrogen.

Depth (m)	Total Se $\mu g \cdot g^{-1}$ ($nmol \cdot g^{-1}$)	Total Se flux ($\mu mol \cdot m^{-2} \cdot yr^{-1}$)	Total C	Org. C	Total N
			(%)		
50	1.69(21.5) 0.07 as +4 0.09 as +6	1.40	30.1	23.5	5.72
100	2.98(37.8)	0.98	29.1	24.4	5.32
470	6.17(78.1)	0.94	18.7	14.5	2.10
970	3.64(46.0)	0.44	18.1	11.5	2.02

Table 3. Monterey-Tahiti dissolved selenium data (in nmol·kg^{-1}).

Sta. No.	Station location (distance from Monterey, km)	Se(+6)	Org. Se(−2)
2	35°40.4′N, 124°26.9′W (250)	0.37	0.38
3	35°16.9′N, 125°27.0′W (350)	0.41	0.29
4	34°31.4′N, 127°15.2′W (535)	0.37	≤0.01
5	34°3.5′N, 128°20.6′W (648)	0.51	0.03
6	33°12.5′N, 130°31.9′W (879)	≤0.01	≤0.01
7	32°46.1′N, 131°38.2′W (983)	0.05	0.43
8	31°58.1′N, 133°38.0′W (1,191)	0.07	0.10
9	30°30.9′N, 137°2.7′W (1,554)	0.05	0.27
10	29°3.4′N, 140°28.7′W (1,921)	0.12	0.52
11	27°33.0′N, 144°2.0′W (2,306)	0.15	0.42
12	26°15.4′N, 146°56.5′W (2,626)	0.11	0.26
13	23°38.3′N, 152°34.5′W (3,260)	0.11	0.16
14	22°31.9′N, 154°46.8′W (3,515)	0.16	0.63
15	20°N, 160°W (4,121)	0.13	0.57
16	17°39.9′N, 160°W	0.17	0.51
17	14°40.8′N, 160°W	0.14	0.45
18	12°49.3′N, 160°W	0.04	0.67
19	10°5.3′N, 160°W	≤0.01	0.65
20	6°56.4′N, 160°W	0.04	0.32
21	3°46.7′N, 160°W	0.04	0.20
22	2°19.8′N, 160°W	0.12	0.62
23	1°10.9′N, 160°W	0.68	0.38
24	0°, 160°W	0.60	0.38
25	1°4.9′S, 160°W	0.58	0.39
26	4°29.4′S, 160°W	0.59	0.36
27	7°41.6′S, 160°W	0.54	0.45
28	10°16.6′S, 160°W	≤0.01	0.52
29	12°43.0′S, 160°W	0.07	0.36
30	16°31.6′S, 160°W	0.01	0.24
31	20°S, 160°W	0.01	0.26

Dissolved selenate and operationally defined organic selenide data are given in Table 3 and Figs. 6 and 7. Selenite data are not included in the table or figures because concentrations were uniformly at or below the detection limits for all stations (i.e. ≤0.01 nmol·kg^{-1}). Selenate concentrations are elevated in the California Current (average of 0.42 nmol·kg^{-1}), drop abruptly to a minimum at station 6, and increase slightly through the transition zone (Fig. 6A). Within the North Pacific gyre (stations 10–15), selenate concentrations are relatively constant with an average of 0.13±0.02 nmol·kg^{-1}. The organic selenide profile (Fig. 6B) shows considerably more variation: the concentration drops rapidly across the California Current, remains at the detection limit to station 6, and then increases across the transition zone into the central gyre, where it shows substantial variability (0.43±0.18 nmol·kg^{-1}).

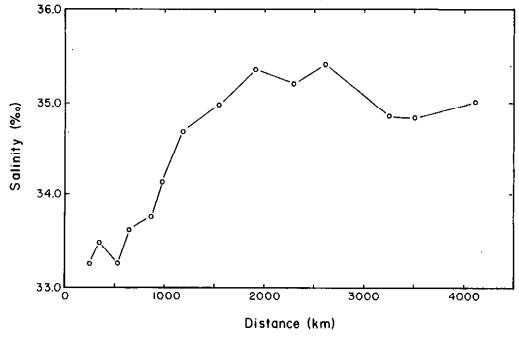

Fig. 3. Mixed layer salinity profile from Monterey, California, to 20°N, 160°W. Position on the transect is expressed as distance from Monterey in kilometers.

Selenate and organic selenide profiles are continued south in Fig. 7. Station 15 (20°N) represents the overlap between the north–south transect and the Monterey–Hawaii leg. Selenate concentrations (Fig. 7A) decrease generally and are quite low (0.04 nmol·kg^{-1}) until the equatorial upwelling zone, where they rise rapidly and average 0.60±0.05 nmol·kg^{-1}. In the South Pacific gyre sele-

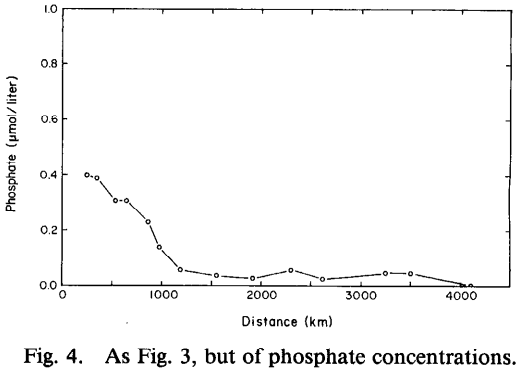

Fig. 4. As Fig. 3, but of phosphate concentrations.

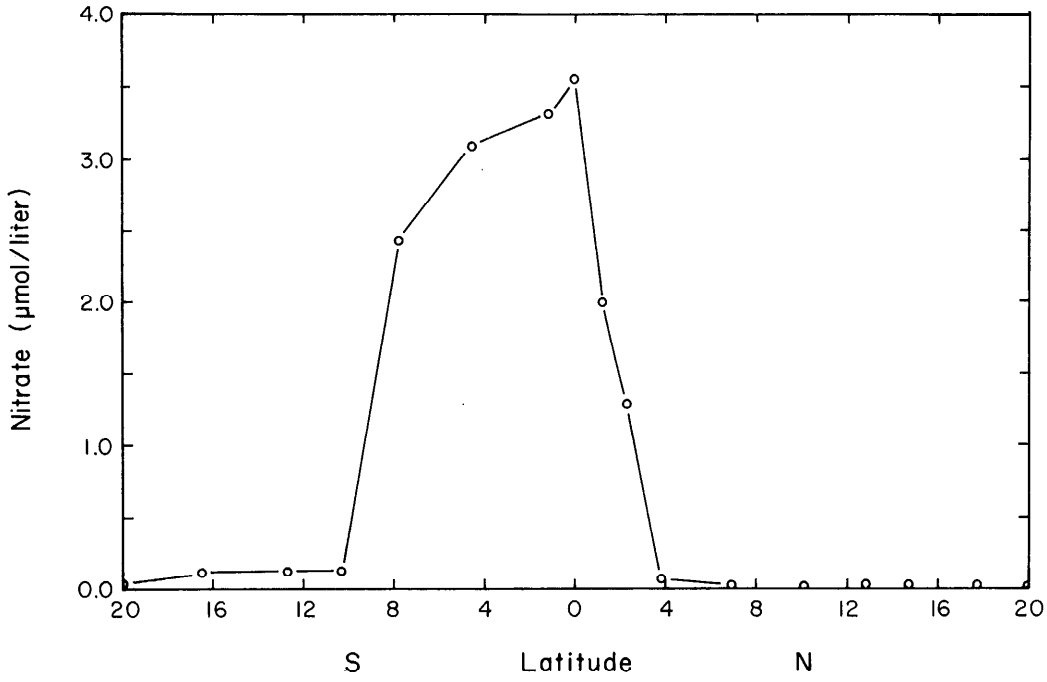

Fig. 5. Nitrate profile in the surface mixed layer on a north–south transect from 20°N to 20°S along 160°W.

nate is nearly nondetectable. Within the upwelling area organic selenide averages 0.39 ± 0.03 nmol·kg^{-1}. The South Pacific gyre has lower organic selenide concentrations than the North Pacific gyre, the average of the two southernmost stations being 0.25 nmol·kg^{-1}, relative to 0.51 nmol·kg^{-1} at the three northernmost stations. If the data for the North Pacific open ocean stations (sta. 7–21) are averaged, values are 0.09 ± 0.05, 0.41 ± 0.18, and 0.50 ± 0.20 nmol·kg^{-1} for selenate, organic selenide, and total dissolved selenium. The total selenium value of 0.5 nmol·kg^{-1} is close to the average surface value reported by Measures et al. (1983). Whereas Measures et al. argued that the major form of selenium in surface waters is selenate, we find that organic selenide comprises about 80% of the total dissolved selenium.

The horizontal data must be interpreted knowing that selenite and selenate exhibit nutrient-type vertical distributions. Thus, in the California Current and equatorial upwelling areas, selenite and selenate would be delivered to surface waters by the enhanced upwelling and vertical mixing of selenium-rich subsurface waters. In the more stratified oligotrophic waters, vertical mixing is minimal, and thus little selenium is supplied to the surface waters, allowing biological utilization to lead to extreme surface depletion. This is a situation analogous to those of phosphate and nitrate. Selenite is found at concentrations <0.01 nmol·kg^{-1} even within the equatorial divergence and California Current regimes; rapid biological uptake is implied by such low values. The elevation of selenate concentrations is loosely correlated with the intensity of upwelling as reflected in the mixed layer nitrate concentrations. The nitrate data show the equatorial upwelling, and resulting eutrophication, to be more intense than that in the California Current (this has a seasonal dependence, however). This same feature is seen in the mixed layer selenate values, with the average California Current selenate concentration being 30% less than those near the equator. In oligotrophic regions the absence of allochthonous selenite results in the secondary uptake of selenate, and thus in

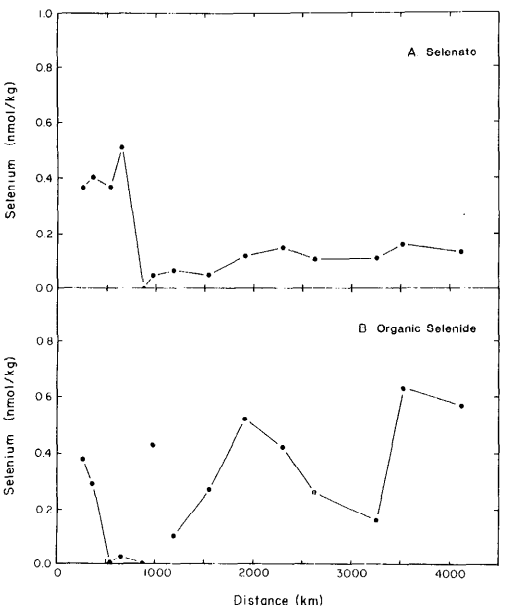

Fig. 6. A. Concentrations of selenate in the mixed layer on an east–west transect from Monterey, California, to 20°N, 160°W (distance in kilometers from Monterey). B. Concentrations of dissolved organic selenide in the mixed layer on the east–west transect.

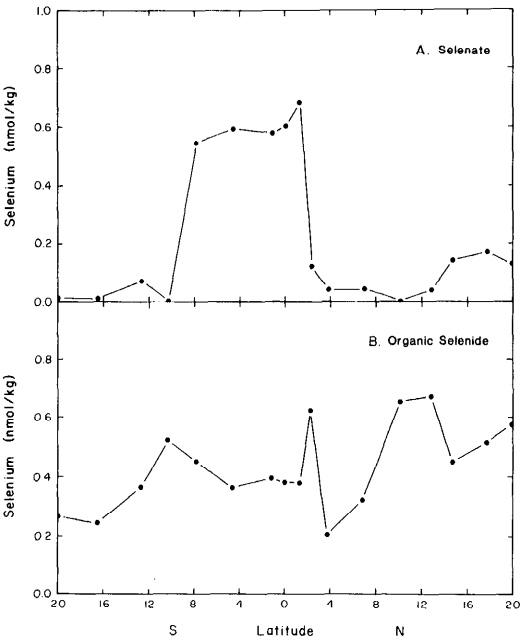

Fig. 7. A. Concentrations of selenate in the surface mixed layer from 20°N to 20°S along 160°W. B. Concentrations of dissolved organic selenide in the mixed layer on the north–south transect.

severe surface water depletion of selenate. The dissolved organic selenide data indicate that it is widely distributed in the ocean and that it is the major dissolved selenium species in the oligotrophic surface waters.

With the data from this work and those of Measures et al. (1980), we can estimate surface water residence times for selenite and selenate in the central gyres and equatorial upwelling region. For these calculations, a 70-m-deep mixed layer is assumed; Table 4 contains other pertinent data. From the SEAREX program, an atmospheric flux of total selenium has been estimated for the North Pacific (Buat-Menard 1983), but the speciation of this input is undetermined. For the central gyres, the atmospheric input term is significant, the input of atmospheric total selenium being up to 37% that from vertical mixing. Some preliminary rain data (Cutter 1978) indicate that selenite might be the dominant form of selenium delivered to the North Pacific from the atmosphere. We use this assumption for the present calculations, but stress that more rainwater speciation data are needed to better understand the role of atmospheric input on the selenium cycle. Using the values in Table 4 and the assumptions stated above, we can make first-order approximations for surface water residence times of selenite and selenate of <0.1 year and 2.6 years in the equatorial upwelling regime and <0.3 year and 2.5 years in the central North Pacific gyre. The short residence times are consistent with the nutrient-type behavior of selenium species and the evidence that selenite is more biologically reactive than selenate. For comparison, the sediment trap data in Table 2 can be used to approximate the residence time for total selenium in the mixed layer. (This includes dissolved to particulate transformation and particulate removal from the mixed layer.) For a 50-m water column at V-II, the total selenium residence time is found to be 39 years. Assuming reductive incorporation with partial regeneration as organic selenide and partial particulate removal, we can use the particulate flux to estimate maximum removal rates of sele-

Table 4. Values used in residence time calculations.

	Se(+4)	Se(+6)	Reference
Average mixed layer concn (nmol·kg^{-1}):			
Equatorial region (sta. 23–27)	≤0.01	0.60	This work
North Pacific gyre (sta. 10–15)	≤0.01	0.13	This work
Average subsurface (200–300 m) concn (nmol·kg^{-1})	0.25	0.90	This work; Measures et al. 1980
Input from vertical mixing (nmol·cm^{-2}·yr^{-1}):			
Equatorial (assuming 18 m·yr^{-1})	0.45	1.60	Broecker and Peng 1982
Gyre (assuming 4 m·yr^{-1})	0.10	0.36	Broecker and Peng 1982
Atmospheric input (nmol·cm^{-2}·yr^{-1}) to North Pacific	0.13	—	Buat-Menard 1983; Cutter 1978

nite and selenate at V-II. In this manner, selenite and selenate have surface residence times of 2 and 5 years. However, total selenium, composed primarily of organic selenide, has a much slower net removal rate (i.e. 39-year residence time).

A kinetic treatment of selenium regeneration and oxidation—The first step in the regeneration of selenium from biogenic particles appears to be the production of dissolved organic selenide (Cutter 1982). Although organic selenide is a regeneration intermediate, it would not be expected to be present at significant levels in oxic waters due to its thermodynamic instability. However, organic selenide might be found if its production rate (through regeneration) is fast, or its removal rate (by uptake or oxidation) is slow. Regeneration rates of nitrogen and carbon have been estimated to be the difference between the rates of primary production and new production (Eppley and Peterson 1979). Such data are available for both the VERTEX II site and the mesotrophic California Current during the VERTEX I cruise in August 1980. The VERTEX I site (36°N, 126°W) was near station 2 on the horizontal transect and was sampled only 2 weeks before station 2. Thus, we can also compare mixed layer organic selenide data. The average primary production was 564 mg C·m^{-2}·d^{-1} at VERTEX I, compared to 832 mg C·m^{-2}·d^{-1} at VERTEX II (Knauer unpubl.). New production estimates for VERTEX I and VERTEX II were 8 and 2.7% of the primary production (Knauer unpubl.). These data indicate that regeneration rates are extremely high at the VERTEX II site. Correspondingly, the mixed layer organic selenide values are higher at V-II than at station 2 (sta. 2, 0.38 nmol·kg^{-1}; V-II, 0.79 nmol·kg^{-1}). This would seem to indicate that organic selenide is acting as a regeneration intermediate. The subsurface nitrite maximum provides a good analogy, nitrite being an intermediate in the regeneration of organic nitrogen to nitrate.

In the deeper waters particulate fluxes and oxygen consumption rates are quite low in comparison to surface waters. Therefore, regeneration rates, and correspondingly the production of dissolved organic selenide, are greatly reduced. This leads to nondetectable levels of the transient organic selenide species in the oxic deep ocean. However, in the V-II suboxic zone a secondary organic selenide maximum is observed. The low oxygen conditions in this region can lead to the stabilization of organic selenide, inhibiting its oxidation to selenite.

The second regenerative step involves the production of selenite by the abiotic or biotic oxidation of dissolved organic selenide species. Extreme depletion of selenite in the V-II surface zone demonstrates that biological uptake is the dominant feature in this region. The low oxygen environment of the V-II suboxic zone affects selenium's multistep regeneration. This type of effect is particularly apparent in the anoxic waters of Saanich Inlet (Cutter 1982), where selenium was regenerated only as organic selenide. In the V-II suboxic region, the oxidation of organic selenide is slower than in waters above and below it. This, in turn, creates the organic selenide maximum and the neg-

ative selenite anomaly. The rest of the selenite profile shows the ubiquitous presence of selenite in deep water, despite its thermodynamic instability. The multistep regeneration of selenium provides a mechanism for the production of selenite. Obviously, selenite must then be kinetically stable in order to persist in oxic systems.

The final step in the regeneration process is the oxidation of selenite to selenate, the thermodynamically stable form of selenium in oxic seawater. The rate of this reaction affects the concentrations of both selenite and selenate in deep seawater. The evaluation of this rate is, therefore, of primary importance. Measures et al. (1980) used a steady state, two-layer box model to determine the rate constant of selenite to selenate. Their model requires that selenite and selenate not change oxidation state during adsorption and transport and that the ratio of selenate to selenite on particles is constrained by the deep water and mixed layer dissolved ratios of the two species. The particulate data presented above show that this model is inappropriate since selenium is reductively incorporated into particles. Therefore, the ratios of dissolved selenate to selenite have no direct bearing on the particulate oxidation states. Using the VERTEX II data, we can propose a more appropriate model.

A chemical kinetic approach with geochemical data can be used to determine the rate constant for the oxidation of selenite in seawater. Some possible reactions relevant to selenium species interconversions (multistep regeneration model) in oxic systems are shown in Fig. 8. The k_1 step is the transformation of particulate selenide to dissolved organic selenide. The rate of this reaction is biologically controlled and therefore of a complex order. However, a regeneration experiment (Cutter 1982) shows this reaction to be fast (i.e. $k_1 > 0.2 \cdot d^{-1}$). The k_2 step is the oxidation of dissolved organic selenide to selenite. The VERTEX II suboxic results indicate that oxygen is involved in the order of the reaction. Protons (pH) would also be expected to participate, but are relatively constant and in large excess relative to selenium in seawater. Thus, pH would not be expected

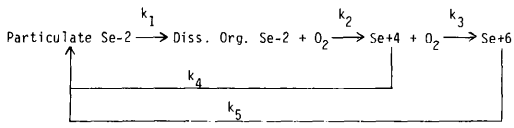

Fig. 8. A possible reaction scheme depicting selenium species interconversions (multistep regeneration model) in oxic seawater. These reactions are not meant to be stoichiometrically balanced. Compounds have been included to indicate that they may contribute to the order of the reaction.

to contribute to the reaction rate. Except in the suboxic zone, dissolved oxygen concentrations are also in large excess relative to organic selenide. Therefore, the k_2 reaction is seen to be pseudo-first-order in dissolved organic selenide for surface and deep waters. The oxidation of selenite to selenate is the crucial step, and the evaluation of k_3 will be the goal of this approach. For the same reasons given in the discussion of the k_2 step, the k_3 reaction can be assumed to be pseudo-first-order in selenite. The k_4 and k_5 reactions are those of reductive incorporation and would only be expected in surface waters. Rate expressions (pseudo-first-order) for the different reactions can now be formulated:

dissolved organic Se(−2):

$$-\frac{d[\mathrm{Se}(-2)]}{dt} = k_2[\mathrm{Se}(-2)] - k_1[\text{part. Se}(-2)];$$

Se(+4):

$$-\frac{d[\mathrm{Se}(+4)]}{dt} = k_3[\mathrm{Se}(+4)] + k_4[\mathrm{Se}(+4)] - k_2[\mathrm{Se}(-2)];$$

Se(+6):

$$-\frac{d[\mathrm{Se}(+6)]}{dt} = k_5[\mathrm{Se}(+6)] - k_3[\mathrm{Se}(+4)].$$

The steady state assumption requires that the concentrations of selenite and selenate not change with time. Therefore

$$[\mathrm{Se}(+4)](2k_3 + k_4) = k_2[\mathrm{Se}(-2)] + k_5[\mathrm{Se}(+6)].$$

In deep waters dissolved organic selenide

can be treated as a very short-lived, transient intermediate (i.e. only selenite and selenate are found in deep water, no other intermediates). Thus

$$[Se(+4)](2k_3 + k_4) = k_1[\text{part. } Se(-2)] + k_5[Se(+6)].$$

In the deep waters, the incorporation of dissolved selenate and selenite into biological organisms is negligible, and the k_4 and k_5 terms can be ignored. Therefore, the expression in the deep waters can be seen as

$$k_1[\text{part. } Se(-2)] = 2k_3[Se(+4)].$$

The above final expression states that in the deep ocean, the rate of transformation for particulate to dissolved selenide is equal to twice the oxidation rate for selenite to selenate. The rate for particulate to dissolved transformation (the "J" term in vertical advection-diffusion models: Craig 1974) can be closely approximated from the average oxygen consumption rate in the deep ocean and the ratios of organic carbon to selenium in deep sediment trap particulate materials. Oxygen consumption in deep waters is due primarily to the oxidative degradation of particulate matter, and it will be assumed that selenium is released along with organic carbon (i.e. selenium is associated with organic phases in biogenic material, as evidenced in the sediment trap data, and the data of Wrench and Campbell 1981). Deep sediment trap samples (this work and Cutter and Bruland in prep.) yield an average atomic organic carbon to selenium ratio of 2.2×10^5, giving a Redfield ratio of carbon to selenium of $106{:}4.8 \times 10^{-4}$. Therefore, the average consumption of oxygen in the deep sea, 450 nmol·liter^{-1}·yr^{-1} (Eppley and Peterson 1979), would result in the transformation of 1.6 pmol Se·liter^{-1}·yr^{-1}; this is the rate of transformation of particulate to dissolved selenium. With an average value of 0.9 nmol·liter^{-1} selenite in V-II deep waters, k_3 has a value of 8.7×10^{-4}·yr^{-1}. Its reciprocal, 1,150 years, is the mean life of selenite in the deep sea with respect to oxidation. Since the average residence time of water in the deep ocean is 1,600 years, this mean life explains the ubiquitous presence of selenite in the deep ocean.

With a 1,150-year residence time we can predict that there should be a selenite to selenate fractionation between the Atlantic and Pacific Oceans. More precisely, if the oxidation of selenite is very slow and the source of deep water selenate is this oxidation, then the ratio of selenite to selenate in the Atlantic (with its bottom water being younger than that in the Pacific) should be much larger than the ratio in the Pacific. Data in the Pacific (this work) and those of Measures and Burton (1980*a*) show that this is not the case. However, the discrepancy can be readily explained by considering the source of bottom water. The primary source of bottom water is from North Atlantic surface waters in high-latitude, eutrophic regions. As shown in data from the horizontal transects, concentrations of selenite in eutrophic water are extremely low, but concentrations of selenate are relatively enriched. Thus, the new bottom water must form with a large amount of selenate already present ("preformed selenate"). In this manner, Atlantic to Pacific fractionation is not observed. The combination of a chemical kinetic and geochemical approach provides a satisfactory answer to the question of selenite oxidation and helps explain the relative abundances of selenate and selenite in the ocean.

Conclusions

The internal marine biogeochemical cycle of selenium includes the processes of selective uptake, reductive incorporation into biogenic material, delivery of selenium to the deep sea as particulate organic selenide via sinking detritus, and a multistep regenerative release of particulate selenium to the dissolved state. A pictorial description of this cycle is given in Fig. 9. In addition, kinetic effects are vital to the existence of thermodynamically unstable organic selenide species (operational definition) and selenite which are produced in the multistep regeneration process. Selenite's ubiquitous presence in seawater can be explained by its slow oxidation rate.

This view of the selenium cycle is by no means complete. For this work, organic selenide has been operationally defined. At least in Saanich Inlet (Cutter 1982), most of the

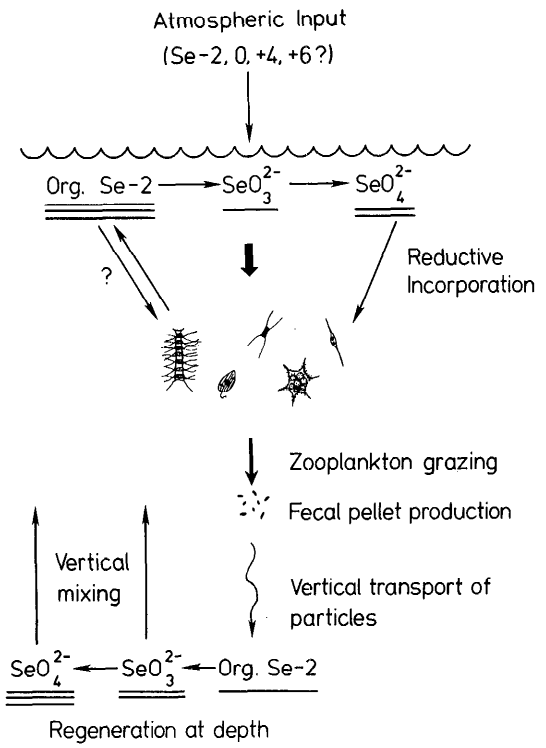

Fig. 9. A diagram of the proposed marine biogeochemical cycle of selenium. Underlining reflects the relative concentrations of selenium species in surface and deep seawater. The preferential uptake of selenite in surface waters is indicated by a larger dissolved-to-particulate arrow.

organic selenide could be accounted for in the total amino acids fraction. The VERTEX II organic selenide profile is similar to that of the amino acids, but accurate characterization of these species in the open ocean is still needed. In similar fashion, elemental selenium may be a transient intermediate in the regeneration of selenium, but current analytical techniques are not capable of detecting such a species (presumably in a colloidal phase). The existence and importance of elemental selenium remains an open question. Finally, the oxidation of selenium during its multistep regeneration may be abiotic in nature or biotically catalyzed. Bacterial catalysis has been observed for the oxidation of manganese (Emerson et al. 1982). A similar biotic catalysis would greatly affect the kinetic stability of organic selenide and selenite, potentially changing their abundances. A biochemically oriented study focusing on transient selenium species oxidation is needed to gain a more complete understanding of the marine biogeochemistry of selenium.

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