800,000-year range under interpretation (i) or into the 1-million-year range under the preferred interpretation (ii).

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15. This may not always be the case. Miotke and Palmer (*1*) argue for fluctuations in the level of the Green River due to downcutting during interglacial periods and partial filling with alluvium during glaciations.
16. Two sites show mixed polarity at about 620 feet. Of four samples taken at one of the sites, three showed reversed polarity and only one showed a weak intermediate direction. These samples were dry and powdery and may have been unreliable. The two samples from the other site gave consistent directions located about 45° from the mean reversed pole. It is not known whether this site represents an actual magnetic field excursion or reflects some external influence such as slumping in the sediment.
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18. I am greatly indebted to park superintendents J. Kulesza, A. Hawkins, and R. Deskins for their cooperation in this project. Many members of their staffs provided valuable advice and assistance, especially L. Cutliff and R. Carson. Twenty volunteer field assistants gave freely of their time in the often tedious sample collecting process, and M. McCamey and R. Selfridge did many of the laboratory measurements. Cave maps and assistance were supplied by the Cave Research Foundation, and J. Quinlan of the Uplands Research Laboratory (National Park Service) gave essential aid in many and unpredictable ways. I thank R. Harmon for his uranium-thorium work on a calcite sample. This project was supported by NSF grant EAR 78-15198.

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Selenium in Reducing Waters

Abstract. *The analysis of selenium species in reducing waters provides important insight into the element's biogeochemical cycle. The absence of selenate and selenite in reducing waters suggests that some removal mechanism could be operative, but the presence in these waters of about 1 nanomole per liter of dissolved organic selenide indicates that the regeneration of selenium in the form of organic species may be the dominant process. The data demonstrate that the regenerative and biogeochemical cycles of selenium are quite complex.*

In recent years attention has been paid to those elements that have multiple oxidation states in seawater [for example, arsenic (*1*), iodine (*2*), chromium (*2*), antimony (*3*), and selenium (*4*)]. This matter is of interest to environmentalists because certain elemental oxidation states may be more toxic than others. In addition, determining the concentrations of individual members of an oxidation-reduction couple may provide information on the oxidation-reduction potential of seawater. Dissolved selenium has three oxidation states: selenate, +6; selenite, +4; and selenide, −2. Thermodynamic calculations (*5, 6*) lead to the prediction that selenate should be the exclusive oxidation state in oxic seawater. These same calculations lead to the prediction that the ratio of selenate to selenite should be unity at an ambient pE of 6.1 (*7*), whereas in anoxic reducing systems selenide should become the stable dissolved form.

These calculations should be considered with caution since they ignore the apparent stability of thermodynamically unstable species as a result of kinetic effects as well as the biologically mediated production of unstable species. Indeed, data obtained by Measures *et al.* (*4*) show that approximately 35 percent of the total selenium found in oxygenated deep seawater is selenite. By examining the speciation of selenium in areas with extreme oxidation-reduction conditions (that is, anoxic basins and fjords), it may be possible to observe both biological and thermodynamic effects and in the process to illuminate details of selenium's biogeochemical cycle. This report presents what I believe are the first data on selenium species in reducing and anoxic waters.

Samples were taken in the Saanich Inlet, an intermittently anoxic fjord located along the southeastern portion of Vancouver Island, Canada, aboard the R.V. *Alpha Helix* in May 1981. The station (48°32.2′N, 123°32.7′W) has a water depth of 196 m. The interface between H_2S and O_2 was at approximately 175 m. A suboxic zone, characterized by low O_2 values ($< 10\ \mu M$) and nitrate reduction (nitrite maximum of 0.5 μM at 130 m), extended from approximately 110 to 170 m. Waters above this depth were considered oxic.

Samples for selenite, selenate, and dissolved organic selenide analysis were passed through 0.4-µm Nucleopore filters and stored in borosilicate bottles at pH 1.5 (HCl). Analyses were completed within 3 months of sampling. Other workers (*8*) have demonstrated that this storage method does not alter the concentration or identity of selenate and selenite over this time period. The method of analysis for selenite and selenate consists of hydride generation, liquid nitrogen–cooled trapping, and atomic absorption detection (*9*). Analysis for total dissolved selenium, which includes dissolved organic selenide, is performed by boiling a 50-ml sample acidified to $4M$ with HCl, to which 1 ml of a 2 percent (weight-volume) potassium persulfate solution has been added, for 1 hour. The resultant solution is analyzed as selenite. The characterization of the dissolved organic selenide entails analyzing 50-ml samples by means of a method developed for free and combined (peptide) amino acids [see (*10*) for an example of its usage with seawater samples]. The seawater is acid-hydrolyzed, rotary-evaporated to dryness, taken up in distilled water with pH adjustment to 9.0, and passed through a copper sulfate–treated Chelex 100 column. This column chelates free amines, which can then be eluted with NH_4OH. The column flow-throughs and elutions are treated as for total selenium.

In order to sample for hydrogen selenide ($HSe^- + H_2Se$), water from the anoxic region was anaerobically transferred into a 1-liter stripping vessel. Helium purged the vessel and was routed into two gas impingers in series, each filled with 20 ml of $7M$ HNO_3. Upon acidification of the sample to $1M$ HCl, H_2Se evolved and was oxidized in the impingers to selenite. This method has been shown to be 100 percent efficient for hydrogen selenide concentrations up to 100 ng per liter. The HNO_3 solutions were taken to dryness, and distilled water portions analyzed for selenite. Samples from the anoxic region were also analyzed for dimethyl selenide. In the procedure one uses the gas stripping vessel with 1 liter of seawater, 90 minutes of helium stripping and liquid nitrogen–cooled trapping, gas chromatographic separation, and photoionization

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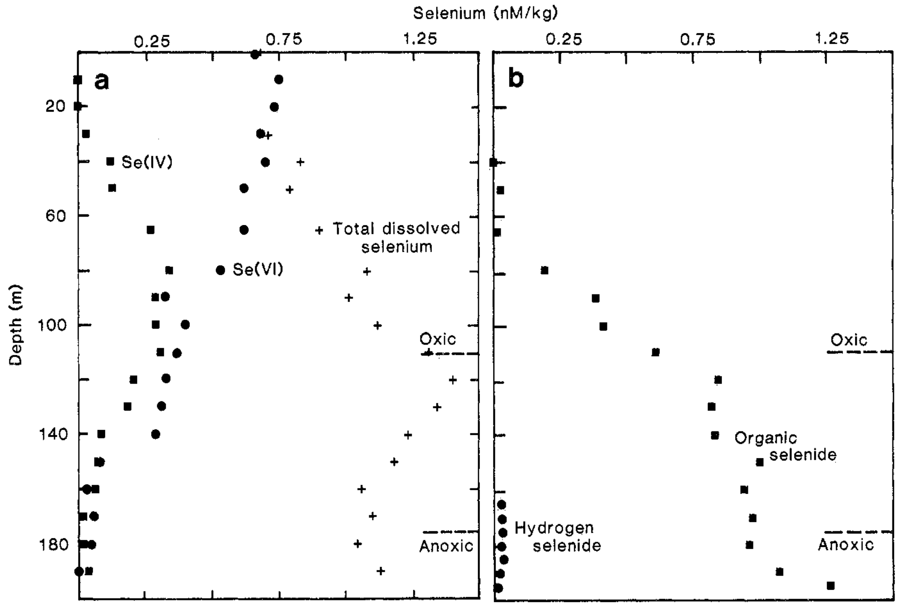

Fig. 1. (a) Saanich Inlet profile of selenite [Se(IV)], selenate [Se(VI)], and total dissolved selenium. (b) Profile of hydrogen selenide ($HSe^- + H_2Se$) and organic selenide in the Saanich Inlet. Waters above the oxic line have O_2 concentrations greater than 10 μM. Waters below the anoxic line have O_2 concentrations below the limit of detectability ($< 0.4\ \mu M$) and H_2S is present (8 μM maximum in the bottom water).

detection. With a relative detection limit of 9 p*M*, no dimethyl selenide was found in the anoxic water.

Figure 1, a and b, shows the selenium depth profiles for the Saanich Inlet. The profile for total dissolved selenium (Fig. 1a) shows an increase in concentration with depth into the suboxic zone but a general decrease within the deeper reducing and anoxic waters. The selenite profile [Se(IV)] in the upper 110 m (Fig. 1a) basically resembles that of oceanic waters, with marked depletion in the surface waters and an increase with depth through the thermocline. However, the selenite concentration decreases within the suboxic zone and is near the detection limit (0.01 n*M*/kg) in the anoxic zone. Selenate [Se(VI)] exhibits a general decrease in concentration from the surface maximum to values at the detection limit in the anoxic zone. Contrary to what was expected on the basis of thermodynamic predictions, hydrogen selenide concentrations are almost below the limit of detection in the anoxic region (Fig. 1b). In waters below the still depth (70 m), dissolved organic selenide (the difference between total dissolved selenium and selenate plus selenite) begins to increase rapidly with maximum values through the suboxic and anoxic zones (Fig. 1b); none could be detected in the surface waters.

To my knowledge, the existence of a dissolved organic selenide species has not been reported in the literature, and its identity was puzzling. The analytical technique used in this study requires that selenium be in the form of selenite. The selenide fraction is oxidized to selenite with persulfate in an acidic medium. The list of environmentally plausible selenium compounds that contain selenide, are soluble, and are relatively stable to oxidation in the water column (the selenide fraction was found into the oxic zone) is rather limited. [No detectable dimethyl selenide, a possible reduced form thought to be a result of biomethylation (*11*) was found.] Several of the possible compounds are selenium-containing amino acids [that is, selenomethionine and selenocystine, where selenium (oxidation state -2) is covalently bonded to carbon], primarily in the form of dissolved peptides. To check this possibility, total amino acids from acid-hydrolyzed samples (175, 180, and 190 m) were chelated on copper sulfate–treated Chelex-100 columns and eluted, and the eluate was analyzed for total dissolved selenium. An average of 65 percent ($N = 12$) of the dissolved organic selenide could be accounted for in the total amino acids fraction. I believe that this is a minimum value for two reasons. First, the samples were not properly stored for optimal amino acid preservation (*10*). Second, the selenium amino acids are not stable with respect to acid hydrolysis and tend to degrade.

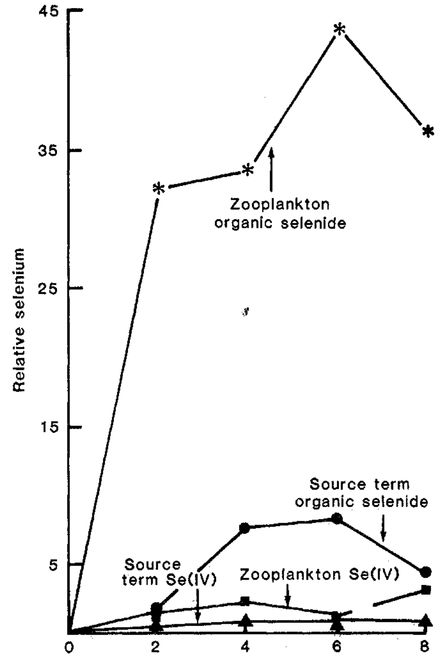

Fig. 2. Results of the selenium regeneration experiment. Fresh zooplankton (euphausiids) and source term particles (almost exclusively fecal material) were collected and processed by S. Fowler and J. LaRosa on the *Vertex* I cruise off the central California coast in August to September 1980. The zooplankton (total selenium, 3.60 μg/g) and source term material (total selenium, 1.79 μg/g) were incubated in aerated filtered surface seawater at 18°C. Portions of these water samples passed through 0.4-μm filters (stored frozen) were analyzed as described in the text.

The profiles of the various selenium species in the Saanich Inlet show the complex nature of selenium's biogeochemistry. In the oxic waters, both selenate and selenite are present, even though selenate is the only thermodynamically predicted form. Selenate and selenite are present at close to the limit of detectability in the anoxic waters, an indication that some removal process is operative. However, very little hydrogen selenide, the thermodynamically predicted form, is found in this region. Instead, the dominant species in the reducing waters is organic selenide.

There are several possible scenarios that might help to explain these profiles. An examination of the total dissolved selenium distribution with depth shows that it resembles those of other trace elements (*12*), with depletion in the surface waters and enrichment at depth. This is typically explained as due to a process consisting of the incorporation of the dissolved elements into biogenic particulates in the surface waters, vertical transport, and regeneration from the particulate to dissolved state in deeper waters as a result of particle degradation. The profiles can be affected by the input rates of the dissolved components at the surface, particle degradation rates, and physical mixing processes. In addition to particulate removal and regeneration, selenium can also undergo oxidation-reduction reactions, which transform it from one dissolved species to another or to insoluble forms such as elemental selenium or metal selenides (this may be the mechanism that removes selenate and selenite from the anoxic zone).

The data in Fig. 2 provide insight into the particulate and species interconversion processes affecting the distributions of selenium species. These data are from an experiment on the regeneration of selenium from two types of marine particulate matter, zooplankton and source term material (fresh biogenic particles produced by these zooplankton). The collection and handling procedures for both the zooplankton and source term material have been detailed in (*13*). Organic selenide is rapidly and primarily released during biodegradation, selenite begins to increase during the time of the experiment, and no selenate is produced during this time (Fig. 2).

These data suggest that at least some of the selenium in biogenic matter undergoes a multistep regeneration. The significance of this idea for the Saanich Inlet data is that each of the species produced has its own thermodynamic and kinetic stability. Dissolved organic selenide would be most stable under anoxic conditions, and perhaps the regeneration would only proceed to this step. Correspondingly, the production of selenite and selenate by the oxidation of organic selenide might be the final regeneration step in oxic waters. This scenario would also necessitate that selenium's uptake into biological particulate material include an oxidation state change (that is, reductive incorporation). The exact nature of the biogeochemical cycle of selenium, and the determination of whether the cycle includes some of these features, remains to be elucidated.

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Organic Matter in a Coal Ball: Peat or Coal?

Abstract. *Chemical analyses of morphologically preserved organic matter in a Carboniferous coal ball reveal that the material is coalified to a rank approximately equal to that of the surrounding coal. Hence, the plant tissues in the coal ball were chemically altered by coalification processes and were not preserved as peat.*

During the Carboniferous and Permian periods, extensive deposits of peat accumulated and were later transformed to coal. Early in their development, some of these peat deposits were impregnated with pore fluids from which primarily calcium carbonate was precipitated. The calcium carbonate permineralized some of the peat, leading to the formation of the carbonate nodules now known as carbonate coal balls. The mineral also preserved the morphological characteristics of some of the plant remains, providing paleobotanists with an insight into the anatomy of vascular plants in the late Paleozoic (*1*).

Most carbonate coal balls contain 1 to 5 percent organic matter (*1*) which has a brownish, cellular appearance similar to that of some Holocene peat. Consequently, this organic matter commonly has been called "fossil peat" (*2*). Although the organic matter in coal balls generally is thought to have been altered chemically (*3*), some have argued that the material was preserved as peat and is, therefore, lignocellulosic in nature (*4*). Baxter (*5*) claimed to have identified microscopic "starch grains" in a coal ball, implying that the starch was chemically preserved even though chemical tests for starch were negative.

Table 1. Elemental composition of each sample on a dry, ash-free basis. Compositions were determined with a Carlo Erba C, H, N, O, and S analyzer.

Sample	Composition (percentage by weight)			
	C	H	N	O
Cellulose	44.4	6.2		49.4
Cypress log (Holocene)	50.2	6.1	0.17	43.5
Periodate lignin	63.0	6.1		30.9
Lignitic log (Oligocene)	70.0	4.3	0.34	28.3
Fine cellular fraction	75.3	5.5	1.2	18.1
Herrin coal	76.4	5.1	1.4	15.5

Clearly, the chemical character of organic matter in coal balls has not been resolved, and uncertainty exists as to whether this material is peat or coal. We now report the results of an investigation that conclusively identifies the chemical composition of organic matter entombed in a carbonate coal ball. In our study we also examined the relation between the organic constituents of the coal ball and the coal from which it was taken.

We selected the petrified stem of a medullosan seed fern in a coal ball from the Herrin (No. 6) Coal Member of the Carbondale Formation (Middle Pennsylvanian) in Illinois (*6*). Xylem, sclerenchyma, resin rodlets associated with sclerenchyma, and parenchymal tissues were isolated from residue that remained after the stem was treated with 2*N* aqueous hydrochloric acid to remove the carbonate matrix. These and small fragments of the coal attached to the outer rim of the coal ball were subjected to petrographic, elemental (C, H, N, and O), and solid-state ^{13}C nuclear magnetic resonance (NMR) analyses.

A small fraction that settled rapidly in the aqueous acidic medium consisted mostly of pyrite grains and woody splinters—mainly xylem tissue—impregnated with pyrite. The amount of organic matter recovered in this fraction was insufficient for complete chemical analysis; therefore, its chemical composition is not addressed. Much of the residue from the acid treatment was flocculent and settled more slowly. This fraction, hereafter termed the fine cellular fraction, consisted of parenchyma, xylem, and unidentified organic matter. A few fragments of brownish thick-walled tissue with a honeycomb appearance (probably sclerenchyma), brownish angular fragments derived from the stem, and unidentified sporelike bodies were present

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