and comparative results. The increase in Antarctic sea ice and decrease in Arctic sea ice reported here are consistent with results from a General Circulation Model (GCM) study in which CO₂ levels were increased gradually (4). Other GCM simulations, though, show slight decreases in Antarctic sea ice extent and thickness (3). GCM simulations of CO₂-induced climate change patterns generally agree on some large-scale features such as the amplification of wintertime warming at high northern latitudes but disagree particularly at high southern latitudes (25). This study also indicates a surface air cooling over the Atlantic sector of the Southern Ocean in austral summer (the season when we observe a maximum positive trend in the ice extents). In these GCM experiments, the hemispheric difference in the climate response results in part from the influence of the thermal inertia of the much larger ocean area in the Southern Hemisphere. Sea ice growth in the Southern Ocean, along with slight lowering of the surface water temperature, are attributed to a general freshening of southern circumpolar surface water and the resultant reduction of convective mixing (3, 4). The continuing sea ice data record shows significant interannual and decadal variability that helps provide the basis for developing a better understanding of the various processes driving the observed changes.

REFERENCES AND NOTES

10. Correction for ice extent and area differences from the various sensors during the overlap periods was critical to obtaining unbiased long-term trends. In Bjergo et al. (7), a correction for SMMR-SSMI differences was mentioned but none for SSMI F8-F11 differences. Bjergo et al. used a two-step procedure to match ice concentrations for the SMMR-SSMI correction. Our matching of algorithm coefficients was somewhat comparable to their procedure, but then we additionally matched ice extents and areas during the overlap periods.
11. Each data set was subjected to careful quality control, including the identification and subsequent correction or removal of bad data. Residual instrumental drift in the SSMR radiances used in the sea ice algorithm was reduced, by means of a procedure used previously (26), to less than the instrument noise levels (8). The SSMI drifts similarly determined were found to be below or at the instrument noise values (9) for the SSMI radiances used in the sea ice algorithm (19 GHz horizontally and vertically polarized, 22 GHz vertically polarized, and 37 GHz vertically polarized) and so were ignored. Data gaps were filled by performing spatial and temporal interpolations. Additional corrections made to the SMMR and SSMI single-day sea ice concentration grids included the removal of false ice signals in the vicinity of the shoreline and over ice-free ocean areas. These were accomplished through the application of a coastline correction algorithm operating on the three image pixels nearest the coast, and also of monthly climatological sea surface temperature thresholds.

The calculation of Arctic and Antarctic sea ice concentrations required to compute sensor intercomparisons and sea ice areas utilizes methods used previously for the SMMR (29) and SSMI (27) data sets. The details of generating a consistent set of sea ice extents and areas from the SMMR and SSMI sensors are discussed elsewhere (29). Since the publication of this report (28), DMSP F13 SSMI data through 31 December 1996 were added, but we followed the same procedure in preparing the data for analysis.

13. Other differences giving rise to different ice concentrations include differences in sensor altitudes and viewing angles; differences in weather filter thresholds and algorithm tie points; and different overpass times, tidal phases, and diurnal effects.
14. The upper limit of the ice extent and area errors for both the Arctic and Antarctic is obtained by calculating the standard deviations of the ice extent and area differences from the F11 and F13 SSMIs during their 5-month overlap period. The estimates are all about 0.3% of the annual mean value. It is noteworthy that the equatorial crossing times of the two spacecraft differ by 45 mm, so that even this estimate includes real fluctuations of the ice covers. Of central importance in this study is not absolute accuracy but the consistency of measurements throughout the data record.

28. The confidence level was determined with a Student's t test in which the number of degrees of freedom is obtained by subtracting the number of calculated parameters from the number of windows used in the multiple window filtering.
29. The SSMI data sets were provided by the National Snow and Ice Data Center in Boulder, CO. We thank S. Fiegles, M. Martin, and J. Saleh for their efforts in reprocessing and correcting the SMMR and SSMI data sets and J. A. Maslak and J. Stroeve for their help in checking the final sea ice concentrations. This work was supported by NASA's polar program.

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Abiotic Selenium Redox Transformations in the Presence of Fe(II,III) Oxides


Many suboxic sediments and soils contain an Fe(II,III) oxide called green rust. Spectroscopic evidence showed that selenium reduces from an oxidation state of +VI to 0 in the presence of green rust at rates comparable with those found in sediments. Selenium speciation was different in solid and aqueous phases. These redox reactions represent an abiotic pathway for selenium cycling in natural environments, which has previously been considered to be mediated principally by microorganisms. Similar green rust-mediated abiotic redox reactions are likely to be involved in the mobility of several other trace elements and contaminants in the environment.

The redox chemistry of polyvalent elements determines their solubility, bioavailability, and toxicity in geologic environments (1, 2). This is apparent in the case of Se, which occurs in the environment in +VI, +IV, 0, and −II oxidation states and in several organic forms (2–4). Their concentration and biogeochemical transformations determine the activity of Se in the environment. Although Se is essential to animal life at low concentrations and its deficiency is known to cause white muscle disease in sheep, Se compounds at high concentrations are carcinogenic and teratogenic (4). The higher valent Se forms are more soluble, and their reduction in soil to the less reactive Se(0) form has generally been considered to be facilitated primarily by soil organic acids (5) and microorganisms (6, 7). However, many suboxic geologic environments contain green rust (GR), which is a mixed Fe(II), Fe(III) oxide, and it has been shown to catalyze redox reactions (8–10). Here we show how GR medi-
The measured peaks 1, 2, and 3 in the XANES spectra reflect Se(0), Se(IV), and Se(VI), respectively. Except for (A), the intensities of peaks 2 and 3 decrease with time. The XANES spectra of aqueous phase in contact with GR show Se(VI) only (not shown here). The Fourier transforms of XAFS spectra shown in (B), (D), and (F) are uncorrected for phase, and the peaks represent complexing atoms around the central X-ray absorber Se. After phase correction, the actual bond lengths are 0.25 to 0.4 Å longer than those shown. (B) Bond length = 1.29 Å, Se–O as in SeO\textsubscript{3}\textsuperscript{2–}. Note that Se(VI) reagents contain traces of SeO\textsubscript{3}\textsuperscript{2–} (<2%), which exhibits a shoulder at the 1.29 Å Se–O peak (~1.35 Å). This also complexes with Fe and produces a weak feature at 3.30 Å corresponding to Se–Fe as in Fe-SeO\textsubscript{3}\textsuperscript{2–}. (D) Bond length = 1.35 Å, Se–O in SeO\textsubscript{4}\textsuperscript{2–}; 2.08 Å, Se as in metallic Se; 3.12 Å, two Fe atoms as in bidentate binuclear Fe–SeO\textsubscript{3}\textsuperscript{2–} complex; 3.56 Å, distant Fe probably around Se(0); 4.03 Å, distant Fe or Se atoms. (F) Bond length = 2.67 Å, Fe polyhedra edge sharing with SeO\textsubscript{4}\textsuperscript{2–}; and other peaks around 1.35, 2.08, 3.12, 3.54, and 3.97 are the same as those mentioned for (D). R and Δ represent the distance and phase shift correction for an absorber and backscatter pair, respectively.

A survey of standard state redox potentials of Fe and Se species (Fe, species 0, +II, and +III; Se, species −II, 0, +IV, and +VI) suggests that Fe(II) can reduce Se from the +VI oxidation state to the −II form (1, 11, 12). The overall reaction can be written as

\[ \text{SeO}_4^{2–} + 8\text{Fe}^{2+} + 9\text{H}^+ \rightarrow 8\text{Fe}^{3+} + \text{HSe}^– + 4\text{H}_2\text{O} \]  

Although Fe(II) is present primarily as Fe(H\textsubscript{2}O\textsubscript{6})\textsuperscript{2+} in acidic solutions, it precipitates as GR, Fe(II), Fe(III), and Fe(OH)\textsubscript{2} in the presence of Fe(III) and at pH > 4.0 and as Fe(OH)\textsubscript{3} in the absence of Fe(III) and pH > 8.0 (13). The common presence of Fe(III) in all iron-containing soils and sediments prevents the formation of Fe(OH)\textsubscript{2} and promotes precipitation of GR. Hence, Se(VI) reduction at pH > 4.0 may occur by homogeneous reactions in aqueous phase and by heterogeneous reactions either on GR surfaces by absorption and reduction or in GR interlayers by coprecipitation and reduction. GR converts to goethite (α-FeOOH), lepidocrocite (γ-FeOOH), maghemite (γ-Fe₂O₃), or magnetite (Fe₃O₄), depending on the rate of oxidation and dehydration of GR (13, 14). In our experiments, Se(VI) reduction with GR primarily produced magnetite. On the basis of these mechanisms Se(VI) reduction can be described by the following reaction:

\[ \text{HSeO}_3^- + 4\text{Fe}^{2+} + \text{OH}^- + 3\text{H}_2\text{O} \rightarrow \text{HSe}^- + 8\text{Fe}^{3+} + 4\text{SO}_4^{2–} + 8\text{H}^+ + 32\text{H}_2\text{O} \]

which has a Gibbs free energy change (ΔG\textsubscript{pH}) of ~−671.1 kJ.

We examined these Fe(II)-mediated Se(VI) reduction reactions in closed systems and monitored changes in aqueous- and solid-phase Se speciation as a function of several variables pertinent to natural systems (15). The GR we used had interlayers of FeOOH, goethite (α-FeOOH), lepidocrocite (γ-FeOOH), maghemite (γ-Fe₂O₃), or magnetite (Fe₃O₄), depending on the rate of oxidation and dehydration of GR (13, 14). In our experiments, Se(VI) reduction with GR primarily produced magnetite. On the basis of these mechanisms Se(VI) reduction can be described by the following reaction:

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which has a Gibbs free energy change (ΔG\textsubscript{pH}) of ~−671.1 kJ.
SeO₄²⁻ (Table 1 and Fig. 1B).

In contrast, aqueous Se(VI) was unstable in the samples prepared at pH > 5.0. Under these conditions GR precipitated initially and, in time, converted to magnetite and lepidocrocite at pH 7.0 and to only magnetite at pH 9.5 (Table 1 and Fig. 2). The presence of GR and its oxidized products in these samples strongly influenced aqueous and solid-phase Se speciation. When Se(VI) was present during GR precipitation, the aqueous Se concentration dropped quickly [more than 48% in the first 0.01 hour (36 s)] and thereafter decreased slowly with a first-order rate (average rate constant 

\[ k = 1.31 \pm 0.63 \times 10^{-2} \text{ hour}^{-1} \] 

(Tables 2 and 3). However, the aqueous Se concentration gradually declined at a similar rate (average 

\[ k = 1.15 \pm 0.42 \times 10^{-2} \text{ hour}^{-1} \] 

when Se(VI) interacted with already precipitated GR. Although Se(VI) can be lost from the aqueous phase by homogeneous reduction to insoluble Se(0) in the presence of high pH Fe(II) species, such as Fe(OH)⁺ and Fe(OH)₆⁶⁺, this reaction was not observed. These solutions were also below saturation for the known Se solids; hence, precipitation is not the mechanism for Se loss (17, 18). These studies demonstrate the necessity of GR for Se(VI) transformations, which may be occurring both in the interlayers and on the external surfaces of GR.

Although aqueous Se speciation did not change at pH > 5.0, all precipitated GR samples exhibited Se(VI) reduction. The degree of reduction varied with pH, the nature of the reaction (coprecipitation versus adsorption), and the initial Fe(II) concentration (15) (Fig. 1, C to F). Se-coprecipitated GR samples reduced Se(VI) rapidly to Se(IV) at high pH when compared with those precipitated around neutral pH (Fig. 1, C and E). Reduced Se(IV) formed bidentate binuclear (at pH 7.0 and 9.3) and edge-sharing complexes (at pH 9.3) with Fe polyhedra, but no Fe-selenite precipitate (Fig. 1, D and F).

This coordination environment changed as the solid-phase Se(IV) was further reduced to Se(0), and GR oxidized simultaneously to magnetite and lepidocrocite. The EXAFS data indicate that the reduced Se(0) atoms occurred as amorphous Se clusters. At reaction times of more than ~60 hours, the Se-absorption edge of the solids shifted to energies lower than that of Se(0), which indicates that trace quantities of Se(−II) were in the system.

In reactions with previously precipitated GR surfaces, Se(VI) reduced directly to Se(0) without detectable accumulation of the Se(IV) intermediate (Fig. 3). Also, Se(0) formed at a slower rate during these adsorption reactions than during the coprecipitation reactions discussed above. Such major changes in the Se speciation of the solid phase may have been a result of incorporation of Se(III) into the interlayers of GR during coprecipitation and weaker Se(VI) interactions on GR surfaces during adsorption. The interlayer-trapped Se(VI) formed bidentate binuclear and edge-sharing complexes with structural Fe(II) and was reduced immediately to Se(IV), which in turn slowly converted to Se(0) and Se(−II). The invariance in the x-ray diffraction profiles of pure and Se-reacted GR and magnetite and the longer Se(0)–Fe distances of 3.85 Å (from EXAFS, Fig. 1, D and F) suggest that Se(0) substitution in these mineral structures is unlikely. Se(0) substitution in iron oxides was also not observed from electron microscopy studies (19). On the basis of these results, we hypothesize that the reduction of interlayer-substituted Se(VI) to Se(0) may have promoted magnetite formation at the expense of GR, and the reduced Se(0) atoms formed clusters on surfaces. Although no direct
physical evidence was available, similar re- 
action mechanisms have been proposed for 
NO$_3^-$ reduction in the presence of GR (9, 10).

We conclude that Se(VI) reduces to Se(IV) and Se(0) in the presence of GR. Although elemental Fe and Fe(OH)$_2$ are absent in nature, their reactions with Se(VI) in the laboratory produced similar redox transformations (15, 19). Thermody- 
namically, Se(VI) should reduce to the most stable Se(−II) form in the presence of Fe(II), but we did not observe this species at high concentration. However, it can be a dominant species when the Fe(II) concentration is much higher and the reaction times are longer than those we considered. Se(VI) reduction by coprecipitation and adsorption pathways can occur when anoxic conditions are created in Se-contaminated sediments (16) [reductive dissolution of Fe(III) oxides precipitates GR with Se], as compared with the ion movement into the previously existing anoxic zones containing GR (dominantly adsorption). The Se(VI) transformation rates we measured are within the range of those reported from other laboratory and field studies on Se speciation in sediments and soils (20–23). The pore waters of several natural samples are also saturated with respect to GR, which indicates its probable presence in these systems. The rapid precipitation kinetics (13) and the flexible crystal structure of GR (24) may allow its formation under a variety of geochemical conditions. The reductive dissolution of Fe(III)-oxyhydroxides forms GR steadily in the anoxic sediments; hence, the concentration and final oxidation products of GR are not the limiting factors for the trace element redox reactions. GR-mediated redox reactions similar to those presented here can occur for other trace elements. For instance, studies on Cr(VI) and As(V) reduction have identified the importance of sediment Fe(II)-containing mineral phases as mediators of redox reactions, but attempts to identify these mineral phases are not complete (25, 26). The rapid oxidation of GR poses a problem for its identification during conventional sediment mineralogical analysis, and for this reason this mineral has not been commonly recorded in sediments. However, recent thermodynamic and spectroscopic studies give direct evidence for the existence of GR in soils (8, 13). The abiotic redox reactions we present provide direct evidence for the formation of reduced Se species in anoxic sediments. Although various strains of bacteria have been identified to facilitate Se(VI) reduction in soil and sediment systems, abiotic reactions with GR should be considered when evaluating trace element and major element redox dynamics in sediments and soils.

REFERENCES AND NOTES

27. The images of mineral grains in 10-μm-thick films of reaction solutions were taken with the high-resolution zone plate microscope, XM-1, which was built and is operated by the Center for X-ray Optics, Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA. See also W. Meyer-Ilse et al., Synchrotron Radiat. News 8, 29 (1995).
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High-Pressure Transformation of Al$_2$O$_3$

Nobumasa Funamori and Raymond Jeanloz

X-ray diffraction measurements indicate that ruby (Cr$^{3+}$-doped α-Al$_2$O$_3$) transforms to the Rh$_6$O$_{12}$ (II) structure when heated to temperatures exceeding ~1000 kelvin at pressures above ~100 gigapascals, in agreement with previous ab initio quantum mechanical calculations. The high-pressure phase did not quench upon decompression to ambient pressure, and the occurrence of this phase transformation may affect interpretations of static (diamond-anvil cell) and dynamic (shock-wave) experiments at ultra-high pressures.

Corundum (α-Al$_2$O$_3$), space group R$ar{3}$c is important in many fields of research, for example serving as a model material in ceramic science (1). In high-pressure research, it is used as a window in shock-wave experiments (2), and also as a pressure-transmitting medium for static compression in the diamond-anvil cell (DAC) (3). Moreover, the pressure-induced shift of the Cr$^{3+}$ fluorescence wavelength of ruby (Cr$^{3+}$-doped α-Al$_2$O$_3$) is used as a pressure calibrant in DAC experiments (4). Theoretical calculations on the behavior of corundum at high pressures (5–7) predict that α-Al$_2$O$_3$ will transform to the Rh$_6$O$_{12}$ (II) structure (space group Pbnm) (8). Recent calculations, based either on pseudopotential (7) or on linearized augmented plane-wave (6) methods, yield a transition pressure of 78 to 91 GPa, raising the possibility that the ruby-fluorescence pressure scale may be contaminated by the effects of a structural transformation. However, no evidence of a transformation was observed in a high-pressure x-ray diffraction study on ruby to 175 GPa (9), and it has therefore been assumed that the α-Al$_2$O$_3$ structure is stable to this pressure. To clarify whether there is a transformation, we carried out a high-pressure in situ x-ray diffraction experiment on ruby that had been heated to a temperature exceeding ~1000 K while at high pressure (10).
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Editor's Summary

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