Microbial Reduction of Elemental Selenium to Selenide in Anoxic Sediments - A XANES Study

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BACKGROUND

Elemental selenium [Se(0)] is the dominant species of selenium present in anoxic sediments. The forms of Se in sedimentary rocks similarly contain high proportions of Se(0), but much of the Se is also in the form of metal selenides, Se(-II). It is not clear if the occurrence of these selenides is due to microbial reduction of Se(0), or a purely chemical process.

In previous studies with a Se(IV)-respiring haloalkaliphile, *Bacillus selenitireducens*, we observed formation of a reduced soluble selenide (HSe^-) when the cells were given Se(IV) or Se(0) with a molar excess of electron donor, lactate (Herbel et al., in press). To investigate if a similar bacterial reduction phenomenon could occur in anoxic sediments, we collected San Francisco Bay sediments and amended them with chemically-formed, red amorphous Se(0) [$Se(0)_{Chem}$], biologically-formed, red amorphous Se(0) [$Se(0)_{Biol}$], chemically-formed black crystalline Se(0) [$Se(0)_{Black}$], and selenite [Na_2SeO_3 or Se(IV)] (TABLE 1).

EXPERIMENTAL SET UP

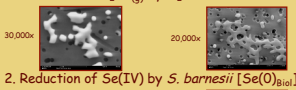
Organic-rich, reducing sediments were obtained from the Palo Alto Baylands Nature Preserve, and mixed with anoxic Artificial Bay Water and Se(0), Se(IV), and lactate (Table 1).

Table 1

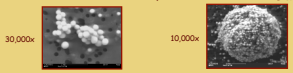
Replicate	Additions to 50 mL sediment slurries (total vol. 100 mL) N_2 headspace, flushed weekly	Total Se (mM) in suspension after additions (0 d, 31.6 d)
1-3	$Se(0)_{Chem}$	3.5, 4.9
4-6	$Se(0)_{Chem}$ + 20 mM Lactate	3.4, 4.8
7-9	$Se(0)_{Chem}$ + 20 mM Lactate + 3.7% formalin (killed controls)	3.1, 4.4
10	$Se(0)_{Biol}$ + 20 mM Lactate	1.3, 3.7
11	Na_2SeO_3/$Se(0)_{Chem}$ + 20 mM Lactate	19.6, 21.0
12	$Se(0)_{Black}$ + 20 mM Lactate	3.5, 12.6
13	20 mM Lactate only	0.0, 0.00

Formation of Se(0) for Reduction Experiments

1. Oxidation of $H_2Se_{(g)}$ by O_2 in Alkaline Water [$Se(0)_{Chem}$]



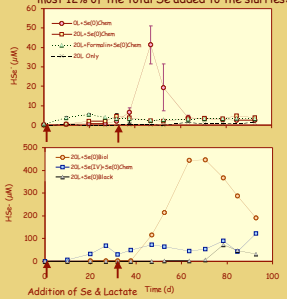
2. Reduction of Se(IV) by *S. barnesii* [$Se(0)_{Biol}$]



3. Reduction of Se(IV) by Ascorbic Acid [$Se(0)_{Black}$]

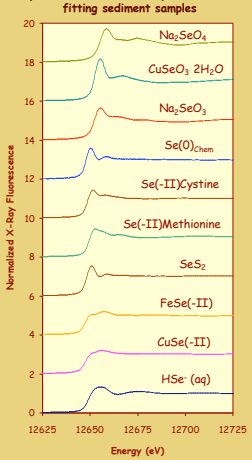
RESULTS - SOLUTION PHASE

Soluble HSe^- concentrations, as determined by ICP-MS analyses of filtrates, were transient and accounted for at most 12% of the total Se added to the slurries:



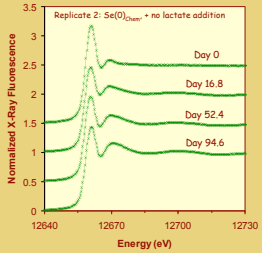
If reduction of Se(0) to Se(-II) did occur, a high proportion of the selenides would combine with metals and organics to form solid phase selenides, which would require solid phase analytical techniques (e.g., XANES or sequential extraction) to quantify.

XANES Spectra of model Se compounds used for curve fitting sediment samples

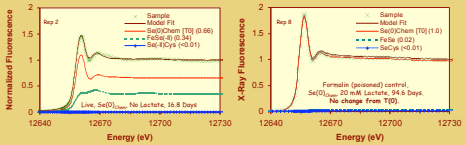


RESULTS - SOLID PHASE

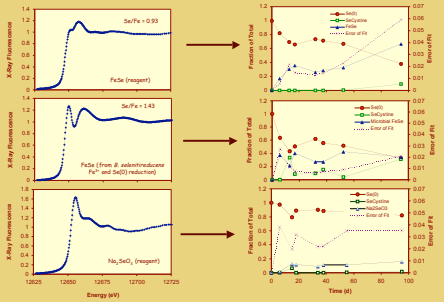
XANES analyses showed decreasing primary X-Ray absorption edge peak intensity and an increase in secondary structure over time:



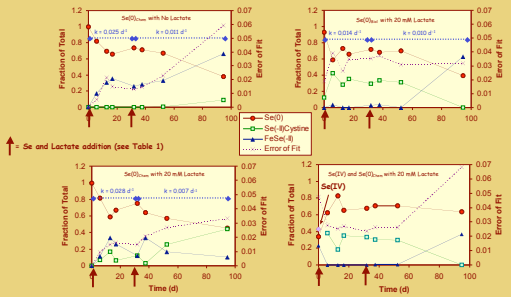
Using the R-Space X-Ray Absorption Package (Booth, unpublished), the sample data were fitted with up to three selenium standards. A fit error parameter was generated to determine which combination of standards best approximated the sample data. In most cases, the standards which best fit the data were Se(0) (after verification, using the sample at Day 0 as the Se(0) standard), FeSe(-II), and Selenocystine [Se(-II)Cys].



Comparison of Se-XANES data fitting using $FeSe_{reagent}$, microbially-formed $FeSe_{1.43}$ or Na_2SeO_3 $_{reagent}$ with Se(0) and Selenocystine for Replicate 2



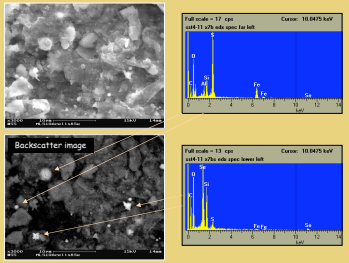
Estimation of Solid Phase Se(-II) Production and Speciation from Se reduction in SF Bay Estuary Sediment Slurries



↑ = Se and Lactate addition (see Table 1)

Note: Samples amended with $Se(0)_{Black}$ await XANES analyses.

SEM images of the sediment slurry amended with Se(IV) and lactate showed reduced Se/Fe/S particles formed separately from FeS_2 particles (day 12.8):



SUMMARY

- We now have evidence that microbial reduction of Se(0) to Se(-II) can occur not only in pure cultures of anaerobic bacteria, but also in organic-rich, anoxic sediments.
- The significant proportion of sedimentary Se(-II) as revealed by Se XANES spectra compared to freely soluble Se(-II) concentrations measured by ICP-MS or acid volatile Se(-II) indicate most of the reduced Se was present in the solid form, primarily as FeSe- and selenocystine-type compounds.
- Using XANES, we measured rates of Se(0) reduction semi-quantitatively. For samples amended with $Se(0)_{Chem}$, reduction rates of 0.025 d^{-1} (0-37 d) and 0.011 d^{-1} (37-95 d) were determined, and only slight stimulation was found upon addition of lactate, indicating the sediment had sufficient ambient electron donor concentrations for Se(0) reduction processes to occur.

REFERENCE

Herbel, M., Blum, J., Borglin, S., and R. Oremland. 2003. Reduction of elemental selenium to selenide: Experiments with anoxic sediments and bacteria that respire Se-Oxyanions. Geomicrobiology Journal. 20(6). In press.