

## Effect of iron on reduction of Se(IV) by *Shewanella putrefaciens*

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Microbial reduction of highly soluble selenate ( $\text{SeO}_4^{2-}$ ) and selenite ( $\text{SeO}_3^{2-}$ ) to insoluble elemental selenium and to selenide (Se (-II)) is an important phenomenon affecting the mobility of selenium. In this study, we examined the influence of Fe (II) on the reduction of selenite by *Shewanella putrefaciens*.

*Shewanella putrefaciens* was grown anaerobically in defined mineral media containing 1 mM  $\text{Na}_2\text{SeO}_3$ , 20 mM sodium lactate, and 20 mM HEPES at pH 7.0 with or without 1 mM  $\text{FeSO}_4$ . Aliquots were removed from the media and passed through a 0.20  $\mu\text{m}$  filter. Total Se concentration in the aliquots was determined by ICP-AES. Precipitates occurred in the media were analysed by X-ray absorption spectroscopy.

In the media with or without Fe (II), the total Se concentration decreased with time and formation of insoluble red precipitates was observed within one day incubation. Se K-edge XANES analysis showed that the white lines of the red precipitates appeared at the almost same energy of that of Se (0) powder. These results indicate that Se (IV) was reduced to Se (0) in the both media. The reduction to Se (0) was also supported by Se K-edge EXAFS analysis. After two months incubation, however, the color of precipitates in the Fe (II) containing medium had changed to black while the red precipitates in the medium without Fe (II) had not changed. Se K-edge XANES spectrum of the black precipitates was different from that of the red precipitates. Se K-edge EXAFS analysis revealed that Fe atoms existed neighbor of Se atoms. These results suggest that FeSe like precipitates were formed by further reduction of Se (0) in the presence of Fe (II).

## Attachment of acidic amino acids to mineral surfaces: Implications for prebiotic chemistry

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We report the results of an integrated experimental and theoretical study of the adsorption and surface speciation of glutamic and aspartic acids on rutile surfaces in NaCl solutions, the extrapolation of the results to other minerals and to more complex aqueous solutions, and the implications of this study for prebiotic chemistry.

Potentiometric titration and batch adsorption experimental results have been integrated with surface complexation models to obtain a thermodynamic characterisation of the adsorption of glutamic and aspartic acids on rutile. Two reactions with identical stoichiometry and the corresponding thermodynamic equilibrium constants were derived. Interpretation of the surface species involved in these reactions has been enabled by the results of ATR-FTIR spectroscopic and theoretical molecular calculations and confirm that the surface speciation is a function of environmental conditions.

The adsorption equilibrium constants have been extrapolated to a wide range of oxide and silicate minerals using Born solvation theory. Together with previously established results for the alkalis, alkaline earths and oxyanion species in natural waters, quantitative predictions can be made involving competitive and cooperative adsorption effects (e.g. at pH=8 in a simple NaCl solution adsorption of glutamate is negligible, but in a solution also containing Ca or Mg, which can adsorb and alter the surface charge of a mineral from negative to positive, the adsorption of glutamate is predicted to be significantly enhanced). Overall, our results point to the need for a thorough characterization of the surface speciation of amino acids and its dependence on mineral identity and aqueous solution chemistry in order to evaluate the role of mineral-organic interactions in prebiotic chemistry.