Competition between enzymatic and abiotic reduction of uranium(VI) under iron reducing conditions

P. VAN CAPPELLEN AND T. BEHRENDS

Utrecht University, Faculty of Earth Sciences, Department of Geochemistry, P.O. Box 80021, NL-3508 TA Utrecht, The Netherlands

Reduction of U(VI) under iron reducing conditions was studied in a model system containing the dissimilatory metal-reducing bacterium *Shewanella putrefaciens* and colloidal hematite. We focused on the competition between direct enzymatic uranium reduction and abiotic reduction of U(VI) by Fe(II), catalyzed by the hematite surface, at relatively low U(VI) concentrations ($<0.5\ \mu M$) compared to the concentrations of ferric iron (>10 mM). Under these conditions surface catalyzed reduction by Fe(II), which was produced by dissimilatory iron reduction, was the dominant pathway for uranium reduction. Reduction kinetics of U(VI) were identical to those in abiotic controls to which soluble Fe(II) was added. We propose that strong adsorption of U(VI) at the hematite surface favored the abiotic pathway by reducing the availability of U(VI) to the bacteria, hence inhibiting the enzymatic reduction pathway. Aqueous complexation of U(VI) in 45 mM bicarbonate solution slowed down enzymatic U(VI) reduction, as well as abiotic surface catalyzed U(VI) reduction by Fe(II). However, in experiments containing bacteria and hematite U(VI) reduction was more efficient in 45 mM bicarbonate solutions compared to solutions without added bicarbonate. We attribute the enhanced U(VI) reduction to the formation of magnetite, which was observed in the experiments. Biogenic magnetite produced as a result of dissimilatory iron reduction may be an important agent of uranium immobilization in natural environments.

On the nature of variation in geochemical soil survey data

G. VAN DER VEER[1], P.F.M. VAN GAANS[1], G.T. KLAVER[2]

[1]Centre for Geo-ecological Research, Department of Physical Geography, Utrecht University, P.O.Box 80115, 3508TC Utrecht, the Netherlands (g.vanderveer@geog.uu.nl) (p.vangaans@geog.uu.nl)
[2]TNO-NITG, National Geological Survey, Department of Geo-environment, P.O.Box 80015, 3508TA Utrecht, the Netherlands (g.klaver@nitg.tno.nl)

Introduction and methods

One of the most striking features of regional geochemical data is the strong correlation found between most elements. Besides other statistical features common to such data, this adds to the well-discussed problems for multivariate analysis. We have therefore chosen for a stepwise regression approach in order to explain trace and minor elemental variation in the soil compartment.

Within the framework of an ongoing geochemical soil survey in the Netherlands, 110 locations were sampled at two depths in four polders that were reclamated from a marine sedimentary environment during the last century. Samples were analyzed for major and trace elements (XRF and ICP-MS) using a broad quality control scheme.

Forward stepwise linear regression was applied to all trace and minor elements by first selecting the best explaining variable, after which more variables were added and tested for significance. To circumvent the multicolinearity problem, higher order variables were chosen from a restricted group of elements that were uncorrelated with elements already in the model.

Results and conclusions

The regression approach showed that a simple bivariate relation could explain the observed variation of minor and trace elements in the majority of cases. For few elements addition of a second independent variable yielded significant model improvements. The regression models could be grouped according to the major mineralogical phase(s) present in the soil compartment that were indicated by the explanatory variable(s). Strong deviation from these linear relations occurred only for specific trace elements in the topsoil, which was ascribed to anthropogenic input. From this, the enrichment of these elements could be quantified.

Regional variation of elements can therefore be regarded as either bi- or trivariate, indicating both the strong selectivity of elements towards one specific mineral phase or group of phases, as well as their tendency to preferentially substitute for a specific (group of) element(s).

With respect to a multivariate approach, the stepwise regression is clearly less cumbersome and allows for a better mineralogical interpretation of elemental variation in geochemical soil survey data. It thereby allows for direct quantification of enrichment of elements in the topsoil and the regional variation observed herein.