

From process-oriented laboratory experiments to the modelling of complex natural systems: Incorporation of microbial dynamics in a Biogeochemical Reaction Network Simulator based on the concept of a 'Knowledge Base'

P. REGNIER, A.M. LAVERMAN, C.PALLUD, Y. VAN LITH
& P. VAN CAPPELLEN

Geochemistry Department, Faculty of Earth Sciences, PO Box
80021, 3508 TA Utrecht, The Netherlands
(pregnier@geo.uu.nl)

Knowledge about key reaction processes involved in the biogeochemical dynamics of natural environments is continuously expanding. Field- and laboratory-based experiments are being conducted to identify reaction pathways, quantify reaction kinetics and elucidate the interactions between biotic and abiotic processes. An important challenge is to develop theoretical and computational tools that allow the systematic integration of new knowledge about the coupled biogeochemical processes which, together, determine the cycling of elements in environmental systems. In this framework, a Biogeochemical Reaction Network Simulator (BRNS), based on the novel concept of an evolving 'Knowledge Base' (KB) has been developed. In this approach it is no longer the model itself, but an easily accessible, open resource element, the KB, which contains the conceptual and quantitative understanding of biogeochemical pathways and their interactions. It is through the KB that a continuous learning process and information exchange between experimentalists and modelers can be conducted. In addition to the KB, a newly developed automatic code generator and associated numerical engines constitute the BRNS.

Our current research aims at merging microbial ecology into existing geochemical models of early diagenesis, using the results from process-oriented laboratory experiments. Because essential parameter values are scarce and poorly constrained for many microbial groups, especially anaerobic bacteria, a continuous feedback loop between process implementation and model simulations is needed. Our modeling approach based on the 'Knowledge Base' concept offers the necessary flexibility for this implementation. The BRNS allows to evaluate alternative process formulations, to develop diagnostic indicators of biogeochemical pathways that can be measured in the field or in experimental set-ups, and to assess the propagation of model and experimental uncertainties in predicted system behavior.

Secular variation of Tl isotopes in ferromanganese crusts?

M. REHKÄMPER¹, M. FRANK¹, J.R. HEIN², S. NIELSEN¹,
A.N. HALLIDAY¹

¹ Institute of Isotope Geology and Mineral Resources, ETH
Zurich, NO C61, CH-8092 Zurich, Switzerland

² USGS, 345 Middlefield Rd., Menlo Park, CA 94025, USA

In a recent study we reported that the surface layers of ferromanganese (Fe-Mn) crusts have Tl isotope compositions that differ from seawater by ~2% (Rehkämper et al., 2002). This difference is thought to result from the isotope fractionation that accompanies the adsorption of Tl onto ferromanganese particles.

We have measured time-resolved Tl isotope compositions in six serially sampled Fe-Mn crusts: BM 1969.05 (N. Atlantic, 0-55 Ma), Alvin 539 (N. Atlantic, 0-30 Ma), Antipode 109 D-C (Indian Ocean, 0-14 Ma), DODO 232D (Indian Ocean, 0-17 Ma), D11-1 (Pacific, 0-55 Ma) and CD-29-2 (Pacific, 0-45 Ma). For most Fe-Mn crusts, we did not attempt to obtain high-resolution profiles and one sample was analyzed per 10-15 Ma. One higher resolution 0 to 4 Ma time series for BM 1969.05, however, does not show any significant short-term (0.3 Ma) variations in Tl isotope composition.

The Tl isotope time series of most Fe-Mn crusts show a coherent trend of increasing $\epsilon^{205}\text{Tl}$ with time ($\epsilon^{205}\text{Tl}$ is the deviation of the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio of a sample from the NIST SRM 997 standard in parts per 10⁴). For the two Pacific samples, the trends of $\epsilon^{205}\text{Tl}$ with time are almost identical: $\epsilon^{205}\text{Tl}$ increases smoothly from ~+6 at about 50 Ma to present-day values of ~+14. The time series of the Indian Ocean Fe-Mn crusts are very similar: $\epsilon^{205}\text{Tl}$ increases from ~+11.5 at 15 Ma to ~+13.5 at 0 Ma. The two samples from the North Atlantic show trends that differ somewhat from the Indian and Pacific Ocean results. For BM 1969.05, $\epsilon^{205}\text{Tl}$ increases from ~+5 at 55 Ma to ~+14.5 at 30 Ma. Following this, $\epsilon^{205}\text{Tl}$ is relatively constant to 15 Ma, then it decreases to ~+11.5 at 8 Ma after which $\epsilon^{205}\text{Tl}$ is almost constant again to the present day. In Alvin 539, $\epsilon^{205}\text{Tl}$ decreases continuously from ~+13.5 at 30 Ma to ~+11.5 today.

An evaluation of the significance of the Tl isotope time series results is difficult at present. Three interpretations of the data are possible. (1) The trends are signatures of diagenetic alteration of the Fe-Mn crusts. In this case, the $\epsilon^{205}\text{Tl}$ variations do not reflect changes in paleoceanographic conditions. (2) The Tl isotope variations in the Fe-Mn crusts are due to changes in the fractionation factor of Tl between seawater and ferromanganese particles. Such changes could be due to, for example, variations in ocean temperatures or the mineralogy of the Fe-Mn crusts. (3) The temporal trends of $\epsilon^{205}\text{Tl}$ reflect a change in the Tl isotopic composition of the oceans. This would indicate that the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio of seawater increased significantly during the Cenozoic, by nearly 10 ϵ -units.