Geochemistry at Utrecht University, Netherlands

Biogeochemistry, from Melt Inclusions to Ground Water Salinization

The sun brilliantly illuminated R.V. Navicula as Dr. Thilo Behrends drove up to the ship. It was the last day of April, and the 35-foot Navicula – part of the fleet of the Royal Netherlands Institute for Sea Research (NIOZ) – was in the Haringvliet Lake for three days of sediment sampling. The sampling was part of the ongoing collaborative research project RESIN (Restoration of Estuarine Systems in the Netherlands) between Utrecht University's Geochemistry Department and the Netherlands Institute for Inland Water Management and Waste Water Treatment (RIZA). Thilo, an Assistant Professor in Geochemistry, was lending a hand to his colleague Dr. Caroline Slomp, a Research Fellow of the Royal Academy of Arts and Sciences (KNAW), and one of the Department's Ph.D. students, Rick Canavan.

Originally, the Haringvliet was a major outlet to the sea for the Meuse and Rhine rivers. In 1970, the mouth of the Haringvliet was closed by a dam, as part of the Dutch Delta Plan. The Delta Plan was designed to protect the low-lying areas of the Netherlands from tidal flooding. As a result, the Haringvliet turned from a tidal estuary into a semi-stagnant freshwater lake. During the 1970s and 1980s, fairly contaminated sediments accumulated in the Haringvliet. In particular, fine-grained sediments in the lake exhibit elevated concentrations of Zn, Cu, Cr, Pb and Cd.

Current Dutch environmental policy emphasizes the ecological health and biodiversity of aquatic ecosystems. In line with this policy, it has been proposed to recreate estuarine conditions in the Haringvliet, by opening the sluices of the dam. This restoration would take place in successive steps, with the ultimate goal of establishing a salinity gradient extending 30 km inland of the dam. A major concern, however, is that salinization would mobilize metals currently locked in the sediments, with subsequent transfer to the food chain.

In order to address this concern, a research project was developed, which involves a detailed chemical characterization of fine-grained sediments and their pore waters, a quantification of the rates of the major biogeochemical processes, and experiments where sediments are subjected to a series of environmental perturbations. The analytical and experimental results are then used as the basis for building an early diagenetic model, capable of simulating the response of the benthic environment to the anticipated chemical changes in the water column.

Although the RESIN project aims at contributing scientific knowledge that is directly relevant to the environmental management of the Haringvliet, the researchers involved are quick to point out that their results have worldwide significance. For example, in Vietnam, floodgates are under consideration to keep seawater out of the Mekong Delta, while surface and subsurface waters in coastal areas are increasingly undergoing salinization, as a result of river damming and excessive pumping of groundwater. The biogeochemical consequences of these human interventions in the hydrological cycle are still poorly understood.

With the field component of RESIN nearly completed, Rick Canavan and Caroline Slomp are now focussing on incorporating trace metal dynamics into an existing early diagenetic model, as well as setting up reactor experiments in the laboratory. RESIN is a typical example of the type of research conducted in the Biogeochemistry group of Professor Philippe Van Cappellen in Utrecht. Research projects usually integrate controlled laboratory experimentation with modeling and fieldwork. For example, Postdoctoral Fellow Anniet Laverman, together with former Ph.D. student Christof Meile, have combined microelectrode measurements in sediment cores, reactive transport modeling and reactor experiments, in order to derive kinetic expressions that allow them to pre-

Royal NIOZ research vessel **Navicula**

Prof. Philippe van Cappellen

dict rates of denitrification across the range of environmental conditions encountered along estuarine salinity gradients. Denitrification is a crucial process in many aquatic environments, because it removes nutrient nitrogen by transforming it into dinitrogen gas, which escapes to the atmosphere.

The major research thrust of the Biogeochemistry group is to understand and quantify the functioning of natural biogeochemical reaction systems. Not only do experimentalists and modelers work closely together, but members of the group also have diverse backgrounds. For instance, before joining the Biogeochemistry group in Utrecht, Ph. D. students Parisa Jourabchi, Steeve Bonneville and Claudette Spiteri studied geophysics, biology and chemistry, respectively. Parisa, who is from Canada, is now looking at ways to incorporate uncertainty analysis in reactive transport modeling, in order to objectively compare observational data and model simulations, and to address the thorny issue of parameter identifiability in geochemical models. Claudette, who comes from Malta, focuses on geomicrobial and geochemical processes in the mixing zone between fresh and salt water in coastal aquifers, while Steeve, from France, studies the effects of mineralogy and surface chemical properties on the microbial reduction of ferric iron minerals.

Philippe Van Cappellen took over from Professor Kees van der Weijden as Chair of Geochemistry in Fall of 1999. Philippe is originally from Belgium, although he is also a Canadian citizen via his mother. He has worked in Belgium, Morocco, Switzerland and, predominantly, in the United States where he obtained his Ph.D. (Yale, 1991). Prior to his appointment in Utrecht, he was an Associate Professor at Georgia Institute of Technology in Atlanta. Utrecht University dates back from 1636 and has a long tradition of research in the earth sciences. The Faculty of Earth Sciences has a permanent academic staff of about 35, and about 65 Ph.D. students and Postdoctoral Fellows.

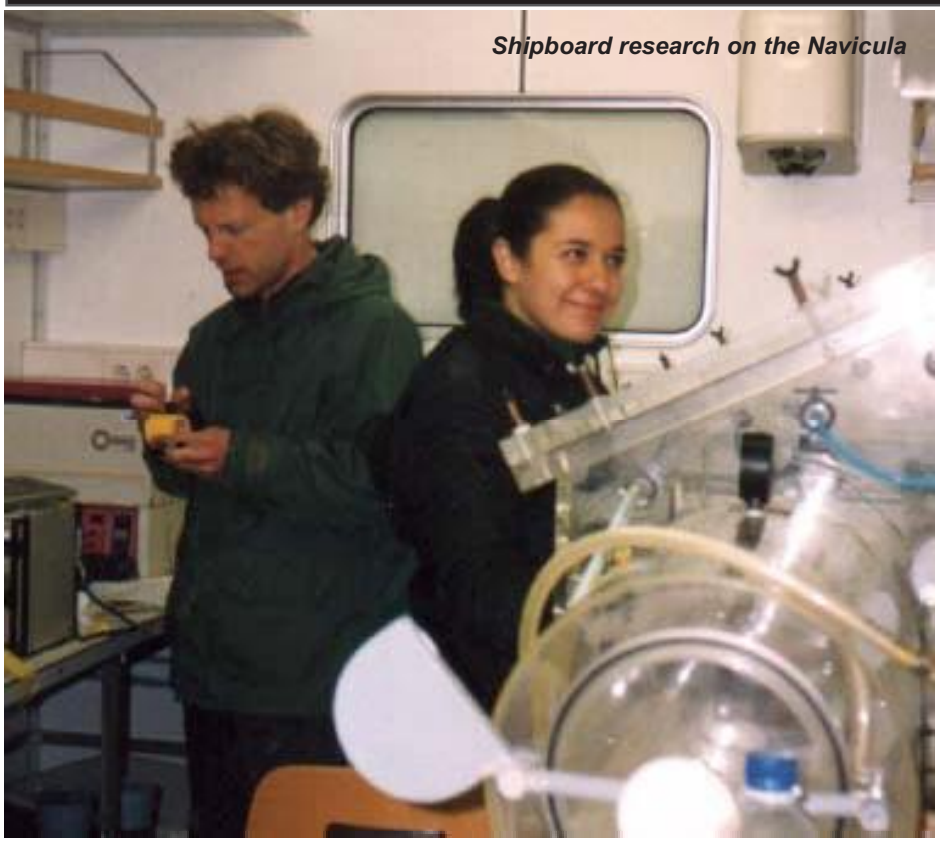
Pushing the envelope

At the moment, there are 13 Ph.D. students and 15 Postdoctoral Fellows in the Geochemistry Department, with about ten different nationalities represented. The Department is subdivided in four units: Biogeochemistry, Marine Geochemistry, Organic Geochemistry and Environmental Geochemistry. Of these, the Biogeochemistry group is by far the largest. Its permanent staff, besides Philippe, comprises two Assistant Professors, Dr. Thilo Behrends, who oversees the Laboratory of Experimental Biogeochemistry, and Dr. Pierre Regnier, who directs a growing group of students and postdocs in reactive transport modeling.

From a Dutch perspective, Philippe is a phenomenon; one of his colleagues calls him “an institution within an institution”. It is probably the result of American-style work ethics, combined with a driven personality and an enthusiasm for science. Despite some inevitable clashes with local traditions and entrenched interests, he keeps pushing the envelope of Dutch geochemistry, by continuously exploring new research avenues and crossing traditional disciplinary boundaries.

One of the hallmarks of Philippe’s arrival in Utrecht has been the revival of a weekly seminar series, with speakers from around the world. The Geochemistry Department also stays in touch with the Dutch geochemical community though its extensive e-mail list – something other Dutch groups in the earth sciences seem to have difficulty to accomplish. Philippe chairs the Dutch counterpart of the Geochemical Society, which meets twice a year in Utrecht for a series of

Dental fluorosis



Shipboard research on the Navicula

lectures. The last meeting, for example, explored the reactivity of organic and mineral substances in soils and aquifers.

A few years ago, Philippe received a prestigious "Pioneer" grant from the Netherlands Organisation for Scientific Research (NWO) to investigate global effects of biogeochemical processes at redox interfaces. This funding signaled the beginning of a strong biogeochemistry program at Utrecht. Since then, Philippe has also become involved in several European-wide research projects and networks. Among his various functions, it is worth mentioning that he is a Board member of the *International Symposia on Environmental Biogeochemistry*, and that he serves on the F. W. Clarke Award Committee of our Society. He is currently co-Editor-in-Chief of *Journal of Hydrology* and Associate Editor of *Geomicrobiology Journal*.

Since Philippe's arrival, some say, the emphasis has shifted from applied to pure geochemistry. Professor Olaf Schuiling, who retired two years before Philippe's arrival, used to be almost synonymous with applied and engineering geochemistry in the Netherlands. While his scientific interests certainly deviate from those of his predecessors, Philippe points out that almost all the research in the Biogeochemistry group has implications for environmental issues. This is also true for the modeling work carried out under the supervision of Dr. Pierre Regnier. Recently, a student working with Pierre, Ms. Inge Folmer, was awarded the 2003 Escher Price from the Dutch Geological Society (KNGMG) for the best Master's thesis in applied earth sciences, proving that in the geochemistry department fundamental and applied research go hand in hand.

Besides the Biogeochemistry and Environmental Geochemistry groups, research in low-temperature processes is also conducted within the Marine Geochemistry group of Prof. Gert de Lange and the Organic Geochemistry group, headed by Prof. Jan de Leeuw. Marine research focuses on the Mediterranean Sea, where scientists from Utrecht have for many years been investigating the nature and paleoenvironmental significance of organic-rich sediment layers, known as sapropels. Research in organic geochemistry deals with the diagenetic processes responsible for the preservation of organic matter in the geosphere, as well as with the development and validation of molecular proxies – biomarkers or molecular fossils.

Melt inclusions and volcanic pollution

The Utrecht campus harbors at least two other geochemistry groups. High-temperature geochemistry is the research domain of the petrologists. Professor Bernard de Jong's Petrology group conducts research in material sciences, thermodynamics and volcanic and magmatic systems. Dr. Paul Mason, who is responsible for the daily operation of the Laser Ablation ICP-MS, is involved in numerous interdisciplinary projects. Studies of melt inclusions at the Free University of Amsterdam, for example, are conducted in close collaboration with Paul.

An interesting example of research at the interface between high- and low-temperature geochemistry is carried out by Ph.D. student Sri Sumarti,

Sampling from a shuttle core

under the supervision of Dr. Manfred van Bergen. Sri, who is from Indonesia, is investigating a remarkable situation in her homeland. The Ijen crater lake in East Java severely contaminates its environment. From this reservoir – about 35 million cubic meters of highly acid (pH<0.5) sulphate- and chloride-rich water – springs a long acid river that transports large amounts of dissolved chemicals, including arsenic, selenium, fluoride and other potentially toxic elements. Long term geochemical monitoring has shown that downstream concentration and pH trends are regulated by influxes of pH-neutral tributaries and that seasonal variations in rainfall play a role as well.

The quality of river water remains poor until the coastal plain at about 40 km from the source. There, virtually all of the water is used for irrigating rice fields and other cropland. The pH records show that since the early 1990s, the pH has decreased from about 4.5 to (occasionally) 2.5 at this site. This has had dramatic effects on crop yields. Continuous irrigation during more than a century has brought large quantities of metals onto the land and has led to soil acidification.

Ijen crater lake, East Java

Locally, the groundwater contains fluorine concentrations that exceed the WHO guideline for safe drinking water. Dental fluorosis is, indeed, widespread. The geochemical signatures of local well waters suggest that the fluorine originates from the Ijen crater lake.

Netherlands Institute of Applied Geoscience

Another player in geochemistry in Utrecht is the Dutch Geological Survey, now renamed the Netherlands Institute of Applied Geoscience (TNO-NITG). At the end of last year, its research facilities and entire staff moved into a new building on the Utrecht campus. After a series of reorganizations and the realization of the new building, the staff moved to Utrecht from various parts of the country – 150 years after the Dutch government commissioned the first geological map of The Netherlands. An example of what it does is the Nabron project. The soils of the Dutch coastal provinces often contain elevated concentrations of arsenic, occasionally at great depths. The Nabron project intends to determine the extent and cause of these naturally high arsenic levels, and to look at the implications for environmental policy makers.

Future plans

What has Utrecht's geochemical 'phenomenon' in store for his Department? 'We've just started a new international Master's program in Biogeochemistry', Philippe says. 'The challenge will be to attract the best students from Europe and beyond. The Master's reflects our research strengths. In the first year, the students take theoretical courses in aquatic chemistry, biogeochemistry, organic geochemistry, geochemical kinetics and geochemical modeling. The first year finishes with a hands-on fieldwork on the Lee estuary, near Cork, Ireland. The second year is devoted to individual research projects and advanced courses. For example, we have just finished putting together a specialized MSc. course in geomicrobiology with colleagues from the Faculty of Biology'.

'Another of my goals is to convince my fellow earth scientists in Utrecht that geochemists do more than just perform chemical analyses. The last three years, Pierre Regnier, Caroline Slomp and I have worked hard to build a strong modeling research group. We have been fortunate to be able to hire some superb young Ph.D. students and Postdoctoral Fellows. Thanks to the constant interactions with experimentalists, we are building models that reflect as closely as possible the reality from the lab or field."

Not all is rosy in Utrecht, however. 'Universities in the Netherlands are top-heavy structures, where administrators spend their time inventing one reorganization after another. North American visitors sometimes marvel at the number of support staff in Utrecht. Yet, the potential benefits for the scientists are pretty much offset by all the layers of bureaucracy.'

Utrecht geochemistry information on the web:

- *TNO-NITG:*
  www.nitg.tno.nl/eng/

- *Haringvliet:*
  www.haringvlietsluizen.nl/

- *Petrology in Utrecht:*
  www.geo.uu.nl/Research/Petrology/

- *Low-temperature geochemistry in Utrecht:*
  www.geo.uu.nl/Research/Geochemistry/