Building and using biogeochemical reaction-transport models

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Rather than being isolated systems that can be described entirely by thermodynamics, environments in the Earth's crust act as open biogeochemical reactors where chemical change is driven by the interactions between migrating fluids, solid phases, and organisms. The complexity of biogeochemical phenomena taking place in nature, particularly that which derives from coupling of transport and biogeochemical processes, suggests that we need a new generation of models to interpret observations from natural systems. Rather than focusing on building and using biogeochemical reactive transport models for predictive purposes (as in risk assessment analyses of nuclear waste repositories), here we stress the uses of reactive transport modelling as interpretive tools.

Modelling approaches

The first question the would-be biogeochemical reaction-transport model developer must face is what physical and biogeochemical processes to include. In certain cases, it may be possible to decouple parts of the biogeochemical reaction system, focusing on individual reactions within the overall reaction network. There is strong evidence, however, to suggest that in some systems, multiple reactions are coupled, making it impossible to simplify the global behaviour of the sytem. Wang and Van Cappellen (1996) showed, for example, that in order to quantify Fe and Mn cycling in marine sediments, it was necessary to account for a number of tightly coupled biogeochemical reactions. The same can apply to the physical processes to be included, since at certain sites one can show that a more sophisticated treatment of transport processes (whether involving physical heterogeneities in a subsurface aquifer, or non-local transport processes in a marine sediment) is required. While it is not possible to make an a priori statement of what level of complexity is needed, in general one wants to construct models which do not assume a decoupled or simple behaviour in advance.

After choosing the physical and biogeochemical processes to be included in the model, the next important step in building a reactive transport model is to decide how to couple the reactions and transport. Here there is clearly no single way to proceed, as evidenced by the large number of hydrogeochemical and early diagenetic models which have been proposed and applied successfully to a variety of natural systems. The choice of how to proceed is also affected by the particular physical and biogeochemical system to be considered. In modelling transient flow, transport, and biogeochemical reactions in a groundwater aquifer, it may be necessary to use a transport algorithm that minimizes numerical dispersion, since the error associated with this effect may completely alter the conclusions obtained. In these systems, many of the most successful algorithms for high Peclet number transport (advection-dominant) involve explicit methods, or those in which information from the preceding time step is used rather than solving globally for all the unknowns. These algorithms, however, are not easy to couple directly to biogeochemical reactions, so the preferred approach has been to use decoupled approaches like the two-step or sequential non-iterative approach (SNIA) (Steefel and MacQuarrie, 1996). Since time steps are required to be small in order to fulphill stability requirements associated with the transport, it generally introduces only small amounts of error (referred to as operator splitting error) to decouple the reaction and transport within a single time step. These approaches have the advantage of using a minimum of physical computer memory and of being very fast in completing a single time step, even if these time steps are relatively small.

Where the interest is in the evolution of the rock properties rather than in the transient propagation of a concentration front, the time splitting approaches are often too restrictive in terms of the time step which can be used. In these cases, computationally more efficient schemes involving one step or global implicit methods should be used (Steefel and MacQuarrie, 1996). Since there is no specific

restriction on the time step to be used in these approaches, the ability to take larger time steps makes the overall calculation much faster. In modelling of biogeochemical reactions taking place in the weathering of a sulphide pile, it was found that the decoupled approach required nearly 24 hours to complete while the global implicit approach produced nearly identical results in as little as 3 hours. The main restriction here is on the available physical memory, since the global implicit or one-step approaches require significantly more memory than the decoupled approaches.

The decision on how to proceed in coupling reactions and transport, then, can be affected by the transport process which dominate a particular system. In early marine sediments, diffusive tranport dominates in most cases. Since the stability requirement for diffusive transport using explicit schemes is of the order ΔX^2, the time step requirements for stability become nearly impossible to meet. In one dimensional diffusion-reaction systems, the one-step or global implicit approach will be far superior to other approaches, particularly since little error in transport results. One-dimensional problems of almost any biogeochemical complexity can be readily handled by modern computers.

Similar decisions on whether to use either explicit or implicit methods to solve the biogeochemical reaction networks arise. Where all of the reactions of interest have rate constants of similar orders of magnitude, it is possible to use very efficient explicit methods. However, if any significant range of reaction rates occurs, these explicit methods quickly become unworkable and fully implicit methods are preferred (Steefel and MacQuarrie, 1996). Modern biogeochemical reaction models will normally include both relatively slower reactions, involving for example electron transfer reactions, and relatively faster reactions (e.g. aqueous complexation reactions). These kind of systems generally require an implicit approach.

Using biogeochemical reaction-transport models

While considerable progress has been made recently in developing and applying reactive transport models to biogeochemical systems, there have also been a number of influential publications recently which have been used to question the usefulness of modelling. For example, Oreskes *et al.* (1994) recently argued that models can never be validated

because this would be an example of "affirming the consequence". While this conclusion is completely defensible, it should be pointed out that these statements apply to all scientific conclusions, not just to quantitative models. The authors rightly point out that the quantitative aspect of some models gives them an aura of believability which they shouldn't have. The article, however, has been used by some to dismiss the role of modelling altogether, or at least to restrict modelling to the realm of an amusing pastime which may have some pedagogic benefit for the user. We believe it is important, therefore, to make a more concrete statement of the potential role of biogeochemical reactive transport modelling in elucidating important processes in the Earth's surficial and subsurface environments.

The complexity of natural processes often make the system behaviour non-intuitive, so one must resort to increasingly sophisticated and complicated models in order to unravel the behaviour. It should be pointed out, however, that the increasing complexity of these models is driven by complexity observed in nature, i.e. there is no motivation to complicate the models unnecessarily. But sometimes the system behaviour really is complex, and misleading conclusions are possible if the overall system dynamics are not taken into account. For example, the occurrence of methane at a specific point in time and space within a groundwater aquifer is often taken as evidence that methanogenesis is occurring locally. In fact, the methane may have been produced far upstream from the actual sampling location (Hunter *et al.*, 1998). Both spatial and temporal patterns, therefore, need to be taken into consideration, and reactive transport modelling provides a tool to do this.

Reactive transport modelling can also be used to calculate more accurate elemental budgets which take into account both reaction and transport processes. Noteworthy successes are the studies by Wang and Van Cappellen (1996) who quantified Fe and Mn cycling in early marine sediments and Regnier and Steefel (1998), who used biogeochemical reactive transport modelling to arrive at an improved inorganic nitrogen budget for the Scheldt estuary in Belgium and the Netherlands. These estimates in both cases are based on interpretation of comprehensive multicomponent data sets. As argued by Wang and Van Cappellen (1996), simpler models may no longer be justified, as they do not make full use of the information within the data sets.