

# Reactive transport modeling: An essential tool and a new research approach for the Earth sciences

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Received 4 February 2005; received in revised form 2 September 2005; accepted 16 September 2005

Available online 10 November 2005

Editor: A.N. Halliday

## Abstract

Reactive transport modeling is an essential tool for the analysis of coupled physical, chemical, and biological processes in Earth systems, and has additional potential to better integrate the results from focused fundamental research on Earth materials. Appropriately designed models can describe the interactions of competing processes at a range of spatial and time scales, and hence are critical for connecting the advancing capabilities for materials characterization at the atomic scale with the macroscopic behavior of complex Earth systems. Reactive transport modeling has had a significant impact on the treatment of contaminant retardation in the subsurface, the description of elemental and nutrient fluxes between major Earth reservoirs, and in the treatment of deep Earth processes such as metamorphism and magma transport. Active topics of research include the development of pore scale and hybrid, or multiple continua, models to capture the scale dependence of coupled reactive transport processes. Frontier research questions, that are only now being addressed, include the effects of chemical microenvironments, coupled thermal–mechanical–chemical processes, controls on mineral–fluid reaction rates in natural media, and scaling of reactive transport processes from the microscopic to pore to field scale.

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*Keywords:* reactive transport; water–rock interaction; contaminant transport; magma transport; coupled processes

## 1. Introduction

In recent years, the Earth sciences have benefited from the strong interest in fundamental research that focuses on individual features and mechanisms considered to play a critical role in the overall system behavior (e.g., mineral or bacterial surfaces, the morphology of nanoparticles, or the rate of a process as a function of a

single environmental variable). While such an approach is absolutely crucial in advancing our fundamental scientific understanding of natural processes, there is also a need to take a broader view of integrated system behavior. Often thought of as an engineering concept, system integration also has a role in scientific investigations of complex natural systems where individual time and space-dependent processes are linked and where the relative importance of individual sub-processes cannot be fully assessed without considering them in the context of the other dynamic processes at work. It can be argued that the complex interplay of

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material flow, transport, and reactions at multiple spatial and time scales which characterize most Earth systems requires an integrated approach.

A key task in developing an integrative scientific approach is to build capabilities for computer simulation of complex and often large-scale natural systems and then to link these to laboratory and field studies. In the Earth sciences, the complex natural systems that are accessible to direct study include soils, groundwater reservoirs, volcanoes, the ocean floor, faults, mountain ranges, oceans, glaciers, the atmosphere, and ecosystems. Deeper in the Earth are the mantle and core, and within them dynamical features like subduction zones and mantle plumes. These systems are characterized by mass transport processes such as diffusion and flow of gases, fluids, and solids, and within the material flow and transport system there are chemical, mechanical,

and/or biological interactions. In many cases, the transport, chemical, mechanical, and biological processes in these Earth systems are coupled—for example, the metabolic activity of a biofilm at the pore scale may depend on some combination of advective and diffusive transport combined with local biogeochemical reactions providing electron donors and acceptors. These processes may then result in changes in the physical properties of the medium through biological growth and/or mineral precipitation or dissolution, providing a feedback between flow, transport, and reaction (Fig. 1).

What is referred to as “reactive transport modeling” is then an important set of interpretive tools for unraveling complex interactions between coupled processes and the effects of multiple space and time scales in the Earth. But reactive transport modeling can also be viewed as a research approach, a way of organizing

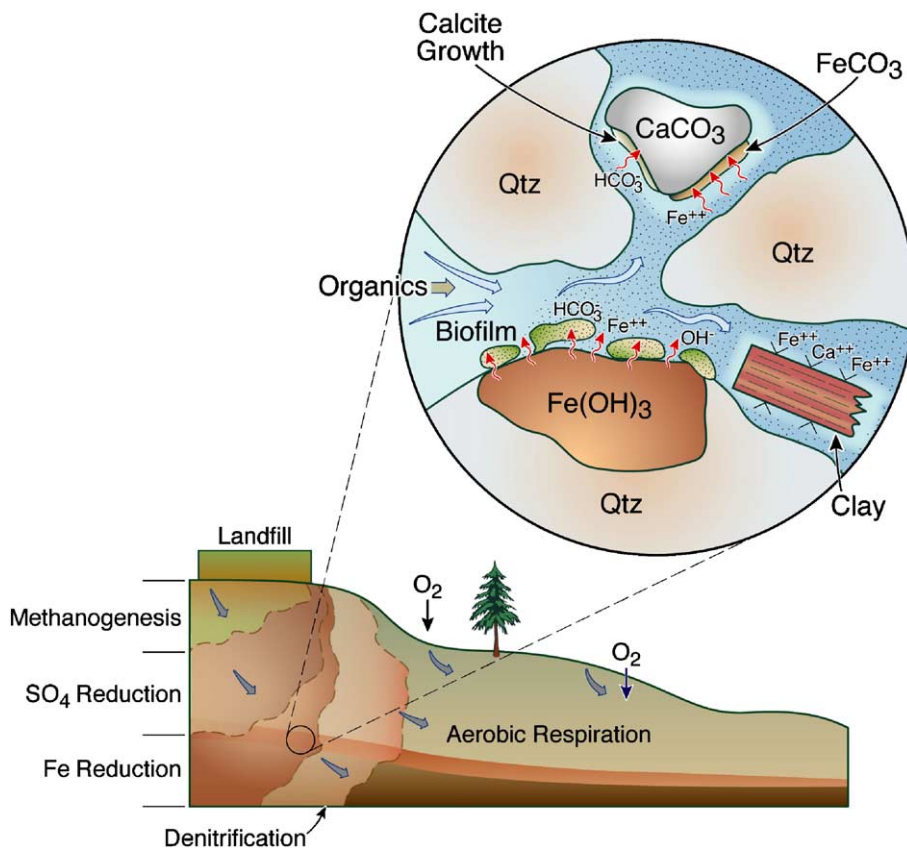


Fig. 1. Schematic representation of the oxidation–reduction zones that may develop in an aquifer downstream from an organic-rich landfill. Closest to the landfill may be a zone of methanogenesis, which is progressively followed downstream by zones of sulfate reduction, dissimilatory iron reduction, denitrification, and aerobic respiration that develop as the plume becomes progressively oxidized through the influx of oxygenated water. Within the dissimilatory iron reduction zone, a pore scale image is shown in which the influx of dissolved organics provides electrons for dissimilatory iron reduction mediated by a biofilm. The dissolution of this phase leads to the release of  $\text{Fe}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{OH}^-$  into the pore fluid, potentially driving siderite or calcite precipitation downstream, and thus reducing the porosity and permeability of the material. Sorption of  $\text{Fe}^{2+}$  may also occur on clays, displacing other cations originally present on the mineral surface. Where reactions are fast relative to local transport, gradients in concentration, and thus in reaction rates, may develop at the pore scale.

and evaluating the effects of coupled dynamic geochemical, microbiological, and physical processes in the Earth sciences. Recently there has been an increased interest in using reactive transport modeling as a synthesizing activity for fundamental Earth science research, in addition to its potential and perhaps more obvious uses in forecasting. From this point of view, reactive transport simulation provides means to apply fundamental Earth science research to natural systems, and an objective and systematic means of evaluating the relative importance and role of fundamental processes that are normally studied in isolation.

## 2. Historical development of reactive transport modeling

Although it is beyond the scope of this paper to provide a thorough review of the historical development of reactive transport modeling, a few observations are in order to provide some context. Several distinct analytical approaches or “threads” have merged in recent years to form what we think of as modern reactive transport modeling. One thread is that of physically based models that are used to describe the transport of fluids, gases, solids, and heat in various Earth environments ranging from the near-surface, to the deep metamorphic, to the interiors of magma chambers. These models have typically treated geochemical and biogeochemical/microbial reactions (or reaction networks) using rather simple formulations, if they are treated at all. In describing contaminant retardation, for example, linear distribution coefficients, or  $K_{dS}$ , were used historically because of the simplicity with which they could be implemented computationally and because data on sorption often came in this form [1–3]. Linear distribution coefficients are also routinely used to describe chemical partitioning in simulations of magmatic systems [4,5]. In applications related to bioremediation and natural attenuation of contaminants, reactions are typically represented with linear kinetic terms [6], an approach that fails to account for coupling between various dissolved organic and inorganic species in solution, reactive mineral phases that might be present, or the biomass itself. In other words, these models provide only a limited description of the *multi-component reaction network and its time dependence*. What the models do provide in the best examples is a rigorous treatment of material (water or melt) flow and mass and heat transport, thus capturing the physical dynamics of a wide range of Earth systems.

Another “thread” that has had a profound impact on modern reactive transport modeling is that of geochem-

ical modeling [7–9]. Initially, this modeling involved time-independent, equilibrium speciation of a multi-component system including dissolved species, minerals, and gases. Similar calculations have been carried out in magmatic systems [10,11]. Such distribution of species calculations was intended to provide a description of the thermodynamic state of a particular multi-component system and is still in wide use today, particularly in the interpretation of the composition of natural waters. An important next step was the development of “reaction path” models that captured the sequence of chemical/mineralogical states resulting from such irreversible processes as chemical weathering and hydrothermal alteration. Early versions of the reaction path models, pioneered by Helgeson and co-workers, did not include an explicit treatment of real-time kinetics, quantifying the system evolution instead as a function of reaction progress [12,13]. These models provided a way of interpreting quantitatively the sequence of minerals observed in nature as the natural consequence of the dissolution of some primary phase (e.g., feldspar), which is itself out of equilibrium due to either the initial state of the system, or more commonly, due to the flux of reactive constituents.

An explicit treatment of transport processes is not factored into the reaction path approach. The reaction path approach can be used to describe chemical processes in a batch or closed system (e.g., a laboratory beaker), however, such systems are of limited interest in the geosciences where the driving force for most reactions is transport. Lichtner [14] clarified the application of the reaction path models to water–rock interaction involving transport by demonstrating that they could be used to describe pure advective transport through porous media. By adopting a reference frame which followed the fluid packet as it moved through the medium, the reaction progress variable could be thought of as travel time instead. This approach has now been generalized to heterogeneous, multi-dimensional flow fields, using both deterministic [15] and stochastic approaches [16–21].

Multi-component reactive transport models that could treat any combination of transport and biogeochemical processes date back to the mid-1980s. Lichtner [22] outlined much of the basic theory of a continuum model for reactive transport. Yeh and Tripathi [23] also presented the theoretical and numerical basis for the treatment of reactive contaminant transport. Steefel and Lasaga [24] presented a reactive flow and transport model for non-isothermal, kinetically controlled water–rock interaction and fracture sealing in hydrothermal systems based on simultaneous numer-

ical solution of both reaction and transport. These studies were largely focused on developing the theoretical and numerical tools for simulating reactive transport in a range of environments.

A number of seminal studies have explored the use of transport theory in interpreting spatial patterns in geologic environments. In groundwater aquifers, the studies of Valocchi and co-workers [25] and Appelo [26] demonstrated that ion exchange could be used to interpret the spatial and temporal patterns of dissolved species in groundwater systems. In the case of contaminant plumes developed from organic-rich landfills, Engesgaard and co-workers [27,28] showed that the spatial zonation of redox zones in an aquifer downstream from an organic-rich waste plume could be rigorously interpreted as the result of the natural sequence of microbially mediated redox reactions as the system gradually becomes less reducing. Beginning with the seminal work of Berner [29], reactive transport modeling helped to make sense of the redox zonation found in marine sediments in terms of a coupling of transport processes and microbially mediated oxidation of organic matter. Reactive transport theory has also been applied to the interpretation of isotopic spatial patterns in soils and groundwater [30,31], although only very recently have these models developed explicit accounting of the various reaction mechanisms that control isotopic exchange [32].

The application of transport theory to the interpretation of mineralogical, chemical, and isotopic spatial patterns in metamorphic rocks is an example of where reactive transport modeling has had profound impact. The interest in the role of transport and its effect on spatial patterns dates back to Thompson [33], Korzhinskii [34], and Weare and co-workers [35]. At the regional scale, the classic study of the distribution of oxygen isotopic values in the Skaergaard intrusion conducted by Norton and Taylor [36] had a profound impact on the field and was quickly followed by a succession of papers exploring mineralogical and isotopic patterns in deep crystalline rocks [37–40].

The types of problems that can be treated with reactive transport modeling has grown, and now includes multi-phase flow, heat transport, and multi-component reaction in fractured media [41–44], and flow and reaction in highly resolved, heterogeneous porous media [45,46]. The recent advances appear to have had the most impact in the groundwater and contaminant transport, but are likely to have much broader impact in the near future on many other situations where water–rock interaction is important.

### 3. Current status of reactive transport modeling

#### 3.1. Coupled processes in reactive transport

The discipline of reactive transport modeling draws on numerous fields in the Earth sciences, including hydrology, geochemistry, biogeochemistry, soil physics, and fluid dynamics. Numerical formulations of reactive transport in porous media inherit all of the difficulties associated with these individual disciplines and then introduce additional complexities related to the coupling of processes [47,48]. Fig. 1 presents a schematic representation of coupled geochemical, microbiological, and hydrologic processes operating at both the aquifer and pore scale. At the aquifer scale, the migration of an organic-rich plume results in reaction with subsurface materials, resulting in a series of distinct redox zones arrayed in space. Physical, chemical, and biological heterogeneities operating at this scale can result in irregular reaction fronts or zones, or even variable extents of reaction over fairly narrow spatial scales (e.g., 1 m). At the pore scale, reactions may also be separated in space, as in the example shown in the figure where dissimilatory iron reduction at one point contributes to the precipitation of siderite ( $\text{FeCO}_3$ ) through the generation of  $\text{Fe}^{2+}$  and alkalinity, to calcite through the generation of alkalinity and the increase in pH, and the sorption of  $\text{Fe}^{2+}$  onto clay particles, all downstream of the iron source. The precipitation reactions, along with the growth of biomass in the pores, may cause a local decrease in permeability, thus affecting the local micro-flow regime. Sorption of  $\text{Fe}^{2+}$  (and potentially other contaminants present in the aqueous phase) not only changes its concentration in solution, it may also change the reactivity and bioavailability of the ferrous iron [49]. These complex series of coupled reactions, often referred to as a “reaction network”, are linked by transport processes that may vary significantly in space, in some cases resulting in gradients in concentration and thus reaction rates at the pore scale. The development of pore-scale gradients in solute concentrations is one of the possible explanations for the scale dependence of reaction rates [50–52] and perhaps even the “discrepancies” reported between laboratory and field rates [53].

The coupling between processes is evident in the governing equations describing reactive transport in porous media (Fig. 2). Represented in this figure are the equations for conservation of energy, conservation of solid and fluid mass, conservation of solute mass, conservation of momentum (the Navier–Stokes equation applicable to flow at the pore scale, Darcy’s Law

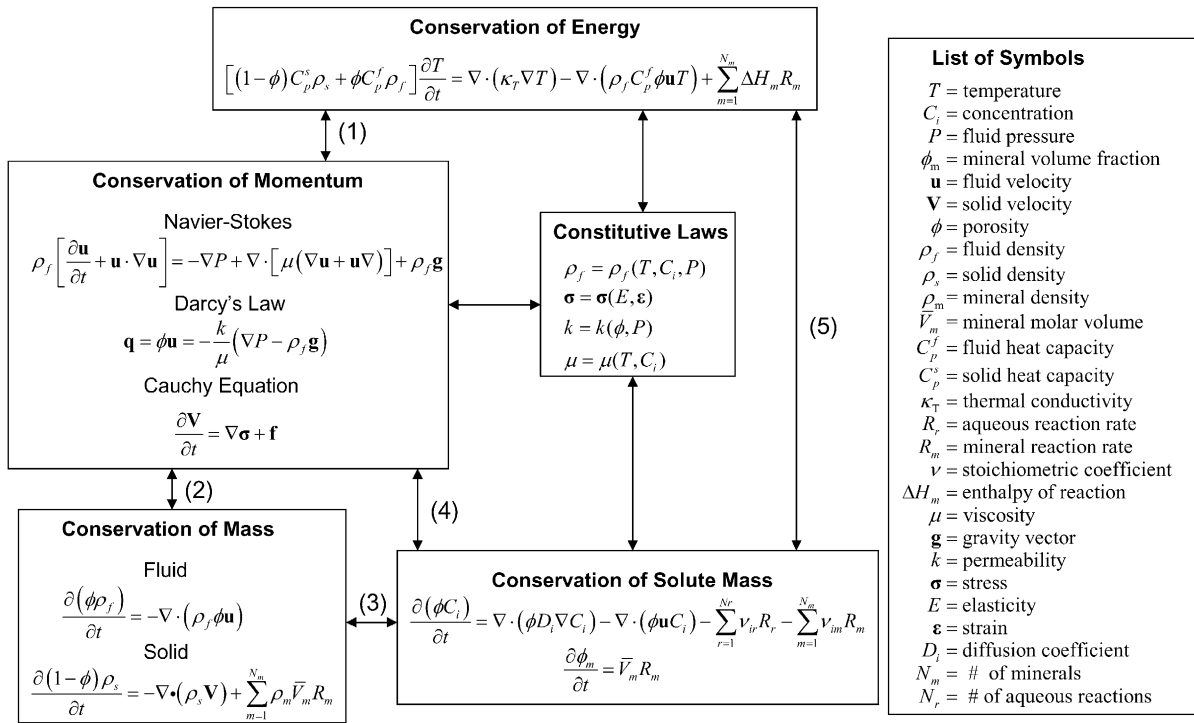


Fig. 2. Governing equations for a single phase coupled reactive transport system, including conservation of momentum (Darcy's Law, Navier-Stokes, and Cauchy equation), the conservation of energy, the conservation of solute mass (the convection–diffusion–reaction equation), conservation of solid and fluid mass, and constitutive laws. See text for discussion of coupling between the various processes shown as numbered arrows in the figure.

applicable to flow in porous media at the continuum scale, and Cauchy's equation describing the deformation of the solid phase), and a variety of constitutive laws for key parameters. A partial list of some of the important feedbacks between the equations/processes (shown with numbered arrows in Fig. 2) include:

1. Coupling between energy and fluid flow (conservation of momentum), primarily through the advection of heat and the effect of temperature on the fluid density,
2. Coupling between the conservation of momentum and the conservation of fluid or solid mass, typically treated by solving the two together to obtain the flow field or the deformation of the solid phase,
3. The effect of dissolution or precipitation of minerals on concentrations of solutes and the mass of minerals,
4. Coupling between fluid flow and solute concentrations, primarily through the advection of solutes and/or colloids and the effect of concentration on fluid density and coupling between the deformation of the solid matrix and solute concentrations through the effect of stress on reactions (i.e., pressure solution) and through modifications in the porosity and per-

meability as a result of mineral dissolution or precipitation, and

5. Coupling between temperature (conservation of energy) and solute concentrations through the effects of temperature on the thermodynamics and on reaction rates and the effect of chemical reactions on the thermal regime where heats of reaction are significant.

These constitute some of the first order couplings between individual field variables and processes that render the system more complex and nonlinear, although it depends on the individual case whether the full range of couplings needs to be considered.

Some workers make a significant distinction between “forward” and “inverse” reactive transport modeling. Forward modeling typically involves stepping forward in time, perhaps for the purpose of forecasting future events. Inverse models involve fitting various dynamic quantities (reaction rates, diffusion rates, etc.) to data like aqueous or mineral concentrations distributed in space or time. The distinction between inverse and forward modeling, however, is somewhat artificial, since modern reactive transport modeling is

only rarely used purely as a predictive tool, even if the eventual goal is to make it sufficiently robust that this is possible. Even with a forward model, data is typically used to calibrate or validate the model in advance of predictive modeling, whether by trial and error or a more formal fitting procedure [44,54,66,77]. The artificiality of the distinction is also apparent from the fact that a common approach to inverse modeling now involves the use of model-independent software like PEST, which is run iteratively in conjunction with a “forward” model to obtain a best fit of a data set [55].

### 3.2. Spatial scales in reactive transport modeling

Arguably, the most difficult challenge now is to capture the scale dependence of reactive transport processes, a topic that has only recently been recognized as an important one [56]. As with the numerical implementation of reactive transport, the scaling behavior of reactive transport processes inherits dependencies related to physical transport in heterogeneous media, but also those related to the heterogeneous distribution of chemical and biological agents in the subsurface. And the coupling of these processes at multiple scales introduces new scale dependencies that are not clearly recognizable in the individual physical, chemical, and biological sub-processes. A related difficulty is that, because of the inherent randomness manifested through heterogeneous material properties, it is fundamentally impossible to fully characterize these systems in most cases. A consequence of this randomness and sparsity of data is that it is impossible to predict the temporal and spatial evolution of a system with any certainty at any particular point in space and time. In addition, what field data are available are often collected at a scale that does not match the scale at which the calculation is to be carried out. As a consequence some form of upscaling or downscaling must be used to properly incorporate the data into the model.

Three different types of models depending on the scale of interest are used to describe reactive transport in porous media today, 1) continuum models, 2) pore scale models, and 3) multiple continua or hybrid models involving a combination of scales. Flow, transport, and reaction are conventionally described by macroscale models based on a continuum formulation of the underlying microscale equations. The continuum approach is the most advanced in terms of its treatment of multicomponent chemical processes. The continuum equations are often derived intuitively by averaging over a representative elementary volume (REV) or control volume resulting in effective macroscale para-

eters. Pore scale models include pore network and lattice Boltzmann models, but few efforts in reactive transport have been attempted. Multiple continuum models have been in use for some time [57]—hybrid models which combine pore scale and continuum scale behavior are only now beginning to be considered seriously. These different approaches are considered in more detail in what follows.

#### 3.2.1. Continuum models

Subsurface reactive flow and transport models are most commonly based on the continuum representation of porous media. This approach depends on averaging system properties over a macroscopic length (control volume or REV) containing many solid grains [47]. Because of this averaging of properties, however, the continuum approach is not valid for length scales on the order of a single pore dimension. Since many of the physical, chemical, and biological processes actually take place at the pore scale, developing averaging approaches for these coupled processes at larger scales is essential.

Solid properties may be either fixed (frozen) or evolving. The latter is much more difficult to simulate and involves using various phenomenological approaches for describing changes in such macroscale parameters as porosity, permeability, capillarity, tortuosity, and reactive surface area. The formation of wormholes, which takes place in carbonate rocks due the infiltration of fluids undersaturated with respect to the carbonate minerals, is an extreme example of evolving heterogeneity (Fig. 3). The wormholes form as a result of a reactive infiltration instability in which the enhancement of permeability resulting from mineral dissolution causes the wormholes to capture progressively increasing amounts of flow, thus accelerating their propagation [47,58–61]. Wormholes are observed in ideally homogeneous materials, such as plaster of Paris (gypsum), indicating that only slight variations in pore size are needed to form wormholes given the presence of high flow velocities and fast reaction kinetics.

Basic assumptions invoked in the continuum formulation are:

- Solid, liquid, and gaseous phases all coexist at a single point (control volume) in space;
- Heterogeneous reactions involving two separate phases which interact across a common interface are treated as if they were homogeneous reactions uniformly distributed throughout a control volume. Interfacial surface area is represented as a uniform surface area concentration;

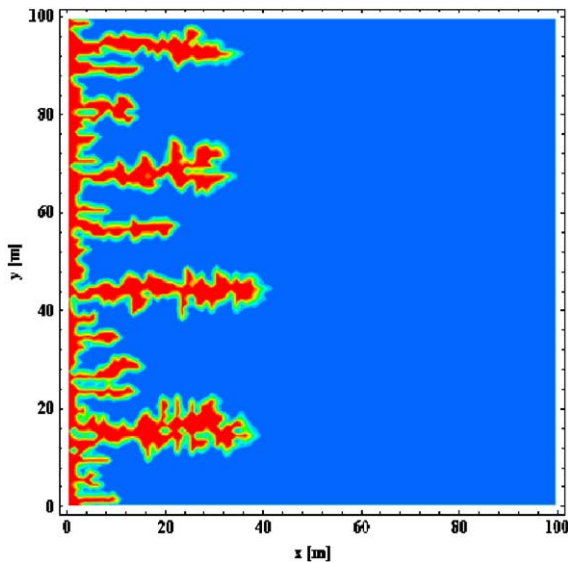


Fig. 3. Continuum calculation of wormhole formation in a porous medium that is initially statistically almost homogeneous. The unaltered host rock is colored blue and wormholes in which complete dissolution occurs are in red. The wormholing is a natural consequence of the “reactive infiltration instability” discussed by Ortoleva et al. [58] and Steefel and Lasaga [59].

- Flow is described in terms of Darcy’s law with velocity proportional to the pressure gradient. The proportionality coefficients are the permeability divided by the fluid viscosity. An exception is the case of flow resulting from compaction of sediment;
- The fluid, solid, and gas phases are well-mixed and therefore without concentration gradients, thus resulting in uniform reaction rates within the control volume.

The continuum description breaks down at the pore scale where the Navier–Stokes equations derived from fluid mechanics are required and where it may be nec-

essary to capture microscopic-scale gradients in concentration resulting from transport and a non-uniform distribution of reactive material.

### 3.2.2. Pore-scale models

Pore scale models have been considered for some time in hydrology and petroleum engineering, but only very recently have such models included coupled reactive transport processes. Network models aim to capture pore scale behavior through a set of rules governing mass transport and chemical/biological reactions within and between individual pores. While they do not capture sub-pore scale gradients and processes that might be present, they offer the advantage of being able to treat processes like wormholing described above with only modest computational expense [51,52]. Li and co-workers used this approach to investigate various upscaling procedures for reactive transport processes controlled by a combination of transport and reaction kinetics at the pore scale. They demonstrated that continuum or volume averaging approaches often introduce significant errors, in some cases not even capturing the correct reaction direction. A more rigorous approach because of its ability to capture intra-pore gradients and geometries is offered by lattice Boltzmann methods [62–64], but these are limited with present-day computational facilities to relatively small scale problems on the order of millimeters. The lattice Boltzmann approach has not yet been applied to systems involving complex chemistry. In addition, there is some question how far up in scale the approach can be extended due to the computational difficulties associated with resolving enough pores to describe the equivalent of a representative elementary volume. The approach is potentially very powerful for developing formulations for use in hybrid models where pore scale processes such as biofilms, diffusion, and fracture or pore sealing can

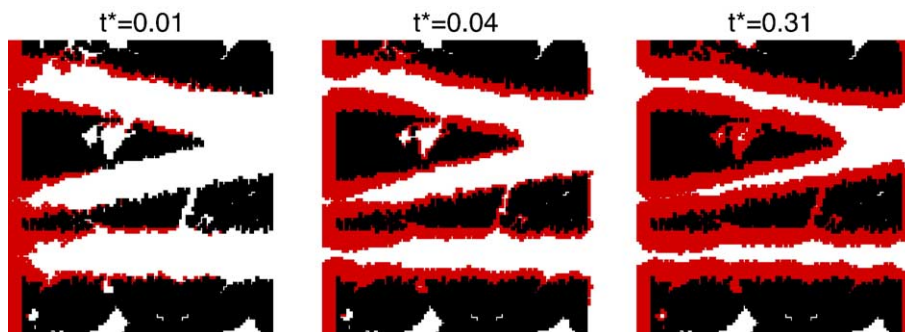


Fig. 4. Lattice Boltzmann simulations of progressive sealing of micro-fractures as a result of mineral precipitation reactions leading to a progressive decrease in bulk permeability [64]. In the lattice Boltzmann approach, the pore space is discretized so as to capture pore-scale gradients in concentration and reaction rate. The lattice Boltzmann approach retrieves the Navier–Stokes equation for pore-scale flow.

occur. Kang et al. [64] presented a recent example of how the lattice Boltzmann approach can be used to study porosity–permeability relationships at the pore scale (Fig. 4).

### 3.2.3. Multiple continuum or hybrid models

Fractured porous media, and more generally hierarchical media involving multiple length scales, play an important role in subsurface flow and transport processes. Fracture-dominated flow systems are involved in numerous subsurface geochemical processes, including contaminant migration, ore deposition, weathering, enhanced oil recovery, geothermal energy, degradation of concrete, and subsurface carbon sequestration. These systems are characterized by bi- or multi-modal distributions in physical and chemical properties, with distinct values associated with the fracture network and rock matrix (Fig. 5). A description based on a single continuum formulation is unable to capture the unique features of a fractured system, and more generally, a hierarchical system involving multiple characteristic length scales, and can lead to serious error. A single continuum approach may be based either on average properties of the total system (e.g., average of fracture and matrix properties), or on the most dominant continuum (e.g., fracture network) neglecting completely other continua (e.g., the rock matrix). Either approach is unsatisfactory and introduces error. The former results in underestimation of the extent of migration



Fig. 5. Example of a reactive fractured rock requiring the use of a hybrid or multiple continuum approach. Actinolite veins (dark green) associated with Fe-metasomatism cutting diopside-rich (tan) rock in the metamorphic aureole of the Bingham porphyry copper deposit. The rock sample is about 10 cm across.

of a contaminant plume and the latter overestimates migration, in some cases so drastically as to be useless in aiding the decision making process for remediation, for example.

If it were possible to model subsurface reactive flow problems at the micro scale over any desired macro length scale, there would be no need to consider other approaches. However, this is obviously not the case even with access to the world's fastest computers. Consequently, the problem must be simplified and approximations made in such a way that at least the first order effects of multi-scale processes are accommodated. One mathematical formulation of this problem is through a hierarchical set of continua, with each characteristic length scale represented by a different continuum that is coupled to the next continuum in the hierarchy. These models are referred to as multiple interacting continua, or in the case of two continua, as dual continuum models [57].

## 4. Has reactive transport modeling had an impact?

The success of any new tool or approach is measured by the impact it has on science. Does the new approach provide a more complete and scientifically defensible interpretation of observations? Does the approach improve the accuracy with which predictions can be made? Or to demonstrate a truly profound impact, does the approach provide an entirely new way of looking at an important process in the geosciences? The impact of reactive transport modeling on the geosciences is growing but still limited. Its full value awaits better integration with fundamental research on Earth materials and processes. Examples of where reactive transport modeling has had a major impact are discussed below.

### 4.1. Migration of contaminants in the subsurface

Understanding and predicting the transport of reactive contaminants is one of the most important practical tasks facing Earth scientists today. At many contaminated sites it is essential that hydrologists and geochemists arrive at an understanding of what is controlling contaminant migration so as to provide sound guidance to policy makers on the best strategy for dealing with it. Will naturally occurring retardation, the degree to which reactive contaminants are slowed relative to non-reactive contaminants, be sufficient to keep the contamination from affecting drinking water supplies? If natural retardation and attenuation are insufficient, what strategies can be used to remediate efficiently and



cost-effectively the contaminated ground, without inadvertently mobilizing the contaminants?

At the Hanford Reservation in eastern Washington, USA, extensive contamination of the vadose zone and groundwater has occurred as a result of accidental releases of radionuclides from storage facilities. The appropriate treatment of sorption is a critical issue in developing and applying performance assessment models for radionuclide migration. The issue has been brought to the fore recently with regard to the enhanced migration of the radionuclide  $^{137}\text{Cs}$  observed in the vadose zone below leaking high level waste (HLW) tanks [65–69]. Various explanations were initially advanced to explain the expedited transport of  $\text{Cs}^+$  in the vadose zone at Hanford, but further study has demonstrated that the bulk of the effect is due to suppression of  $\text{Cs}^+$  sorption as a result of the high concentrations of  $\text{NaNO}_3$  in the HLW contaminant plume [65,66,68]. The strong competitive effect of  $\text{Na}^+$  in solution has been demonstrated unequivocally in both batch [65] and column experiments [66]. In addition, the effect is clearly seen in the field as well, with  $\text{Cs}^+$  below very highly concentrated  $\text{NaNO}_3$  tanks (SX-108, with  $\text{NaNO}_3=20$  to  $25$  mol/kgw) showing a retardation factor, defined as the ratio of the velocity of non-reactive tracer like nitrate (corresponding here to the position of the  $\text{Ca}^{2+}$  front) to the velocity of the  $\text{Cs}^+$  front, of 2–3 (Fig. 6). In contrast, field measurements of  $\text{Cs}^+$  retardation in other environments indicate  $\text{Cs}^+$  retardation as high as 30 or more. By way of comparison, the retar-

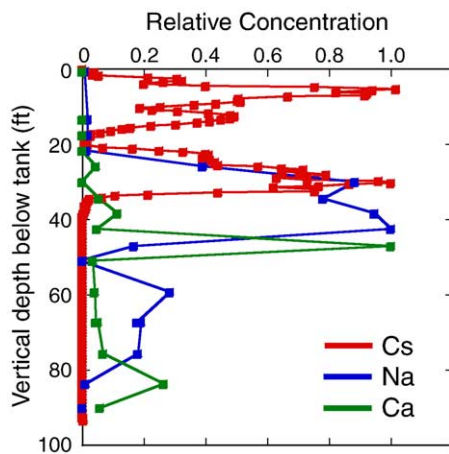


Fig. 6. Chromatographic separation of cations below the SX-108 tank at the Hanford site, eastern Washington, USA. The position of  $\text{Ca}^{2+}$ , which is displaced from exchangers by high  $\text{Na}^+$ , corresponds closely to the position of non-reactive tracer fronts (e.g.,  $\text{NO}_3^-$ ). The high concentration of  $\text{NaNO}_3$  in the tank leak solution results in a much lower retardation for  $^{137}\text{Cs}$  than is typically observed in other settings.

ation factor for  $\text{Cs}^+$  below the less concentrated SX-115 tank at Hanford (concentration of  $\text{NaNO}_3=1\text{--}3$  mol/kgw) is between about 10 and 20.

What kind of model do we need to predict accurately whether contaminants like  $\text{Cs}^+$  will move, and if so, how rapidly and under what conditions? Historically, retardation has been treated in contaminant transport models through the use of linear distribution coefficients, or  $K_d$ s. Mathematically, this takes the form of  $K_d=C_{\text{solid}}/C_{\text{aqueous}}$ , where  $C_{\text{solid}}$  is the concentration associated with the solid phase (adsorbed, or otherwise incorporated into the solid) and  $C_{\text{fluid}}$  is the concentration in the fluid (water or melt) phase. This approach is mathematically and computationally attractive, since the linearity of the expression allows retardation to be treated as a simple correction to the local transport rates. In addition, sorption is often measured and interpreted in terms of these simple linear distribution coefficients, in many cases without explicit accounting for either site saturation (as occurs in the case of Langmuir-type adsorption), or for competitive effects from other dissolved species. The neglect of the site saturation behavior is generally not a problem when the contaminants are present at low concentrations. More problematic is the neglect of competitive effects from other dissolved species. Several publications have pointed out quite clearly some of the problems associated with the use of linear distribution coefficients to describe contaminant retardation. Using a multi-component reactive transport analysis, Yeh and Tripathi [23] showed that an effective  $K_d$  for uranium could vary over orders of magnitude as a result of oxidation–reduction and precipitation processes. Brady and Bethke [70] and Bethke and Brady [71] demonstrated that the constant  $K_d$  approach could not possibly account for pH and other competitive ion effects on sorption and therefore could not adequately describe solute breakthrough curves where spatial and/or temporal changes in groundwater chemistry were present. Similarly, Zhu [72] showed that the  $K_d$  for Zn varied both in space and time as a result of geochemical processes taking place along a groundwater flow path. Many users of the  $K_d$  approach acknowledge that  $K_d$ s are not constant parameters, but it is often claimed that either a site-specific but constant  $K_d$  can be determined, or that the range in values for the  $K_d$  can be captured with the use of a probabilistic approach like the Monte Carlo method.

In contrast, a multi-component cation exchange model is able to capture the important effect of competing cation concentrations on the retardation of exchangeable radionuclides like  $^{137}\text{Cs}$  and  $^{99}\text{Sr}$ . This can

be seen clearly in the effect that differing background  $\text{NaNO}_3$  concentrations have on the retardation of  $\text{Cs}^+$  compared to a non-reactive tracer like nitrate using high resolution reactive transport simulations of the migration of  $\text{Cs}^+$  through the vadose zone at Hanford (Fig. 7). A constant release of contamination, although resulting in two distinct  $K_d$  values for  $^{137}\text{Cs}$  that depend on the background  $\text{NaNO}_3$  concentration, would at least result in individual  $K_d$  values that remain constant as the plume migrates through the vadose zone, except where a changing water content causes the exchanger to fluid ratio to change. Any dilution of the plume by infiltrating rainwater, however, causes the  $K_d$  to increase as the competitive effect of the high  $\text{Na}^+$  is reduced. More importantly, however, is the natural evolution of the  $\text{Cs}^+$   $K_d$  to higher values as a result of the chromatographic separation of the fronts when the HLW leak is of limited duration. In this case the mechanism is not strictly dilution, but rather a consequence of the larger retardation of the  $\text{Cs}^+$  relative to the  $\text{Na}^+$ , which causes the  $\text{Na}^+$  front to move progressively away from the  $\text{Cs}^+$  front once the leak event has stopped. Using a constant but low  $K_d$  value for  $\text{Cs}^+$  within the context of a probabilistic analysis might represent a conservative value, but it fails to capture what is essentially a deterministic and predictable spatial evolution of the  $K_d$  value.

#### 4.2. Improving estimates of elemental and nutrient fluxes

One of the most important demonstrations of the power and utility of reactive transport modeling is its use in estimating elemental and nutrient fluxes in critical natural environments, such as the interfaces between major Earth reservoirs like the atmosphere, ocean, marine sediments, and the continents. The strong

disequilibrium developed at these global interfaces provides energy and food sources for opportunistic biota, which in turn exert a fundamental control on the elemental and nutrient cycling. One of the best examples of such global interfaces is the sediment–water interface at the ocean bottom, where the microbially mediated oxidation of organic carbon buried in the sediments drives a complex reaction network that modifies the fluxes resulting from diffusion, irrigation, and sediment burial [29].

Developing reliable methods for estimating local, regional, and global fluxes of nutrients and other reactive constituents is an active topic of research. For example, the flux of nutrients like N and P from the continents, whether from rivers [73] or from ground water discharge [74], can play a significant role in nutrient cycling and biological productivity in coastal ocean waters. It is essential, therefore, to have a good understanding of all of the processes, including transport and biogeochemical reactions, that can affect these fluxes. Similarly, estimating the transfer of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  between such Earth compartments as the ocean, atmosphere, soils, and biosphere is essential to understanding the importance of each of these in regulating atmospheric  $\text{CO}_2$ . In some cases, these fluxes can be directly measured and a model may or may not be needed. It is impractical to measure nutrient and elemental fluxes everywhere, however, so modeling provides a means to extend the data we have in a rigorous fashion by incorporating the relevant processes that control these fluxes. In other cases, direct measurement of fluxes is quite difficult because of the complexity of the transport processes involved—measuring seaward fluxes of nutrients from estuaries, which are affected by complex, time-dependent dispersive transport, is a case in point. An appropriately calibrated reactive transport model can provide better

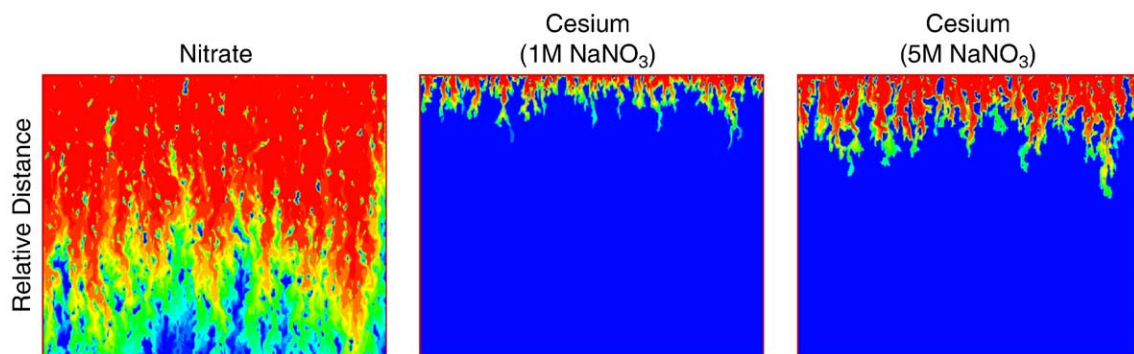


Fig. 7. High resolution reactive transport simulation of the separation of  $\text{Cs}^+$  and nitrate (non-reactive tracer) fronts for the cases of 1 and 5 M  $\text{NaNO}_3$  background electrolyte in physically heterogeneous Hanford sediments. The distance traveled by the non-reactive tracer relative to the  $\text{Cs}^+$  is a direct measure of the retardation of the  $\text{Cs}^+$ , which is less in the case of the 5 M  $\text{NaNO}_3$  electrolyte.

estimates of estuarine fluxes than can be obtained from a limited number of direct measurements [73]. The model in fact can provide a vehicle for making the maximum use of the measurements that are available. The seawater–marine sediment interface was perhaps the first of the important environments where reactive transport models were developed to improve our understanding of nutrient and element cycling and fluxes [29,75–77]. Early reactive transport models to describe the marine sediment–seawater interface dating back to the 1970s were successful in capturing the major elemental profiles as a function of depth in the sediment and provided a first order estimation of fluxes into and out of the sediment. The primary reactions considered in these early models were those involving the oxidation of organic carbon by a series of electron acceptors and mediated by heterotrophic bacteria. Not quantified was the effect of reactions and/or transport processes that were considered “secondary”—for example, when hydrogen sulfide is produced at deeper levels within the sediment as a result of sulfate reduction, it was assumed to combine with iron to form iron sulfide (which it does in part). But where hydrogen sulfide is present in excess of iron, it is possible that the upward diffusion of  $H_2S$  will cause direct reaction with other oxidants in the system like  $O_2$  and/or Fe-oxhydroxide [77]. Similar arguments can be made about other reduced phases like methane—recent studies have shown that anaerobic oxidation of methane by sulfate is an important sink for sulfate over and above that which is reduced via sulfate reduction [78].

A comprehensive attempt to incorporate secondary reactions taking place within the marine sediment and to quantify the effect on fluxes was made by Wang and Van Cappellen [77]. These authors focused primarily on the Fe and Mn cycle, using data from a series of shallow sediment profiles collected by Canfield and co-workers [79,80]. Wang and Van Cappellen were able to demonstrate clearly with their mechanistic reactive transport model that only a portion of the  $O_2$  entering the sediment at the seawater–sediment interface was used up in aerobic respiration (Fig. 8). Their results indicated that 22% to 46% was used up in aerobic respiration, with the remainder consumed by oxidation of either Fe(II), FeS,  $NH_4$ , or Mn(II) oxidation. These “secondary” sinks for  $O_2$ , in turn, depended on the availability of the electron donors, which varies to some extent from site to site. Whether these secondary  $O_2$  sinks come into play also depends on the reactivity of the organic carbon, the transport length scales, and the transport mechanisms. Using a mechanistic reactive transport approach, the authors were able to arrive at flux estimates that matched those observed, but did so with a set of reaction-specific parameters that were applicable to multiple sites once the appropriate site-specific data (e.g., bottom water composition, burial fluxes, etc.) is incorporated. Thus, the model, despite being more complex in its treatment of the biogeochemical reaction network and transport processes, becomes more general and therefore transferable for use in estimating nutrient and elemental fluxes within and between major Earth reservoirs.

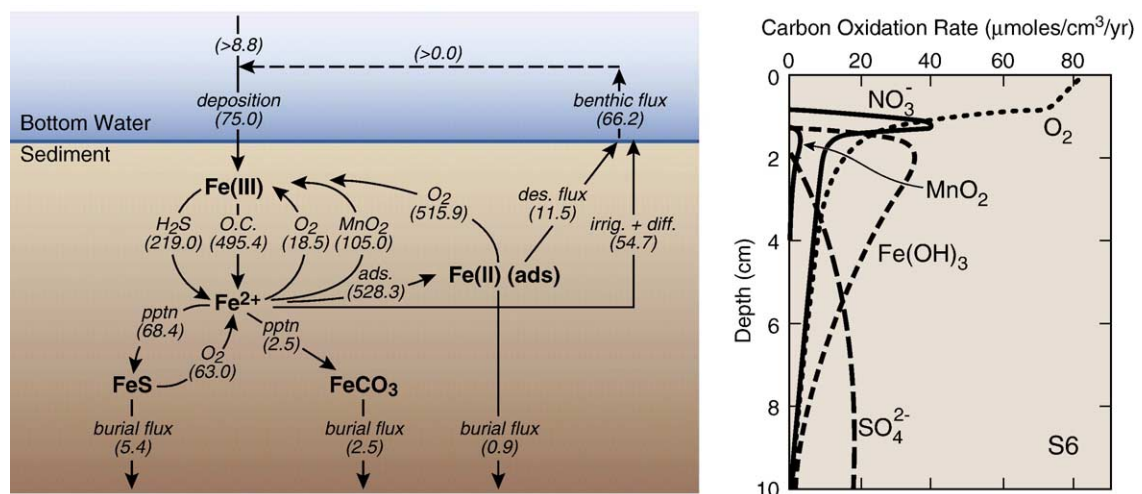


Fig. 8. Cycling of Fe and Mn in marine sediments. Matching of observed dissolved and solid concentration profiles with forward reactive transport simulations is used to define the reaction network in the marine sediments, thus improving estimates of elemental and nutrient fluxes. The simulations demonstrate the “secondary” reactions between  $O_2$  and various reduced species account for a significant portion of the consumption of  $O_2$  in the sediment. The units of flux are  $\mu\text{mol}/\text{cm}^2/\text{yr}$  [77].

### 4.3. Magma transport in the Earth

Reactive transport models have become essential for understanding magmatism in the Earth. The formation of magma in the Earth and its transport to the surface to form volcanoes is a challenging and interesting problem. The process cannot be directly observed to any substantial degree, and so its character must be inferred from indirect evidence. Models rely on the material properties of partially molten rocks, equations for compaction and fluid flow, and the thermodynamics of melting [81–83]. Most of the parameters are not precisely known for the conditions under which melting occurs, and so there are still many uncertainties. An exciting new approach is the use of the trace element and isotopic chemistry of lavas to infer the nature of the melting process and melt migration [84–87]. It is here that reactive transport models come into play. The observables are chemical concentrations and isotopic ratios, and as in the case of water–rock systems, the stimulus is observations that do not conform to simple models.

A major advance came from 1-D treatments of magma flowing through partially molten rock material,

with the magma and solid phases exchanging by solution and precipitation, but without significant changes in the mineralogy of the solid [88]. These models were used to understand the distribution of U-series nuclide concentrations in lavas from mid-ocean ridges, and later from Hawaii [89,90]. More recently Spiegelman and co-workers [60] investigated the effects of changing thermodynamic equilibrium along the flow path. The interesting effects produced in the models stem from the fact that magma is generated gradually due to progressive melting of upward flowing solid mantle rock. Under mid-ocean ridges, liquid starts to be generated at depths of about 100 km, but the liquid percolates upward for 60 or 80 km before entering dikes and being transported to the surface. The magma generated at 80–100 km depth is not in chemical equilibrium with the rock it passes through at shallower depth, and this chemical disequilibrium causes additional melting. The additional melting enhances permeability; zones of enhanced permeability develop, flow is concentrated in these zones which further accelerates melting, and eventually “melt channels” form (Fig. 9). Spiegelman and Kelemen [61] show that this effect can drastically

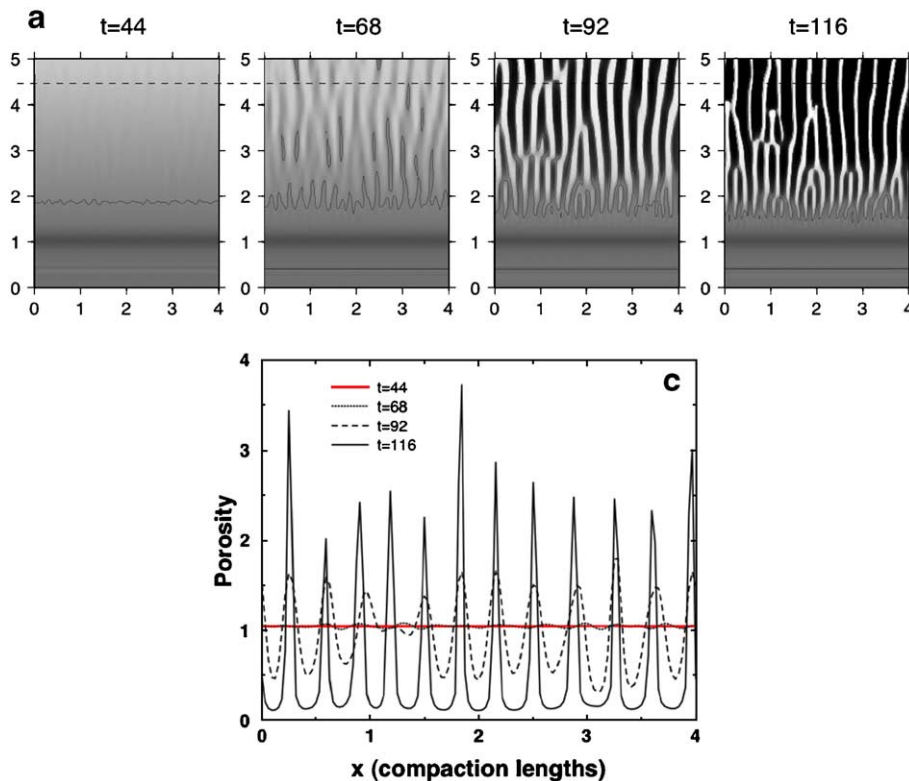


Fig. 9. Time evolution of porosity, giving rise to unusual trace element fractionation in upwelling magma. A dimensionless time of 1 in the simulation is the time required to traverse the box once at the background porosity. Panel C shows a cross section of the porosity at  $z = 4.5$  for the four panels shown at the top of the figure [60].

affect the chemical composition of the lavas, and in fact is a plausible explanation for certain trace element features of the lavas as well as the occurrence of pyroxene-deficient zones in exposed mantle rocks at the Earth's surface. The high  $^{226}\text{Ra}$  contents observed in island arc lavas [91], which apparently relate to migration of both fluids and magmas in subduction zones, is another example of an observation that may not be correctly interpreted until appropriate reactive transport models are developed for the complex subduction zone environment.

## 5. New challenges and directions

### 5.1. Chemical microenvironments

A chemical microenvironment can be defined as a small region in space in which the chemical composition of the fluid differs from the bulk chemical composition. Microenvironments may or may not be physically isolated from the bulk solution. On the sub-micron to micron scale, microenvironments can be found at the immediate mineral interface, the microbial cell surface, and within or between mineral grains. At the nanometer scale, a microenvironment may involve different reacting molecular sites represented by the reactivities of different mineral surface faces or at their intersections. At larger scales, microenvironments could be a clay lens embedded in sandy sediments, or a reducing biofilm. Localized microenvironments exist because reaction rates (either microbially mediated or mineral dissolution/precipitation rates) are fast in comparison to the transport of solutes into or out of the local environment. The result is that chemical gradients develop in the aqueous phase, schematically represented in Fig. 1 as the zones of depletion of  $\text{Fe}^{2+}$  in the vicinity of siderite nucleation/precipitation sites and clays where sorption occurs. Microenvironments are particularly likely to develop in physically heterogeneous systems where flow rates locally can be very slow and transport is dominantly by molecular diffusion. Microenvironments can provide unique conditions for nucleation of mineral phases, for example, microbial cell surfaces or specific nucleation sites on the mineral surface, and in this regard they may provide a fundamental control on the overall reactivity of the system. Thus microenvironments can be viewed as unique systems to evaluate the interplay of flow, diffusion, and reactivity.

Owing to their unique chemical conditions, microenvironments serve as localized sources and sinks for chemical constituents and have a significant influence on the overall behavior of those constituent. For trace

components, the vast majority of the mass of the component can be localized in microenvironments. Examples include the accumulation of uranium in microfractures in mineral grains, the precipitation of minerals at the microbe/mineral interface, and the reduction of uranium, technetium or other soluble contaminants in a cellular/mineral matrix [92].

Unfortunately, microenvironments are difficult to characterize owing to their small size and small total volume relative to the bulk environment in which they are found. Identifying the chemical composition and mineralogical identity of specific components is hampered by their close association with the bulk phases. The transport of chemical constituents to, from, and within microenvironments is an extraordinarily difficult problem to fully integrate with macroscopic transport. From a modeling perspective, microenvironment is problematic because the processes take place at scales that are well below the size of a typical computational grid cell. Therefore, we are faced with the daunting challenge of describing reaction rates in a chemical environment whose composition is difficult to probe or predict, and inferring how these reactions affect the chemistry of the bulk fluid.

### 5.2. Coupled mechanical–chemical systems

One of the major stumbling blocks in understanding geodynamic processes on scales ranging from that of subduction zones to crack tip propagation is our present inability to understand adequately how reactive flow influences deformation and in turn how that deformation affects the fluid transport and chemistry. The major challenge in this area is that the coupling of chemistry, flow, and mechanical deformation needs a unified theory that couples the flow of fluids with the chemical reactions between scales and that includes consistent solid mechanics for a wide range of rheologies including elastic, brittle and ductile. Reactive fluids in deforming media are crucial in this regard because as materials fail, they are exposed to changes in stress regime, and new conduits for fluid flow open up. As reactive fluids interact with the primary minerals in the rock, significant changes in matrix mineralogy and thus in the rheology of the material can occur.

Another as yet unresolved problem is that of the space needed for reactions to occur. This is particularly an issue in low porosity materials where there is often insufficient pore space available for the reaction products if the thermodynamically favored reaction were to proceed. Any reactive transport modeler who has investigated metamorphic reactions, especially those involving car-

bonation, knows that unrealistic negative porosities occur unless some feedback to the transport rates or to the porous medium itself is included. This issue seems to have been neglected by most metamorphic petrologists, who historically have paid little attention to the actual pore space required for a reaction to proceed.

Several limiting kinds of behavior are possible. Where the force of crystallization is weak and/or the confining pressure is high, one expects no deformation of the porous medium. In this case, the porous medium may be sealed by precipitation reactions, but there is at least anecdotal evidence that the low porosity of the medium may suppress nucleation and/or precipitation in these cases and complete sealing does not occur [93,94]. A more rigorous treatment of the entire problem is to include a calculation of the local stress field and to incorporate this effect into the thermodynamic analysis [95,96]. With this approach, the local stress field and the strain associated with mineral precipitation is formally considered in calculating the solubility of the neoformed phases, as is implied in Fig. 2. Clearly such a fully coupled approach is a significant challenge, but it will also provide a unified description of chemical and physical processes in deeper environments where the stress field is likely to be important.

### 5.3. Comparing reaction rates in laboratory and field systems

If reactive transport models are going to be used to describe water–rock interaction and other processes like reactive contaminant transport, then they must be able to capture natural, in situ reaction rates adequately. One possible approach is to use reaction rates and rate laws based on direct measurement in the field, in this way skirting the entire issue of how to interpret rates at a variety of scales. But this approach runs counter to the stated role of reactive transport modeling here, which is to use it to integrate fundamental, mechanistic descriptions of the various sub-processes that, coupled together, control the overall system reactivity. This is perhaps the first point to be made, namely that reaction rates in field settings are not to be interpreted as strictly geochemical or microbiological quantities, but are the net result of all of the coupled processes that affect rates. A priori, there is no clear information on whether the rates are even limited by the intrinsic geochemical or microbiological reactivity, or whether the major limitation on rates is transport. Transport limitation of chemical weathering, for example, is strongly suggested by the frequently observed one-to-one correlation of weathering rates with infiltration and/or runoff [97,98]. It is also sug-

gested by detailed studies of chemical weathering profiles where the extent of reaction and therefore disequilibrium decreases with increasing distance along a flow path [99]—consistently far from equilibrium behavior, as is measured in most laboratory experiments, should show uniform extents of rock dissolution along the flow path. Other evidence, however, suggests that slow interfacial reactions are important in the overall weathering process—the development of etch pits, for example, is taken as good evidence that the fluid was locally strongly undersaturated with respect to the dissolving mineral phase [53]. The situation is more complicated in physically and chemically heterogeneous media, where it is possible for both transport and interface reaction control to occur locally [20,51,52]. Unfortunately, much of the discussion about the “discrepancy” between laboratory and field rates has ignored this crucial point for years, with physically and chemically heterogeneous systems treated effectively as well-mixed flowthrough reactors.

Reactive transport models cannot solve the problem of the apparent discrepancy between laboratory and field rates by themselves, but they can be used to rigorously evaluate the importance of individual processes, some of which can be constrained independently. In other cases, the reactive transport modeling can be used to narrow down the possible explanations for the overall rates observed in the field. For example, if the data from a non-reactive tracer transport test could be used to constrain the travel (and thus residence) time distribution of dissolved species moving through a weathering profile, then Malmstrom and co-workers showed that this independent information could be used to quantify the possible effect of heterogeneous flow paths on the overall rate of weathering [20]. By incorporating this statistical information on the range of residence times into a reactive transport model (without attempting to provide a completely deterministic description of actual flow paths), it is possible to evaluate whether this effect could explain the “discrepancies” between laboratory and field reaction rates. Another possible approach is to choose field sites where the transport rates can be modeled accurately and deterministically because gross physical heterogeneities are absent. By representing the independently constrained transport rates accurately, it is possible to focus then on purely geochemical or microbiological effects that influence the overall reaction rates. One such analysis has been presented by Maher and co-workers [32], who studied silicate dissolution rates in un lithified, high porosity marine sediments where the physical heterogeneities discussed by Malmstrom et al. [20] are absent.

#### 5.4. Upscaling reactive transport

Perhaps the most significant obstacle to developing realistic models for reactive transport flow is the need to incorporate the multitude of spatial scales that are characteristic of natural subsurface environments. Spatial scales may range from nanoscale surface chemistry, to pore and fracture apertures of millimeters to centimeters, to fracture spacing and matrix block sizes of tens of centimeters to meters, to reservoir or basin scales of kilometers to tens of kilometers. Even where a particular system can be discretized with a reasonable number of grid cells in a numerical model, it may be that physical and chemical processes occur at much smaller sub-grid scales. These processes may include mass transfer-limited exchange between low and high permeability regions [50], or highly localized chemical microenvironments that are related to a heterogeneous distribution of reactive material [92]. Under such conditions, gradients in concentration can develop at the pore to centimeter-scale, thus causing reaction rates to vary spatially at scales well below the numerical grid size that can be handled with reasonable computational efficiency.

The problem of upscaling from the laboratory to the field-scale has been extensively discussed in the physical hydrology literature, particularly with regard to the scale dependence of macrodispersion [100–102]. Gelhar [101], for example, showed that field-measured values of longitudinal dispersivity depended on the scale of measurement, implying that a contaminant plume migrating through an aquifer must be described by an increasing dispersion with time. Similar arguments can be made for the scale dependence of reactive processes, whether equilibrium or kinetically controlled. Espinoza and Valocchi [103] and Rajaram [104] showed that the presence of chemical heterogeneities could create “pseudokinetic” conditions characterized by a time-dependent effective retardation coefficient, even in the case where local equilibrium is assumed.

A variety of mathematical approaches to upscaling transport and reactive transport in porous media have been used, with ensemble averaging [102,105–109] and volume averaging [110–116] being the most common. These approaches rely on expansion of the local mean concentration, retaining only the linear terms. This approach presents a problem in multicomponent systems, however, where the reaction terms related to mineral dissolution and precipitation, cation exchange, and aqueous and surface complexation are generally nonlinear [117]. For example, U(VI) speciation is

strongly affected by pH and bicarbonate concentrations in pore water, with the result that relatively small variations can have a significant effect on transport [118,119]. Despite the difficulty in applying ensemble (stochastic) or volume averaging procedures in the case of multicomponent reactive transport, particularly if multiple chemical processes are operative, it is essential to deal in some fashion with the issue of physical and chemical heterogeneities if the scale dependence of reactive transport is to be addressed, especially in three dimensions. One approach has been to use high performance computing to carry out deterministic simulations of an aquifer containing both physical and chemical heterogeneities [120]. Often, the high-resolution data set itself is generated stochastically based on geophysical or other high-resolution data [121,122].

High performance computing can help alleviate, but not eliminate, upscaling and multiscale issues. Another approach is to rely on multiple continua models, the simplest of which is the dual porosity model, for capturing sub-grid processes. Such models will be successful only where a detailed understanding of fundamental mechanisms and the supporting data is available, implying that careful experimentation and conceptual model development are necessary first steps.

## 6. The future

Reactive transport modeling is only now emerging as an overreaching research activity in the Earth sciences, although significant obstacles still remain to its acceptance as a mature discipline. Many Earth scientists still regard reactive transport modeling primarily as an engineering tool and have not yet recognized the potential it offers for integrating fundamental Earth science research as it bears on complex natural Earth systems. In this review, we have tried to highlight some of the important scientific problems where reactive transport modeling has already had a significant impact, including 1) the treatment of contaminant retardation in the subsurface, 2) the improvement in estimates of elemental and nutrient fluxes between Earth compartments, and 3) the treatment of reactive magma transport in the Earth. Despite these successes, however, the field continues to evolve, with new interest and effort in developing pore scale and hybrid or multiple continua models to capture the scale dependence of coupled geochemical, biological, and transport processes. In addition, we have identified some frontier research questions that have mostly not been addressed, in-

cluding 1) the issue of chemical microenvironments in the subsurface, especially with regard to their control of contaminant migration, 2) the treatment of coupled mechanical–chemical processes in the subsurface, 3) the oft-cited discrepancy between laboratory and field rates, and 4) the difficult problem of how reactive transport processes scale from the microscopic to pore to field scale. The latter research topics present both special challenges and opportunities for reactive transport modeling in the future. With past and future successes, we believe it is possible for reactive transport modeling to form the basis for a new research approach and perhaps even paradigm in the Earth sciences that goes well beyond its narrower but important role as a tool. The real role of reactive transport modeling comes from its ability to integrate fundamental Earth science research, to provide the dynamical glue that links together fundamental processes in complex natural environments.

### Acknowledgements

Many of the ideas presented in this paper came out of a workshop sponsored by the Geoscience Program of the U.S. Department of Energy Office of Basic Energy Science that was held in Carmel Valley California in June of 2003. We are grateful to Dr. Nicholas Woodward for providing financial support for this workshop and for ensuring that we followed through with a written product that summarized the principal issues that emerged. We are also grateful to the other participants in the workshop: Linda Abriola, Craig Bethke, Edward Bolton, Susan Brantley, James Davis, Dave Dixon, Ron Falta, Andy Felmy, Grant Garven, Janet Hering, James Johnson, Barbara Ransom, Eric Roden, Eric Sonnenthal, Marc Spiegelman, Steve Yabusaki, John Zachara. The first author is also grateful for the direct financial support of DOE Basic Energy Sciences for his time in organizing and conducting the workshop and in producing this review paper. We are also grateful to John Ferry and an anonymous reviewer for their careful and constructive reviews of the manuscript.

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