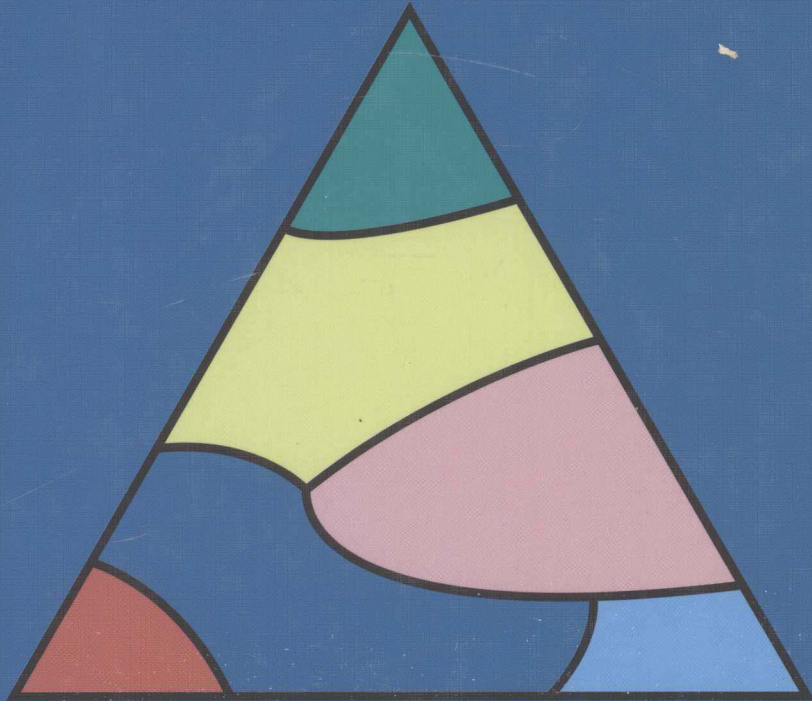


DEVELOPMENTS IN GEOCHEMISTRY 7



GEOCHEMISTRY  
AND FLUID FLOW

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and Aura N. Araque-Martinez

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## Preface

Chemistry is familiar enough; fire and fermentation are cornerstones of human civilization, and the beaker and the test tube are readily recognizable icons in most of the world. Flow is even more familiar; everyone has seen a river, felt the wind, taken a pulse. Though they are rarely on the center stage, fluids that undergo chemical reactions as they flow also impact an astonishingly large number of human experiences. Examples of this include air purification, electro-chemical transport within the human brain, blood and air flow through lungs, flow through kidneys, catalytic converters, tooth decay, deterioration of historic objects, and nearly every large-scale manufacturing process, from semiconductors to paper. Besides the sheer number, the diversity of this list is impressive.

The numerous biological examples reflect an inevitability of Nature's adoption of the flow-with-reaction model in the animal kingdom. Diffusion may provide adequate transport rates at the scale of a single cell, but making viable animals at the meter-scale generally demands quicker ways to deliver nutrients, provide fuel, remove waste, etc. Certain creatures manage to survive reasonably well by rooting themselves to one spot and waiting for food to arrive, in which case the flow-with-reaction model applies to the creature's surroundings rather than the creature's insides. Humans realized long ago the labor-saving and cost-reducing advantages of flow processes over batch processes, as even a brief inspection of the history of the chemical industry would show.

Our interest in this subject is primarily geological: we want to describe what takes place when a fluid is introduced into a permeable medium, reacts with that medium, and thence transports the reaction product downstream, possibly for further reaction. Even when restricted to geologic media, the range of interest is large; it encompasses the weathering of geologic formations by the action of water, the manner in which certain minerals come to occur in commercial quantities, the fate of chemical contaminants once they enter an aquifer, optimal methods to remove (or at least contain) these contaminants, and ways to improve the recovery of hydrocarbons from reservoirs. The last topic usually involves ways to operate and treat the wells that extract the hydrocarbon.

This, then, is the scope of the applications of the material to be covered in this text. But this scope, as important and relevant as it may be, would be an insufficient justification for this text, for it is impossible to believe that all of the applications of geochemical flow can be comprehensively treated in a single document. But it is possible to treat certain features of simplified reactive flow that occur in nearly all applications. Understanding these features will help interpret much more complex flows. Providing the basis for this understanding is the goal of this text.

The central idea in the treatment is waves. Waves are changes in the chemical

composition of the fluid. Focusing on changes, rather than the concentrations themselves, may seem a bit odd initially, but you will see that if we can describe the changes (the size of the change and what is on either side of it), we can also describe the concentrations. All of the waves in this text are moving (propagating). There are no standing waves. The waves propagate by direct flow (convection): all of the waves are affected by how the chemical components contained within them interact with each other and, most especially, how they interact with the permeable medium. The waves propagate through the medium more slowly (sometimes much more slowly) than the fluid carrying the components. Frequently they can change shape, sometimes drastically so. The change in shape is sometimes the most important part of the flow, for it is through this mechanism that chemicals can be broadcast over large areas.

As intriguing as the propagation, though, is the fact that entirely new concentrations can appear as a consequence of chemical interactions. These concentrations need not fall between the concentrations of the fluids initially present and those injected. This behavior would be wholly surprising were it not understood in the context of wave behavior. Framing the discussion in terms of wave behavior is what sets our work apart from others working in reactive transport and flow.

The text itself is a culmination of a research project conducted at The University of Texas at Austin (UT) over the past 20 years. The project began as a study on the requirements of uranium mining, progressed through more than ten graduate students and many other applications, and most importantly for this text, yielded several other general insights. We cannot come anywhere close to replicating the detail in the students' theses and dissertations, but we hope that there is enough information in this text to assist in reading those works, to which we have referred extensively at the appropriate places in the text.

This book is also the text for a graduate course on geochemistry and flow that has been taught at UT. Each of us has taught this course over the past ten years so the material represents a distillation of four teaching styles and emphasis. The progression of a research project through publications, to the classroom and finally to a text represents the type of knowledge flow that is characteristic of a research program at well-functioning universities.

Several acknowledgements are in order. We thank Dr. I. H. Silberberg for numerous editorial suggestions, Ms. Joanna Castillo for the figures, format editing and general computer support. We also thank Claire Jones, Mary Pettengill and the numerous research sponsors the program has enjoyed over the years. Above all, we thank the M.S. and Ph.D. students at The University of Texas for providing the foundation of this knowledge. Most of them are cited too infrequently throughout text, so let us acknowledge them here:

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## **Dedications**

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## Chapter 1

### Introduction

#### 1.1. Objectives and Scope

Making a pot of coffee is like making a cask of whiskey: the process cannot be rushed. The impatient new owner of a drip coffee maker soon acquires a keen appreciation of the trade-off between taste and drip rate. The distiller who increases the flow rate through the filtration section can fill more barrels per year but with a lower-quality product. Both are caught in what a dramatist would recognize as creative tension, in this case arising from the co-existence of two independent time scales, one for flow and another for reaction. This tension, or competition between coupled phenomena, is a hallmark of reactive transport. This book provides a foundation for the qualitative and quantitative understanding of such features.

Though we do not guarantee that you will make better coffee the morning after reading this book, you will at least be in a better position to explain what went wrong, as well as to weigh in authoritatively on the merits of metal vs. paper filters\*. More importantly, you will also be equipped to interpret a broad range of phenomena, for fluid flow accompanied by chemical reaction and mass transfer is ubiquitous. Its practical applications are as mundane as making coffee and as marvelous as moving oxygen through the human body. Moreover, a variety of couplings are inherent in reactive flow and transport, giving rise to as interesting an array of behavior as may be found in any of the engineering sciences.

Our applications deal mainly with flow through the Earth's crust, though many of the ideas are immediately relevant in other systems. The chemical reactions of the Earth's minerals with meteoric water underlie many phenomena that are vital to human enterprise: mineral deposition, weathering, diagenesis, formation of ore deposits, and mobilization, migration, and mitigation of pollutants. Some of these are specifically discussed in Chap. 9. We are thus at a crossroads between chemistry, physics, and geology. This is remarkably fertile territory. It exhibits elegant and subtle mathematical behavior while, at the same time, encompassing many applications.

To keep the treatment manageable, we will examine only a subset of the many problems in which chemistry, transport, and geology interact simultaneously. For example, we mostly treat the limiting case in which the chemical reactions are locally in

---

\* One is inert, the other sorbs oils extracted from the beans. The consequences of this distinction are explored in Chap. 3.

thermodynamic equilibrium. Furthermore, we shall use just enough physics to obtain steady flow of a single fluid phase through a permeable medium, though the behavior of the chemical components will be transient. And we will often boil down the geological description of a stratum or formation to a list of the mineral phases present in that rock. We rely almost exclusively on analytical solutions of the partial differential equations that define the reactive transport problem, resorting to numerical solutions only occasionally to discuss a realistic application.

As discussed above, all solutions are restricted to single-phase, incompressible, isothermal, and one-dimensional flow. Later sections of this chapter discuss these assumptions and their implications in more detail. You might wonder how much substance remains after so many simplifications. A good deal of interesting behavior remains, though. The set of requirements to be explored in this text consists of

- (i) the possibility of transforming one chemical component into another;
- (ii) the possibility of transferring components between phases;
- (iii) a means for perturbing the system from equilibrium; and
- (iv) chemical interaction between moving and stationary-phases.

The first two requirements are met as soon as we allow chemical reactions. Whether the reactions go to equilibrium is less important than the fact that the reactions occur. The assumption of local equilibrium is convenient mathematically, provides a basis for understanding more complex flows (even those not in equilibrium), and is occasionally valid in practical applications. Thus this assumption will permit much insight without sacrificing a key feature of reactive transport problems. Similarly, steadily injecting fluid into a domain with which it is not already in chemical equilibrium is a mathematically convenient way to perturb the system. Such injection is also a good approximation of what happens in many reactive transport applications. Permeable rocks and soils are the oldest examples of media in which a moving fluid phase is in intimate contact with a stationary-phase.

## 1.2. Aesthetics of Reactive Flow

Mathematics is the language of science, and, like other languages, it can be a medium for artistic expression. Coupling between one phenomenon and another is often a source of richness. Consider, for example, the chaotic evolution of simple predator-prey population models or weather models, or pattern formation in self-organizing systems. The mathematical encapsulation of the laws governing these systems can be extremely simple, e.g.,

$$\begin{aligned} dx/dt &= x - xy \\ dy/dt &= xy - y \end{aligned}$$

The term  $xy$  imposes a nonlinear coupling between the two rate laws, and its presence is all

that is needed to produce subtle behavior. Dropping that term from one or both equations, or replacing it with a linear term (e.g., with  $y$  in the first equation and  $x$  in the second), yields comparatively straightforward exponential growth/decay curves.

In the case of reactive transport, a fundamental coupling arises when components in a flowing phase interact with a stationary phase. We chose the simplifying assumptions given above to preserve this particular coupling. Other couplings arise in reactive transport, notably when chemical modification of the medium changes its flow properties (permeability, porosity, wettability) or when reactions change the composition-dependent viscosity of the fluid. These couplings fall beyond the scope of this book.

Let us now briefly tour a gallery of interesting behaviors. Flow with competitive sorption provides a simple example of a situation rarely encountered in life, wherein one can get something for (almost) nothing. It is possible to inject a fluid containing a component at a concentration  $C_1$  into an appropriate permeable medium (ion exchange bed, chromatography column, a bucket of clay mixed with sand) initially containing a solution with that component at concentration  $C_2$ , and extract from the medium (for a limited time) a fluid with component concentration exceeding both  $C_1$  and  $C_2$ . Just how amazing this is may be hard to realize in the modern world, where chromatographic columns and water softeners are commonplace. But consider what effect Twain's Connecticut Yankee could have produced at King Arthur's court with a vial of ion exchange resin, a bucket of fresh well water, and a bucket of seawater!

Another geochemical marvel is the process that petrifies wood. Pieces of petrified wood bear detailed images of the original tree, but there may not be a single molecule of the tree remaining, the cellulose having been replaced by siliceous compounds. The replacement of the original cellulose is so precise that the morphology of the bark or annual rings of the original tree remains. Even the original cells of the wood are distinguishable under a microscope. How is it possible for a geochemical process to so exactly replicate the original texture of the wood when replacing the cellulose?

One other picture in this gallery ends the tour. Some years ago we had an opportunity to view a Texas uranium-roll-front deposit in a sandstone aquifer (Galloway, 1977). The uranium ore was being produced by open-pit mining. Viewing the roll-front from within the mine, we observed the boundary between the ore zone and the reduced zone downstream of it. The boundary or front was easy to see because there was a change in the color of the sandstone from black to a reddish tinge. This sharp change in color is consistent with the presence of iron in different oxidation states in the sandstone. In a reduced valence state iron tends to be dark, whereas iron compounds in an oxidized state are more colorful (for a more quantitative description, see Chap. 9). The most remarkable feature of the boundary was that it seemed to be only a few sand grains thick, which is extremely sharp considering that the ore body dimensions are measured in meters. How has Nature managed to make such sharp boundaries?



### 1.3. Computation of Reactive Flow

You may wonder why anyone should be concerned with analytical solutions to simplified problems in the era of massive computational power. Many computer programs to model the interactions between aqueous solutions and assemblages of minerals exist (e.g., Truesdale and Jones, 1974; Wolery, 1979; Felmy *et al.*, 1983). Besides their usefulness for modeling batch (non-flowing) systems, these programs often are the basis of sophisticated simulators that solve for the transport of an arbitrary number of chemical components in multiple flowing phases in heterogeneous three-dimensional domains, all subject to many chemical reactions. Several of these programs are free, publicly available, and run on a variety of platforms at practical speeds. In more than two decades of work, we at The University of Texas have weighed in with PHASEQ/FLOW (Walsh, 1983), KGEOFLOW (Sevougian, 1992), ALGEFLOW (Novak, 1990; Araque-Martinez, 2001), UTKFLOW (Araque-Martinez, 2001) and IPARS/TRCHEM (Sun, 2002). See also ParSSim (Saaf, 1996). We routinely use simulators and train students to use them. Would not a tutorial on preparing input files for such a program therefore be much more useful than a treatise on theory?

Posing such a question misses a key point: the interplay between computation and theory. Advances in algorithms, raw processing speed, and user interfaces are ushering in an era in which computation will join theory and experiment as a third pillar of science. In our experience, simulation results have on several occasions provided the inspiration for a new theoretical development. Conversely, testing the generality of theoretical predictions obtained in simple, mathematically tractable cases is often much easier at the keyboard than at the laboratory bench.

These remarks should not be misconstrued. Numerical experiments cannot and should not be regarded as substitutes for laboratory or field experiments. Rather, a simulator is most powerful for understanding physical systems when its output is interpreted through a theoretical framework. Thus from our perspective, a User's Guide is neither more nor less useful than a mathematical theorem.

Since no part of this book deals with computational tools, you may yet have doubts about its practical utility. You should consider the following sampler of questions, the answers to which do not appear in any User's Guide known to us.

1. How many gridblocks (cells), the minimum resolution in numerical models, is enough? Features in reactive transport applications, such as the roll-front boundary in Fig. 1.1, can be remarkably sharp. How does one know that the chosen level of refinement is not obscuring important features?
2. Which components can be safely omitted from the simulation? Nature knows all the possible components and thus leaves nothing out. The computer only knows what the user tells it.
3. What if no characterizing data are available for a particular component? How