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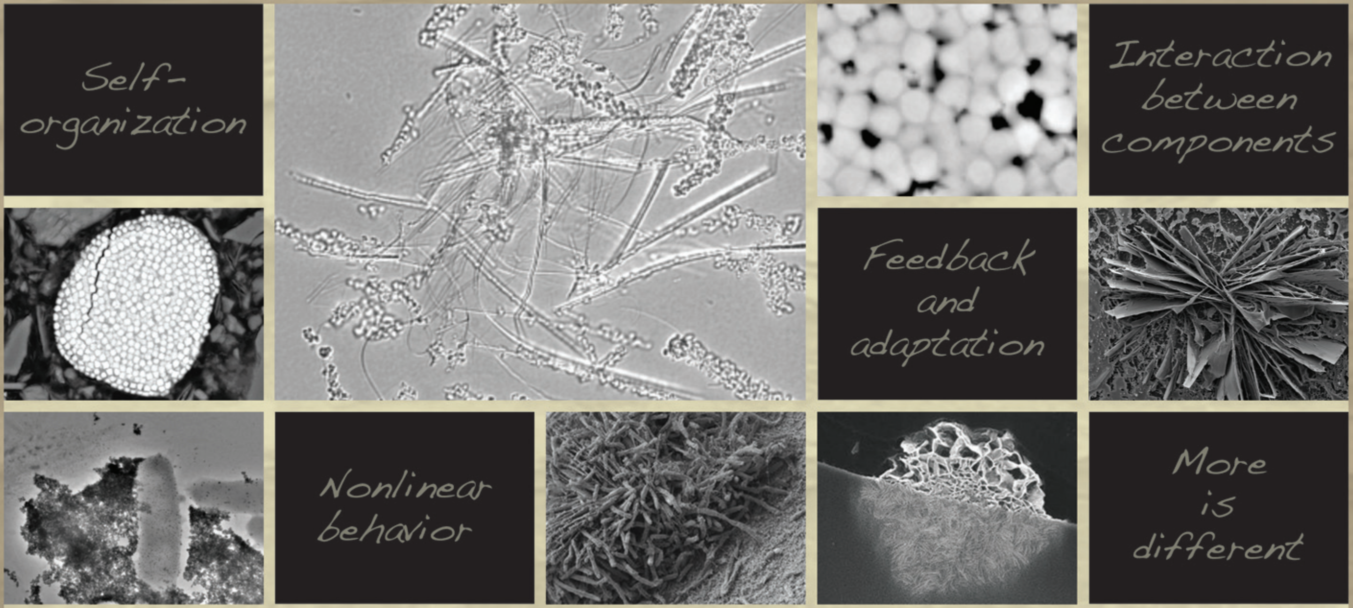

Complex Systems Science for Subsurface Fate and Transport

Report from the August 2009 Workshop

U.S. DEPARTMENT OF
ENERGY
Office of Science

Office of Biological and Environmental Research

Complex Systems Science for Subsurface Fate and Transport

Report from the August 2009 Workshop

Convened by

U.S. Department of Energy
Office of Science
Office of Biological and Environmental Research

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Contents

Executive Summary

The subsurface environment, which encompasses the vadose and saturated zones, is a heterogeneous, geologically complex domain. Believed to contain a large percentage of Earth's biomass in the form of microorganisms, the subsurface is a dynamic zone where important biogeochemical cycles work to sustain life. Actively linked to the atmosphere and biosphere through the hydrologic and carbon cycles, the subsurface serves as a storage location for much of Earth's fresh water. Coupled hydrological, microbiological, and geochemical processes occurring within the subsurface environment cause the local and regional natural chemical fluxes that govern water quality. These processes play a vital role in the formation of soil, economically important fossil fuels, mineral deposits, and other natural resources.

Cleaning up Department of Energy (DOE) lands impacted by legacy wastes and using the subsurface for carbon sequestration or nuclear waste isolation require a firm understanding of these processes and the documented means to characterize the vertical and spatial distribution of subsurface properties directing water, nutrient, and contaminant flows. This information, along with credible, predictive models that integrate hydrological, microbiological, and geochemical knowledge over a range of scales, is needed to forecast the sustainability of subsurface water systems and to devise ways to manage and manipulate dynamic *in situ* processes for beneficial outcomes.

Predictive models provide the context for knowledge integration. They are the primary tools for forecasting the evolving geochemistry or microbial ecology of groundwater under various scenarios and for assessing and optimizing the potential effectiveness of proposed approaches to carbon sequestration, waste isolation, or environmental remediation. An iterative approach of modeling and experimentation can reveal powerful insights into the behavior of subsurface systems. State-of-science understanding codified in models can provide a basis for testing hypotheses, guiding experiment design, integrating scientific knowledge on multiple environmental systems into a common framework, and translating this information to support informed decision making and policies.

Subsurface behavior typically has been investigated using reductionist, or bottom-up approaches. In these approaches, mechanisms of small-scale processes are quantified, and key aspects of their behaviors are moved up to the prediction scale using scaling laws and models. Reductionism has and will continue to yield essential and comprehensive understanding of the molecular and microscopic underpinnings of component processes. However, system-scale predictions cannot always be made with bottom-up approaches because the behaviors of subsurface environments often simply do not result from the sum of smaller-scale process interactions. Systems exhibiting such behavior are termed complex and can range from the molecular to field scale in size. Complex systems contain many interactive parts and display collective behavior including emergence, feedback, and adaptive mechanisms. Microorganisms—key moderators of subsurface chemical processes—further challenge system understanding and prediction because they are adaptive life forms existing in an environment difficult to observe and measure. A new scientific approach termed *complex systems science* has evolved from the critical need to understand and model these systems, whose distinguishing features increasingly are found to be common in the natural world.

In contrast to reductionist approaches, complexity methods often use a top-down approach to identify key interactions controlling diagnostic variables at the prediction scale; general macroscopic laws controlling system-scale behavior; and essential, simplified models of subsystem interactions that enable prediction. This approach is analogous to systems biology, which emphasizes the tight coupling between experimentation and modeling and is defined, in the context of Biological Systems Science research programs under DOE's Office of Biological and Environmental Research (BER), as "the holistic, multidisciplinary study of complex interactions that specify the function of an entire biological system—whether single cells or a multicellular organism—rather than the reductionist study of individual components."

In August 2009, BER held the Subsurface Complex System Science Relevant to Contaminant Fate and

Transport workshop to assess the merits and limitations of complex systems science approaches to subsurface systems controlled by coupled hydrological, microbiological, and geochemical processes. Important objectives were to

- Define complex subsurface systems, identify their distinguishing features, and establish why they are important to different DOE mission outcomes.
- Consider how the coupling of subsurface hydrological, microbiological, and geochemical processes defines complex system response and dynamics, and identify research challenges that, if resolved, would lead to high-impact subsurface science advances.
- Evaluate the need for new research approaches that identify and account for the influence of smaller-scale processes and their mechanisms on larger-scale system behavior.
- Conceptualize models and associated knowledge needed to describe and predict complex system behavior at different scales.
- Identify significant, long-term, interdisciplinary research opportunities associated with complex subsurface systems.

The workshop was attended by participants from universities and DOE national laboratories with broad expertise in the environmental, microbiological, Earth, and marine sciences. These researchers represented different perspectives spanning mechanistic investigations at the molecular level to intermediate-scale laboratory studies to field investigations of natural environments at scales ranging from meters to kilometers. Participants also included practitioners of complex systems science. They concluded that effectively managing subsurface systems requires a comprehensive understanding of their controlling processes, interactions, and response to change as well as a means to predict their integrated effects at multiple spatial and temporal scales within a heterogeneous framework. This great challenge can be met only by first recognizing these attributes and then looking beyond the tenets of any one single research approach (such as reductionism and complexity science).

This report lays out the need, identified by workshop participants, for a new subsurface science research strategy that includes a well-conceived convergence of complementary top-down and bottom-up methods to access and integrate the special insights and understanding provided by each approach. Melding select strengths of reductionism and complexity could enable the understanding of key underlying mechanisms and interactions, while simultaneously providing insights on common macroscopic laws governing complex system behavior at the prediction scale.

To resolve key research gaps and needs that currently limit effective, knowledge-based management of complex subsurface systems, workshop participants identified three high-impact, interdisciplinary research opportunities for advancing subsurface science. These three opportunities, associated challenges, and strategies for resolving them are summarized below. They emphasize hierarchical subsurface systems dominated by coupled processes, the characterization of inter- and cross-scale process interactions and feedback mechanisms that lead to emergent or other complex behaviors, and the development of heuristic and simulation models for system understanding and prediction.

Understand Fundamental Subsurface Process Coupling. Tight coupling occurs between microbiological, geochemical, and transport processes at mineral interfaces, within particle fractures and pores, and within different sediment types that make up the subsurface system as a whole. These complex biogeochemical systems are difficult to understand because of heterogeneities at different spatial scales; highly variable reaction time scales; and nonlinear, biologically catalyzed reactions and their associated feedbacks. Critical priorities are characterizing and measuring biogeochemical dynamics at the mineral-microbe interface, identifying microbial community responses to variable environmental conditions, establishing biogeochemical reaction rates in heterogeneous media, and quantifying and modeling feedbacks between biogeochemistry and water flow.

Identify and Quantify Scale Transitions in Hierarchical Subsurface Systems. Knowledge of how processes occurring at different levels of a hierarchical system link with each other and control higher-level behavior is essential to understand complex systems. Particularly challenging is the ability to quantify the influence of smaller-scale processes on higher-scale behavior across three main scale transitions: molecular to pore, pore to porous medium, and porous medium to field. Required advances include measuring diagnostic variables indicative of complexity, identifying interactions that lead to complexity, and developing scale transition models.

Understand Integrated System Behavior. The interplay between coupled biogeochemical processes in the presence of *in situ* heterogeneity, complex water flow patterns, and flow transients can lead to complex subsurface system behavior. This behavior is further impacted through linkages with the ecosystem and climate. Prerequisites for successful management of subsurface resources and problems are understanding subsurface complexity associated with the movement and reaction of waterborne solutes over scales relevant for many aquifers, plumes, and watersheds and identifying the patterns and emergent behavior that are shared by many systems and that can be predicted by models. Key challenges that must be addressed include identifying and modeling emergence and other complex behaviors, devising innovative strategies to interrogate large-scale system behavior, and developing phenomenological models for understanding and prediction.

Pursuing these research opportunities will enable us to understand how complex subsurface systems behave, identify the properties and processes controlling them, and predict the various consequential aspects of their behaviors. This new understanding will provide critically needed transferable scientific concepts for managing and manipulating complex subsurface systems at all scales, from the kilometer and above. These contributions are important to multiple DOE mission areas focused on the subsurface environment. Additionally, the proposed scientific direction has significant potential to result in high-impact subsurface science advances and the development of a distinguishing BER leadership capability in subsurface science.

1. Introduction

The subsurface environment, which encompasses the vadose and saturated zones, is a heterogeneous, geologically complex domain. Believed to contain a large percentage of Earth's biomass in the form of microorganisms, the subsurface is a dynamic zone where important biogeochemical cycles work to sustain life. Actively linked to the atmosphere and biosphere through the hydrologic and carbon cycles, the subsurface serves as a storage location for much of Earth's fresh water. Coupled hydrological, microbiological, and geochemical processes occurring within the subsurface environment cause the local and regional natural chemical fluxes that govern water quality. These processes play a vital role in the formation of soil, economically important fossil fuels, mineral deposits, and other natural resources.

Cleaning up Department of Energy (DOE) lands impacted by legacy wastes and using the subsurface for carbon sequestration or nuclear waste isolation require a firm understanding of these processes and the documented means to characterize the vertical and spatial distribution of subsurface properties directing water, nutrient, and contaminant flows. This information, along with credible, predictive models that integrate hydrological, microbiological, and geochemical knowledge over a range of scales, is needed to forecast the sustainability of subsurface water systems and to devise ways to manage and manipulate dynamic *in situ* processes for beneficial outcomes.

Prediction is an important goal of subsurface science because of its connection to water resource management in support of human needs. Predictive models are the primary tools for forecasting the evolving geochemistry or microbial ecology of groundwater under various scenarios and for assessing and optimizing the potential effectiveness of approaches to carbon sequestration, waste isolation, or environmental remediation. These models also are the principal basis for integrating scientific knowledge on multiple environmental systems into a common framework and for translating this information to support informed decision making and policies. Predictive models thus are essential components of subsurface research—providing a context for knowledge integration, a vehicle to demonstrate the degree of system understanding and the sensitivities of outcomes to parameters and processes, and a tool to forecast future system behavior either with or without manipulation. An iterative approach of modeling and experimentation can reveal powerful insights on system behavior. State-of-science understanding codified in models can provide a framework for testing hypotheses and guiding experiment design.

Important disciplinary advances in subsurface science over the past decade have allowed the development of sophisticated models. These models describe chemical migration, microbial population dynamics, and other system responses (e.g., CO_2 release or sequestration) based on molecular and microscopic understandings of geochemical and microbiological processes and their coupling with hydrology. Generally reductionistic in nature, the models describe how multiple processes occurring at the microscopic and mesoscopic scales integrate to control field-scale behavior. For even the simplest of these state-of-science models, obtaining the multiscale characterization data and coupled process knowledge needed to adequately and mechanistically represent subsurface systems is challenging. To date, success has been varied in using reductionistic approaches to predict, with the required accuracy, the behavior of hierarchical subsurface systems.

Despite major scientific and technological advances in subsurface science, there is growing evidence that many environmental systems are not predictable using reductionistic or bottom-up approaches alone. This situation can occur when numerical models based on knowledge of small-scale processes and their interactions are inadequate to describe the way in which the larger system behaves. While reductionism provides foundational understanding of component mechanisms and processes that can robustly describe behavior at the studied scale, these relationships alone may not capture the essence of system function and response at the prediction scale. The "system" may be a single microorganism, a soil or sediment column, a coupled groundwater–surface water domain, or a nuclear waste repository, each containing numerous interactive parts or phenomena. In such cases, either the effects of uncharacterized heterogeneity or the collective responses of linked processes or components can yield new, unpredictable features or behaviors that distinguish the system at higher scale. Systems exhibiting behavior as a result of collective responses are considered complex, and a top-down approach termed *complex systems science* has evolved over the past 25 years to investigate, conceptualize, characterize, and model these system types (Bar-Yam 1997). The approach is analogous to systems biology (Bork 2005; Kitano 2002), which emphasizes the tight coupling between experimentation and modeling and is defined, in the context of Biological Systems Science research programs within DOE's Office of Biological and Environmental Research (BER), as "the holistic, multidisciplinary study of complex interactions that specify the function of an entire biological system—whether single cells or a multicellular organism—rather than the reductionist study of individual components."

Driving the evolution of complex systems science is the need to describe and predict the holistic behaviors of natural and biological systems containing a large number of interacting or interwoven components. Occurring at virtually any scale, these systems are difficult to analyze and understand and exhibit higher-scale features or behaviors not readily derived from the sum of their parts. Key to this is the concept of emergence (Baas and Emmeche 1997; Manson 2001): generally unpredictable behaviors or features arising at higher scale from multiple interactions of different types of processes and phenomena. Emergent behaviors might be different in every system, or they might be the same in many systems. Complex systems science is fundamentally an interdisciplinary and integrative approach seeking to understand the primary interactions that determine emergence and overall system behavior at the prediction scale. Without common disciplinary boundaries, this approach has two goals: (1) identify broadly operative macroscopic laws applicable to different systems and (2) predict system-scale behaviors using phenomenological rather than mechanistic models.

In emergent systems, interactions between many components, which themselves may be complex, result in the self-organized formation of distinctive collective structures, patterns, and behaviors different from those associated with individual components or with systems consisting of only a few components (see examples in *Science* 1999). These structures can be manifest across a broad range of spatial scales, and the behaviors can be summarized by the often quoted statement, "More is different," (see Fig. 1.1. Examples of Collective Structures in Emergent Systems, this page, and Appendix A, Complex Systems Science and Subsurface Complexity, p. 21). The greatest intersection between complexity

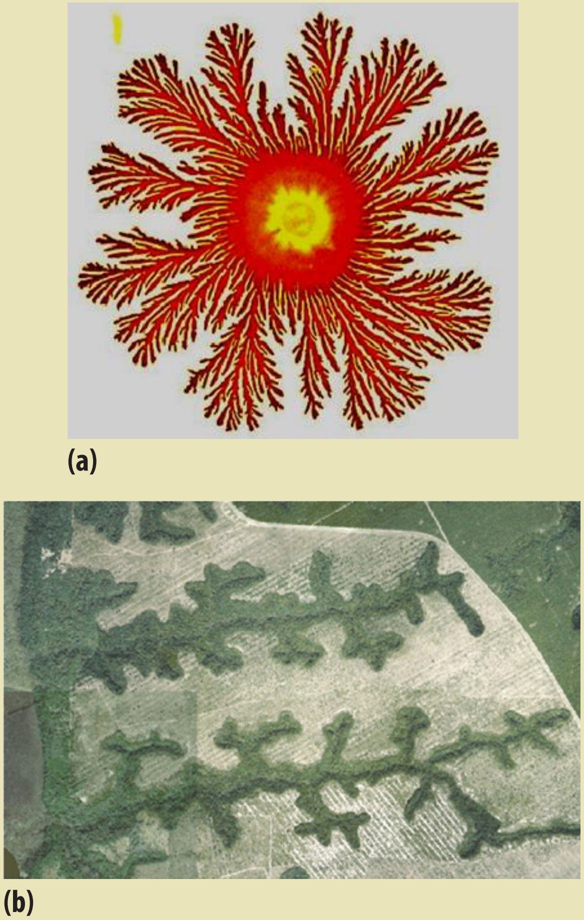


Fig. 1.1. Examples of Collective Structures in Emergent Systems. Self-organizing biological and physical structures are observed across a wide range of spatial scales. Illustrated are patterns observed in association with **(a)** bacterial cell colonies grown in culture [From Ben-Jacob and Levine 2006] and **(b)** river system geomorphology [Published in Howard 2009 courtesy of the Florida Department of Revenue (FDOR). Reprinted by permission from FDOR and Macmillan Publishers Ltd: *Nature Geoscience*. See also Abrams et al. 2009]

science and subsurface science is likely to be found through exploring the causes for and implications of emergence, self-organization, and collective behaviors. While a reductionist approach is applicable in theory, it may not be practical when many components act together and with their environment to generate distinctive structures and behaviors. The differences between complicated and complex systems (see Appendix A) are debated often. However, making this distinction may not be necessary or productive for subsurface systems that are inherently heterogeneous, difficult to characterize and observe, and challenging to understand and model.

The subsurface is characterized by multiple processes operating in a heterogeneous physical framework (see Fig. 1.2. Commonplace Heterogeneities in Physical Properties Resulting from System Geological Processes, this page, and Fig. 3.1. Three Research Opportunities and Selected Challenges, p. 9). These processes function and interact over a hierarchy of scales ranging from the sub-nanometer to kilometer, and their outcomes are spatially variable because of heterogeneity. Even one of these processes alone can exhibit complex behavior. For example, fluid-fluid displacement processes are well known for their ability to generate fractal patterns in homogeneous porous media. These complex fluid-fluid displacement patterns and their three-dimensional counterparts can be simulated using simple models such as the diffusion-limited aggregation model and the invasion percolation model (Witten and Sander 1981; Wilkinson and Willemsen 1983). While these models predate modern complexity approaches, their strategies in describing the higher-level aspects of behavior are similar to those now used in complex systems science (Boccara 2004; Shalizi 2006). Subsurface microorganisms, in particular, possess attributes of complex systems, including (1) properties (i.e., phenotype) not fully explained by component parts (i.e., genotype), (2) dynamic biochemical processes that adapt when subject to evolutionary forces, and (3) robustness arising from adaptation to change that may occur through redundant components able to compensate if primary components fail. The widespread coupling of microbiological, hydrological, and geochemical processes in the subsurface may yield daunting complexity, such as feedback mechanisms, memory effects, and nonlinear behavior at multiple scales. Consequently, collective behavior and self-organization are expected to be common in the subsurface, with emergent features evolving at different scales.

Fig. 1.2. Commonplace Heterogeneities in Physical Properties Resulting from System Geological Processes. Subsurface physical heterogeneity, such as the variations in grain size and sedimentary structure shown here, influences the distribution of fluids, geochemical reactivity, and microbiological activity. Such heterogeneity, coupled with the observational constraints associated with subsurface systems, poses challenges for developing a predictive understanding of emergent behaviors at larger scales. [Courtesy Andy Ward]

In applying the concepts and methodology developed in complex systems science to the subsurface, the interplay between heterogeneity and collective (emergent) behavior is expected to be important and challenging. New research approaches and sensing technologies will be necessary for acquiring a comprehensive understanding, and the development of new experimental, analytical, and modeling methods will be required to detect, quantify, and interpret self-organized spatial and temporal patterns in the subsurface. Also needed are new ways to recognize and quantify emergent behavior to enable us to focus on important systems for which understanding and prediction can be obtained without relying completely on a bottom-up strategy. Addressing these needs will allow identification of systems-level patterns or behaviors that are repeatedly observed in spite of differences in system-specific environmental variables or characteristics. These common behavioral patterns are key findings because they represent a reality that our models must reproduce. Although the exact positions or magnitude of subsurface components may not be predictable, there often will be patterns of important properties or behaviors that are. Understanding the controls on these patterns and building models that describe and predict them are important long-term research goals.

Complementary top-down and bottom-up approaches that include iterative experimentation and modeling are required to evaluate hypotheses on key interactions controlling system behavior. Also needed are subsystem-level concepts and understandings that are based on knowledge of molecular mechanisms but do not require their explicit upscaling for systems-level predictions. New concepts on the function of hierarchical, multiprocess systems that comprise the subsurface must be developed along with ways to effectively characterize and describe such systems in the context of heterogeneity. The anticipated scientific impacts of resolving these research needs are sizeable and include the identification of underlying interactions, principles, and natural laws governing the behaviors of complex subsurface systems of different types (e.g., Murray 2003; Murray 2007). Beyond this, the expected development of new, pragmatic modeling approaches will enable more-robust and defensible systems-scale predictions at the spatial and temporal scales necessary to effectively and sustainably manage subsurface systems for human needs and to protect human health.

This document reports on the DOE BER workshop, Subsurface Complex System Science Relevant to Contaminant Fate and Transport, held August 3–5, 2009, in Gaithersburg, Maryland. The workshop evaluated complex systems science as a potential new approach for subsurface science research. Although comparable approaches have been described as a new direction in environmental biology (Raes and Bork 2008), subsurface science as a discipline exhibits significant differences from this area of biology. These differences include the nature of key science questions and issues, system scale range and framework, types and diversity of interactive processes, accessibility to observation, and need for prediction. Thus, workshop goals were to (1) broadly assess with the subsurface research community the merits and limitations of the complex systems science approach; (2) determine how its concepts might be implemented in subsurface science research; and (3) identify new subsurface research gaps, needs, and opportunities.

In this report, we summarize proceedings of the workshop then present its primary findings. The findings include (1) research needs to integrate concepts of complex systems science into subsurface science research and (2) new scientific opportunities and challenges whose solutions significantly could advance the predictive capability and state of science for such research. We conclude with a description of potential implementation strategies and anticipated benefits. The report is supported by appendices that provide a technical basis for the research needs and opportunities described in the report core. In addition, the appendices describe the scope and goals of complex systems science and characteristics of complex systems (see Appendix A, p. 21). Also discussed are examples of complex subsurface systems and an evaluation of the merit of the complex systems science approach for the subsurface environment (see Appendix B, Complex Subsurface Systems and Merit of Approach, p. 29).

2. Workshop Objectives and Content

The BER workshop on Subsurface Complex System Science Relevant to Contaminant Fate and Transport was motivated by recognition that subsurface systems at all scales display great complexity and often are difficult to predict. Participants explored the question of whether the tenets of complex systems science are applicable to and could advance scientific understanding and prediction of subsurface systems. Overall workshop objectives were to

- Define complex subsurface systems, identify their distinguishing features, and establish why they are important to different DOE mission outcomes.
- Consider how the coupling of subsurface geochemical, microbiological, and hydrological processes defines complex system response and dynamics, and identify research needs and gaps to advance understanding of important disciplinary and interdisciplinary science issues associated with subsurface complexity.
- Evaluate the need for new research approaches that identify and account for the influence of smaller-scale processes and their mechanisms on larger-scale system behavior.
- Conceptualize models and associated knowledge needed to describe and predict complex system behavior at different scales.
- Identify significant long-term interdisciplinary research opportunities associated with complex subsurface systems.

The workshop consisted of a plenary session with lectures on various aspects of and perspectives on complex systems science followed by three breakout sessions (see Appendix C, Workshop Program, 43). Specific topics were discussed during each breakout session, including (1) the identification of relevant complex subsurface systems and their key functional components; (2) major disciplinary research needs that could enable the characterization, monitoring, understanding, and prediction of such systems and components; and (3) the research required to integrate knowledge and models of these systems and their interactive components across scales for improved field-scale predictions. An important outcome for the workshop was to identify new interdisciplinary approaches, concepts, and research needs for subsurface science that address the high degree of process coupling, complexity, and heterogeneity existing in the subsurface.

Workshop participants included scientists from universities and DOE national laboratories with a broad range of expertise in the environmental, microbiological, Earth, and marine sciences as well as in complex systems science. Researcher experience and perspectives spanned mechanistic investigations at the molecular level to intermediate-scale laboratory studies to field studies of natural environments ranging in scale from meters to kilometers. Experts in modeling and experimental science were well represented, and all participants generally were proponents of the merits of interdisciplinary research. BER-invited observers from other DOE offices and government agencies were important members of the audience (see Appendix D, Workshop Participants and Observers, 45).

This report represents the primary product of the workshop. It is not intended to be a research plan for BER's Subsurface Biogeochemical Research activity but rather speaks only to how complex systems science concepts may be implemented within the overall program. The writing team attempted to capture the spirit and content of workshop deliberations focused on the complex systems science approach and to consistently and logically summarize often diverse perspectives and recommendations about scientific need. The topic of complexity and complex systems science does have semantic and conceptual ambiguities discussed in Appendix A, Complex Systems Science and Subsurface Complexity, p. 21. Attempts were made in report preparation to meld the concepts and vernacular of complex systems science with those of subsurface science in Appendix B, Complex Subsurface Systems and Merit of Approach, p. 29, since this issue was debated during the workshop. Technical results of the workshop—supported by citation and post-workshop conceptual analysis—are summarized in Appendix B, with emphasis on the merits of the complexity approach for subsurface systems.

The need for a new interdisciplinary scientific approach and the research gaps, requirements, and opportunities identified as primary workshop outcomes recognize the subsurface as a complex system. This new perspective for subsurface science will face technical challenges in implementation. However, potentially large scientific payoffs may result—for BER's Subsurface Biogeochemical Research activity and for subsurface science in general.

3. Research Opportunities for Subsurface Environmental Systems Science

Scientific study often relies on either bottom-up or top-down approaches and methods. These differ in philosophy and strategy and impact the types of data collected and the nature of conceptual and numerical models developed (see Appendix B, Complex Subsurface Systems and Merit of Approach, Table B.2, Characteristics of Reductionistic and Complexity Approaches, p. 41). The primary goal of the bottom-up, reductionistic approach is to quantify lower-scale fundamental mechanisms, processes, and their interactions. Working upward, reductionistic approaches conceptualize and model system behavior as the result of its lower-scale components and their interactions. In contrast, top-down, complex systems approaches strive to identify diagnostic variables defining high-level system behavior. Working downward, complexity approaches conceptualize and model critical subscale interactions and environmental variables that control system behavior, with an objective to identify transferable macroscopic laws and relationships. Both approaches have value and merit, and each provides unique scientific insights on different aspects of complex system behavior. Given the complexities of the subsurface, it seems prudent to explore the intersection of the two approaches and ways that they can be integrated to provide a more holistic understanding and prediction of system behaviors.

Several Earth science disciplines have explored complex systems approaches for describing emergent and self-organizing behavior, including ecology (Harte 2002; Grimm et al. 2005), landscape geomorphology (Murray and Fonstad 2007), and watershed surface hydrology (Sivapalan 2005; McDonnell et al. 2007). Relative to subsurface science, these fields benefit from data accessibility, such as the ease of collecting samples from or making measurements on Earth's surface or retrieving data collected from satellites. The rich datasets facilitate, for example, recognizing patterns or classifications, exploring the connection between patterns and processes, and testing models that describe complex system behavior.

Perhaps because of inaccessibility, subsurface investigations have been predominantly reductionistic in nature. This approach has led to improved understandings of fundamental microbiological, geochemical, and hydrological processes. However, the reductionistic approach has met with limitations when used to study the integrated behavior of subsurface systems, which are characterized by multiple hydrological, geochemical, and microbiological processes occurring at different scales; significant heterogeneity; and measurement and observational constraints. Although complexity science offers potential for improving our systems-level understanding, unclear is how measurement networks might be developed to identify complex behavior or how models common to complexity would be formulated for reactive subsurface systems.

However, now evident is that subsurface science encompasses systems-level and specialized disciplinary (e.g., microbiology, geochemistry, and transport) challenges requiring broad and diverse knowledge of processes couplings, hierarchies, and controlling properties and features. Consequently, applying multidisciplinary expertise and multiple scientific approaches is now necessary to investigate the high level of complexity commonplace in the subsurface. Workshop discussions supported the need for a hybrid approach in which complexity and reductionistic approaches would be integrated to achieve major advances in the understanding and prediction of subsurface systems. A hybrid approach melding select strengths of both approaches is needed to enable the understanding of key underlying mechanisms and their interactions while simultaneously providing insights on scale transitions and macroscopic rules that govern system behavior at a larger scale. Needed elements of the hybrid approach are

- Integrative, multidisciplinary investigations of subsurface systems to identify common behavioral patterns observed at different scales, regardless of exact system characteristics, and the variables controlling these patterns. This includes identifying features that are diagnostic of complexity and components that control system behavior, determining key process and component interactions that cause emergence or other complex behaviors, and developing and evaluating top-down system models and their predictive power.

- Complementary experimental, theoretical, or field studies of key components or controlling variables of subsurface systems in which important process interactions and their controlling mechanisms are quantified and modeled at lower scales for comprehensive understanding. Upscaling research is performed to learn about scale transitions in hierarchical systems and to discover how to deal with them in the absence of emergence. Simplified abstractions of processes and their interactions are derived to constrain or enrich top-down models.

Three interdisciplinary Research Opportunities (see Table 3.1, this page) were identified at the workshop to improve scientific understanding of complex subsurface systems and their key component interactions (see Fig. 3.1. Three Research Opportunities and Selected Challenges, p. 9). Each Research Opportunity has associated challenges (or research gaps) whose solutions hold potential for high-impact subsurface science. Implicit to all three is a hybrid research approach integrating complex systems concepts with reductionism through iterative modeling and experimentation. These Research Opportunities emphasize hierarchical subsurface systems; the quantification of inter- and cross-scale process interactions (from the molecular to field scale); and integrated, systems-level behavior. Crucial overall research needs are to identify, quantify, and understand emergent behavior and variables diagnostic of such behavior using both top-down and bottom-up approaches. Briefly presented in the sections below are the rationales for selecting each Research Opportunity and a discussion of their key challenges and potential research approaches.

Research Opportunity 1: Fundamental Process Coupling

The coupling of microbiological, geochemical, and hydrological processes exerts a primary control on the chemistry of subsurface systems. This coupling is fundamental to all DOE mission areas concerning the subsurface, and the intimacy of it is great and multidimensional, involving feedback mechanisms at different scales. Water movement delivers nutrients that drive subsurface microbiological activity. This, in turn, influences system geochemistry through oxygen fugacity, pH, mineral dissolution, and other effects. Physical heterogeneities influence water flow paths and travel times and the distributions of microorganisms and geochemical (solid, solute) reactants, thereby controlling the rates and directions of biogeochemical reactions. Microorganisms adapt to their environment but also change it in multiple ways, leading to pathway-specific memory effects.

Research Opportunity 1 identifies challenges associated with four specific coupled processes playing significant roles in complex subsurface system behavior. The first two challenges involve microbiology-geochemistry interactions occurring on scales ranging from the suborganism to the microbial community on mineral surfaces and within the pores and fractures of sediment particles. Challenges three and four focus on the scale where marked variations in subsurface hydro-

Table 3.1. Improving Scientific Understanding of Complex Subsurface Systems

Research Opportunity	Challenge
1. **Fundamental Process Coupling**	A. Coupled Mineral-Microbe Interfacial Processes
	B. Microbial Community Responses to Dynamic Subsurface Conditions
	C. Biogeochemical Reaction Rates in Heterogeneous Media
	D. Feedbacks Between Biogeochemical Transformations and Flow
2. **Scale Transitions in Hierarchical Systems**	A. Measurement Approaches for Key Variables and Diagnostic Signatures
	B. Identification of Smaller-Scale Controlling Variables
	C. Scale Transition Models
3. **Integrated System Behavior**	A. Identification of Field-Scale Emergent Phenomena Using Numerical Modeling
	B. Strategies for Interrogating Large-Scale Behavior
	C. Phenomenological Models for Prediction

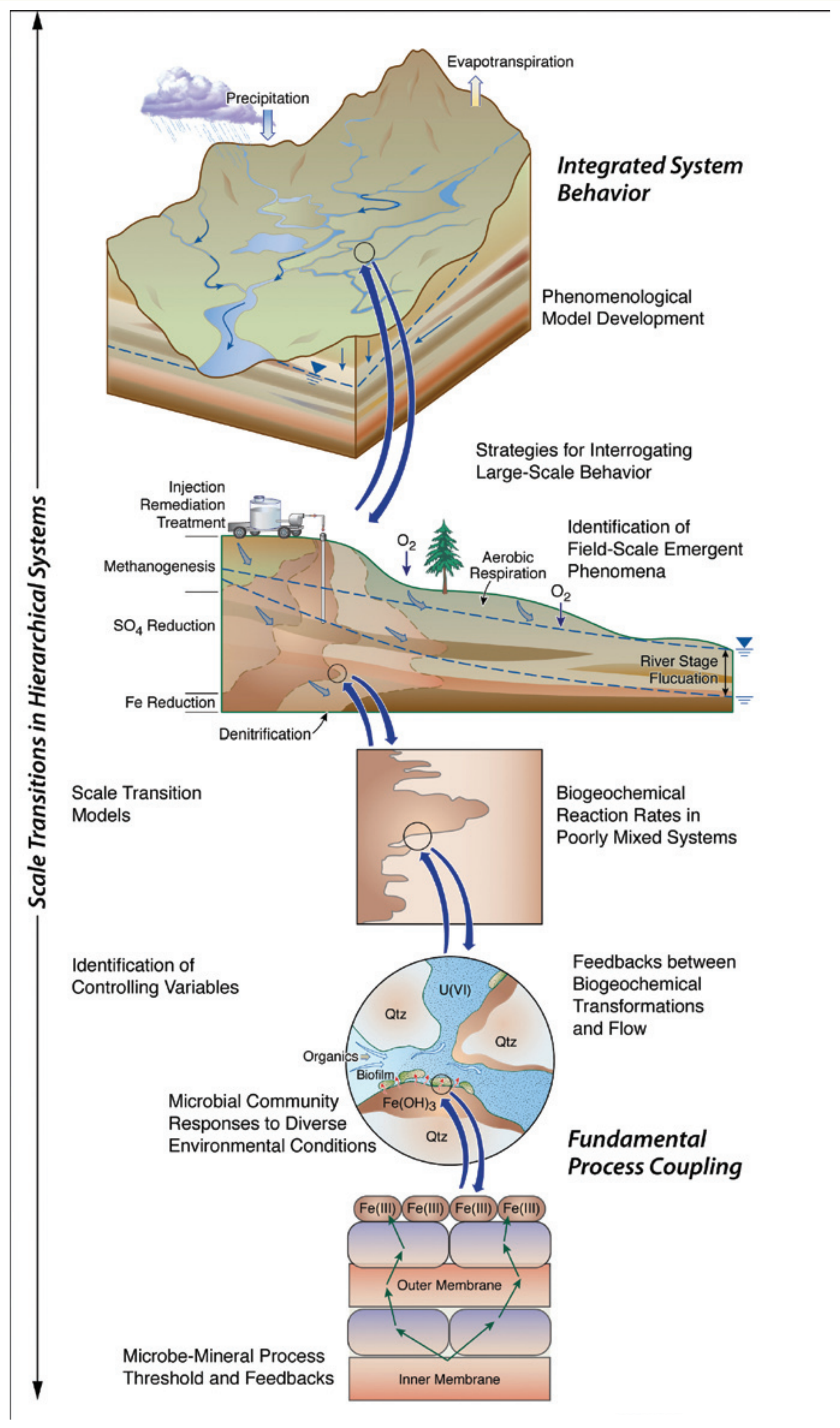


Fig. 3.1. Three Research Opportunities and Selected Challenges. The subsurface is characterized by multiple processes occurring on different spatial scales and operating within a heterogeneous physical framework. Investigation of the identified Research Opportunities (shown in bold) and their associated challenges using a hybrid approach is expected to improve scientific understanding of complex subsurface systems. [Graphic courtesy Susan Hubbard]

geological and mineralogical properties occur over distances of centimeters to meters (e.g., see Fig. 1.2. Commonplace Heterogeneities in Physical Properties Resulting from System Geological Processes, p. 3), causing zones of reduced accessibility, poor mixing, or differential reactivity. Fundamental process coupling related to these cases is emphasized as it occurs in the presence of water flow or geochemical transients where the interplay between biogeochemistry, *in situ* heterogeneity, and advective and diffusive processes can lead to emergent subsurface system behavior. The four challenges for Research Opportunity 1 are described briefly below.

A. Coupled Mineral-Microbe Interfacial Processes

Mineral-microbe interactions are not easily predicted from knowledge of individual cellular components and mineral properties, and process interactions often change dramatically in response to evolving system characteristics (see Appendix B, p. 29). The bottom-up characterization of the interfacial region between microorganisms and reactive solids is a current topic of investigation in Subsurface Biogeochemical Research. New complexity concepts are needed to extend the current research scope to include dynamic and complex interfacial processes involving multiple interactive microorganism types and the bio-organic structures they create. These new concepts should encompass issues like physiological adaptation, evolution, biofilm formation and function, bioweathering, and biomineralization. One significant need is determining how microscale biological, chemical, and physical interactions control macroscale processes, such as the formation and dissolution of minerals (see Fig. 3.2. Microorganisms Involved in the Formation of Minerals, this page).

In systems biology, advances have been made in collecting global datasets of gene activity and protein expression and applying these data to predict cell gene regulatory and metabolic networks. However, such measurements have been taken on populations of cells and assume homogeneity. The ability to make biological, physical, and chemical measurements at very small scales is critical because the interfacial region between living cells and mineral surfaces can

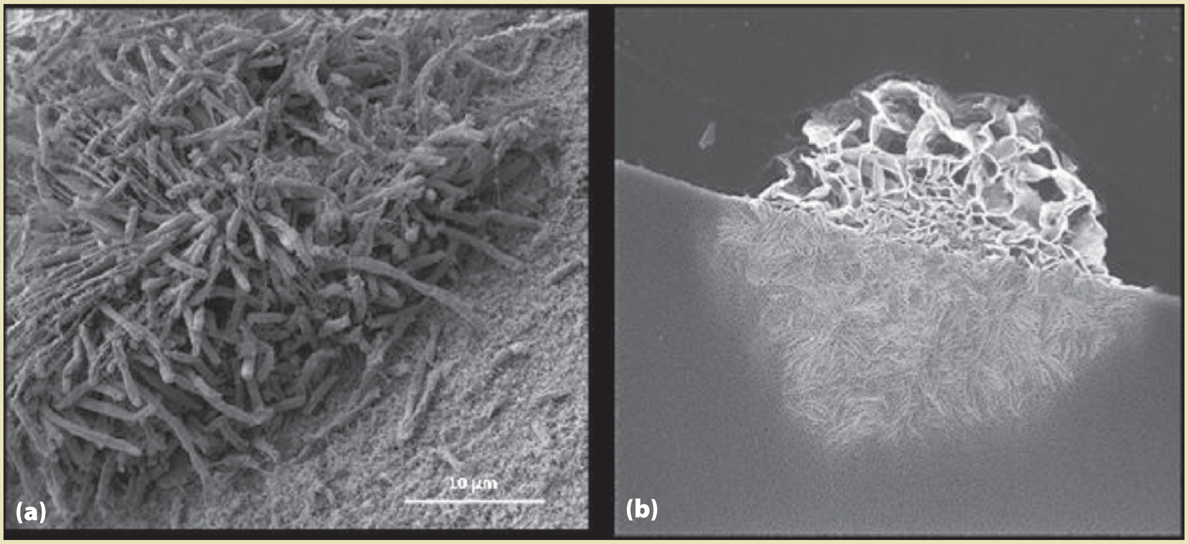


Fig. 3.2. Microorganisms Involved in the Formation of Minerals. These interactions occur through poorly understood microenvironment effects at the microbe-mineral interface. Often the mineral forms demonstrate complex morphology and highly organized structures. Colonies of microorganisms can extract insoluble iron oxide forms from physically inaccessible internal domains of porous silica (**a**) and precipitate them in highly ordered iron phosphate forms [the colony and bioprecipitate (**a**) is shown in cross-section in (**b**)]. The 40-µm crystal shown in (**b**) grows upward into the aqueous phase and downward into the porous mineral substrate from the active colony of microorganisms. [From Peretyazhko et al. 2010, in review. Copyright Elsevier]

be on the order of tens of nanometers and concentration gradients can be steep. New techniques are required to (1) characterize component distributions and interactions (such as co-visualization of cells, key proteins, and mineral solids) and their spatial and temporal variations in the context of local hydrochemical environments; (2) place molecular-level information (e.g., gene expression at the single-cell level) into a spatial and functional context; and (3) measure *in situ* reaction rates. Another recognized research need is the development of statistical methods for analyzing highly multivariate data from multiple sources with differing levels of technical error and spatial resolution.

B. Microbial Community Responses to Dynamic Subsurface Conditions

Subsurface microbial communities exhibit complex behavior resulting from the collective interactions between phylogenetically and metabolically diverse microorganisms and their local microscopic and macroscopic environments (see sidebar 3A, BER's Rifle Integrated Field Research Challenge Site, this page). An important scientific need is to understand how microbial communities respond to dynamic physical and geochemical perturbations commonly occurring in shallow subsurface environments. Systems-level laboratory and field experimentation should be tightly coupled with new top-down modeling strategies to address the following questions:

- Which environmental variables control microbial community structure and function?
- What are the relationships between structural and functional heterogeneity in microbial communities, and how do these relate to the changing properties of the physical and geochemical environment?
- Which forces drive or limit adaptation of individual populations and the microbial community to changing environmental conditions?

Tackling such research needs will allow the prediction and manipulation of specific microbiological activities to achieve desired outcomes in a broad range of subsurface environments.

Sidebar 3A

BER's Rifle Integrated Field Research Challenge Site

The Rifle project has been manipulating the biogeochemical conditions of a shallow, uranium-contaminated aquifer along the Colorado River using local acetate injection into groundwater. Acetate functions as an electron donor for specific organism types (iron and sulfate reducers) and stimulates their activity to reduce and immobilize dissolved contaminant uranium. Stimulation causes major changes to the subsurface microbiological community. These changes have been monitored during and after injection to provide insights on the community profile and its members' relationships to terminal electron acceptor transitions, sediment properties, and groundwater chemistry. Related patterns of simulated microbially mediated acetate consumption and precipitate evolution within the Rifle aquifer are shown in Fig. B.4. Plan View, Model-Computed Map of Acetate and Bromide Transport, p. 35, and Fig. B.5, p. 36. Remote monitoring of the biogeochemical transformations using geophysical methods is shown in Fig. 3.4. Example Illustrating Use of Time-Lapse Geophysical Data to Quantify Microbially Mediated Precipitate Evolution and Permeability Reduction, p. 15, and in Fig. B.6, p. 37. Although the overall scientific strategy has similarities to the hybrid approach (and includes aspects of biological systems science), new methods are needed that permit interrogating and predicting the impact of subsurface community dynamics on overall system behavior manifest at larger spatial scales (see Appendix B, p. 29).

[Image courtesy Phil Long]

High-throughput technologies now permit the gathering of large biological datasets of target microorganisms (typically in laboratory-controlled systems), and significant achievements allow *in situ* genome-level measurements of microbial communities. However, interpreting these data poses challenges, and often only a fraction of the collected data is used. Improving systems-level understanding thus requires new or enhanced data analysis methods for pattern recognition, statistical analyses, data mining, data integration, and gene annotation to integrate geochemical and physical information with "omics" information (e.g., metagenomic, metatranscriptomic, metaproteomic, and metabolomic data). The development of learning models also could lead to important improvements in data interpretation. Placing metaomics measurements into a spatial and temporal context at appropriate scales is key to investigations of subsurface microbial communities and ecosystem biology in general.

Several other research requirements involving microbial community dynamics were identified as potentially valuable. Model communities need to be established to facilitate experimental manipulation and hypothesis testing under well-defined and controlled environmental conditions. Also needed are methods to improve quantification of the rates of *in situ* microbial activities and approaches to connect the various biological components provided via global measurements (such as metaomics approaches). Prioritizing isolation and characterization activities of microbial populations using metaomics approaches is required to identify the subset populations affecting larger-scale behavior. Another high research priority is moving beyond a descriptive understanding of microbes to models that can accurately predict microbial community–wide interactions and responses to environmental perturbations at a systems level.

C. Biogeochemical Reaction Rates in Heterogeneous Media

Subsurface heterogeneity strongly influences system-wide distribution of chemical components and microbial catalysts, the time scales of reactions, and biogeochemical reaction rates (see Fig. 3.3. Tracer Experiment Performed at the Hanford IFRC Field Site, this page). Heterogeneity causes gradients in concentration and rates; it leads to incomplete mixing of reactants at both the pore scale (due to diffusion

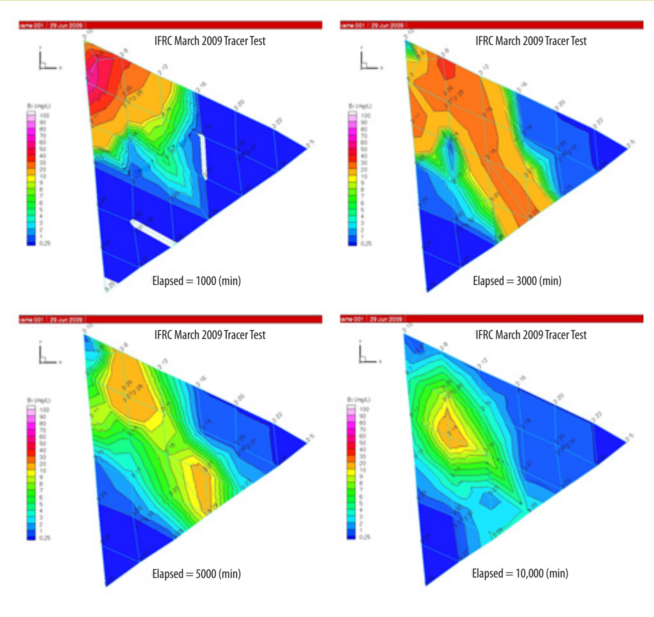


Fig. 3.3. Tracer Experiment Performed at the Hanford IFRC Field Site. Further described in Appendix B, p. 29, the experiment involved injection of nonreactive tracer (red) into the saturated zone near the upper left corner of the 60-m triangular field, which is instrumented with 37 wells. The color contour maps indicate the tracer movement through the well field from 1000 minutes (top left) to 10,000 minutes (bottom right) after injection. Groundwater flow moves from the upper left to the lower center of the triangle. Evident at the later periods of the experiment is a mass transfer–limited domain (lower right panel) that retains the tracer for long periods. Although ongoing submicron- (not shown) to decameter-scale process investigations at the Hanford IFRC are illuminating the hierarchy of existing mass-transfer domains (see Appendix B), a systems approach could lead to an understanding of emergent behavior that may be critical for understanding long-term plume mobility.

limitations) and the field scale (due to preferential flow paths). Complex kinetic processes in heterogeneous subsurface systems depend on the *in situ* rate of coupled reaction and transport and on the rates of mass transfer to and from points of reaction. Mass transfer rates are dynamic, scale dependent, and time variable. Overall reaction rates observed in these poorly mixed, heterogeneous media often are slower than those observed in the laboratory, leading to large uncertainty in field-scale numerical simulations.

Research is needed to measure, understand, and model biogeochemical reaction rates in heterogeneous subsurface environments having different physical and geochemical character and different microbial communities. Controlled experiments in laboratory-constructed heterogeneous systems and in natural systems are needed to quantify scale-specific and averaged transport and reaction rates in the presence of heterogeneity. Related requirements are the development of measurement approaches that can assess *in situ* reaction rates and a better understanding of measurement volume averaging or proxy signatures associated with indirect measurement approaches.

D. Feedbacks Between Biogeochemical Transformations and Flow

Biogeochemical processes can lead to mineralogical changes (e.g., precipitation or dissolution) and biological transformations (e.g., biofilm formation or the generation of gas or extracellular polymeric substances) that impact pore space and fluid flow. These transformations occur at the pore scale, but their impacts are strongly manifest at the mesoscopic and field scales as discussed in Appendix A, Complex Systems Science and Subsurface Complexity, p. 21 (Englert et al. 2009; Li et al. 2009). The interplay between biogeochemical transformations and water advection exhibits intermittent and threshold-governed feedbacks characteristic of complexity.

Important research gaps are quantifying and modeling the process coupling between nonlinear biogeochemical reactions and transport that leads to complex system behavior. Experimentation is needed in which the biogeochemical system is perturbed in ways resulting in mineral precipitation or dissolution and microbial growth across scales. Feedback mechanisms with water advection must be better understood, and new models explaining and describing noted behaviors are required. Resolving these research needs will provide new insights on the dynamic relationships between biophase and biomineral structure and distribution, biogeochemical reaction kinetics, heterogeneity structures, porosity, permeability, tortuosity, and reactive surface area relevant for pore- to field-scale system understanding.

Research Opportunity 2: Scale Transitions in Hierarchical Systems

Knowledge of how processes occurring at different levels of a hierarchical system link with each other and control higher-level behavior is key to understanding complex systems. A critical gap is defining how the effects of process interactions are translated within and modulated across scales. Goals involve identifying and quantifying lower-scale processes that control higher-scale behavior and determining which information about them is necessary to understand emergent system features. For example, experiments (based on our current understandings) are required to identify diagnostic, measurable signatures of effective system response. Drawing on statistical approaches or complex systems analytical tools (see sidebar 3B, Applying Complexity Science Tools, p. 14), new model types are needed that explicitly consider the process, parameter, and scale hierarchies leading to complex behavior.

Transitions within and across three scale ranges need to be considered. The *molecular to pore scale* is the traditional realm of continuum and statistical mechanics. For many well-defined systems, continuum descriptions can be obtained that accurately represent the behavior of complex molecular systems. Although this is perhaps the best understood scale transition of the three, major scientific challenges remain for fundamental biological and geochemical process-coupling research. The *pore to porous medium scale* transition moves from the scale of discrete grains and pores—where continuum mechanics of separate phases can be applied—to the scale of an effective porous medium, where explicit pore geometry is disregarded. In traditional numerical models of subsurface systems, the properties and processes are homogenized

Sidebar 3B

Applying Complexity Science Tools

Complex systems science methods (e.g., Shalizi 2006) can be broadly defined in two categories: methods for analyzing high-dimensional, multivariate datasets and methods for modeling complex systems.

In the first category, statistical learning and data mining methods seek to infer reliable predictive models from large datasets with strongly dependent variables by identifying data patterns. Specific model architectures include neural networks, splines, classification trees, and support vector machines. Methods such as regularization, cross-validation, and structural risk minimization are used to determine the appropriate level of model fit and parameter tuning. Time-series analysis methods include those that envision time series as random samples of underlying stochastic processes (e.g., auto-regressive moving average models), as well as newer methods of nonlinear dynamics that conceptualize time-series data as being generated by a deterministic process with added noise.

Cellular automata (CA) and agent-based models are the most well known in the second category of complexity science tools. CA methods simulate changes in discrete states at each grid cell on discrete time intervals by applying simple transition rules to each cell based on the current states of a limited set of neighboring cells. By specifying rules appropriately, emergent behavior at macroscopic scales can be efficiently simulated. Agent-based models can incorporate the behavior of individual discrete entities and their interactions, where an entity might be an organism or a molecule, as opposed to aggregated (population-level) simulation. These models are particularly useful when individual history or heterogeneity in individual states or behaviors is important to overall system outcomes.

or averaged over a representative elementary volume (REV), within which variations no longer are considered explicitly. One example issue, therefore, is how to handle incomplete mixing of reactants and phases at sub-REV scales, particularly for cases in which reaction rates are nonlinear with respect to local concentration. The final transition is that from *porous medium to field scales*, where recent research has focused on resolution (or stochastic representation) of spatiotemporal heterogeneity and its impact on long-term contaminant behavior. Three challenges are identified within Research Opportunity 2.

A. Measurement Approaches for Key Variables and Diagnostic Signatures

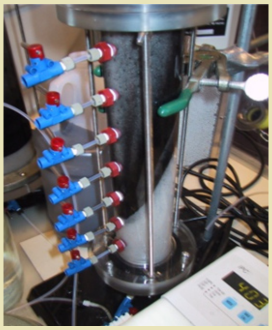
Approaches are needed to measure the features and variables indicative of integrated or macroscopic system behavior at the prediction scale. Emphasis is placed on developing experimental, analytical, or model-based methods that identify and quantify complexity measures such as diagnostic signatures of emergent system behavior. Example research in this challenge might investigate the energy and material balance of representative biofilms to understand their function as dynamic sources and sinks for subsurface chemical agents and nutrients.

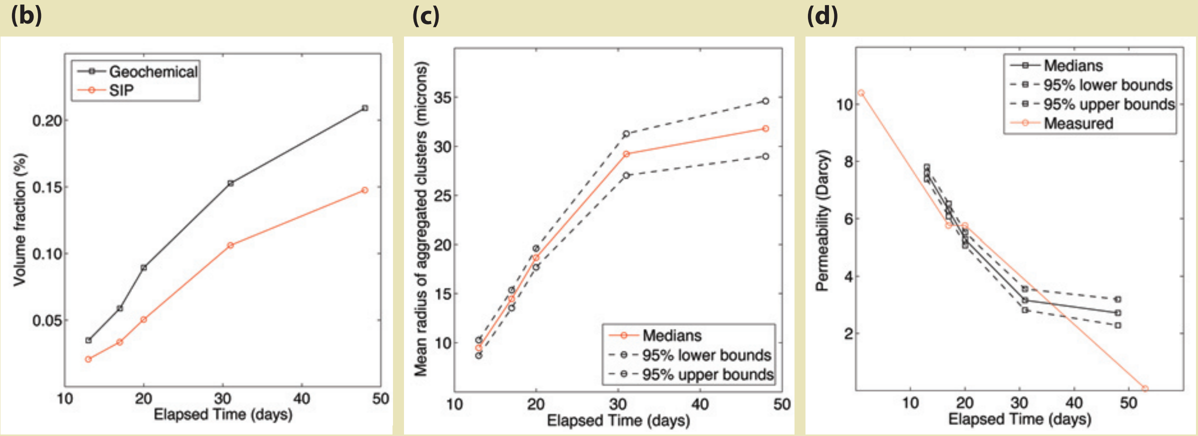
Other needed research is the development of new imaging or interpretation methods for exploring the response of a microbial community to a transition in geochemical conditions across scales. Examples include quantifying geophysical (see Fig. 3.4. Example Illustrating Use of Time-Lapse Geophysical Data to Quantify Microbially Mediated Precipitate Evolution and Permeability Reduction, p. 15) or isotopic signatures diagnostic of critical complex system controls, transitions, and behaviors.

B. Identification of Smaller-Scale Controlling Variables

The robust determination of the integrated or macroscopic behavior of a complex hierarchical system naturally motivates and guides more-detailed hypotheses on processes and variables responsible for system response. These processes and variables may occur at the prediction scale or originate at much smaller scales, with their effects propagated upward through multiple

Fig. 3.4. Example Illustrating Use of Time-Lapse Geophysical Data to Quantify Microbially Mediated Precipitate Evolution and Permeability Reduction. (**a**) Spectral Induced Polarization (SIP) geophysical data were collected synchronously with geochemical data during a Rifle-based column-scale biostimulation experiment. The geophysical data were used within an estimation framework to quantify: (**b**) the volume fraction evolution of microbially mediated FeS precipitates, (**c**) the dynamics of precipitation aggregation, and (**d**) the associated reduction in permeability caused by the biostimulation. Figures (**b**) and (**d**) compare the geophysically obtained estimates with measured geochemical and hydrological measurements, respectively. This study illustrates how diagnostic geophysical signatures potentially can be used to quantify biogeochemical transformations and feedbacks on flow characteristics in subsurface domains where these direct measurements are difficult to obtain. Examples of time-lapse SIP data collected during field-scale environmental remediation at the Rifle site are given in Appendix B, p. 29. [Figures b–d modified from Chen et al. 2009. Reprinted with permission from the American Geophysical Union]


(a)



scale transitions. Many biogeochemical reactions follow this pattern. For example, adsorption or desorption and oxidation or reduction are molecular-level processes, yet their effects on chemical migration can be clearly visible at the field scale through measurement of the aqueous concentrations of diagnostic variables (e.g., dissolved uranium). This challenge builds on the preceding one to identify (1) microscopic components and processes exerting primary control on observed overall system behavior and (2) process, parameter, or hierarchy interactions causing emergence.

For this challenge, research is needed to identify—within and across process hierarchies or scale transitions—the signatures of process interactions or effective system response in DOE-relevant subsurface systems. Associated research might include, for example, quantifying which critical properties or environmental conditions control biofilm or precipitate evolution at the pore scale or redox zonation or contaminant fluxes at the aquifer scale. Iterative comparison of experimental results with process modeling is needed to identify the components and processes that most critically impact larger-scale behavior and the most effective ways to describe them and their interactions in a systems context.

C. Scale Transition Models

Needed developments are models describing how processes and phenomena at different scales influence and couple with each other in hierarchical systems. The models and approaches might be mechanistic, mathematical, statistical, or phenomenological in nature. New variants of volume averaging, hybrid mixture theory, statistical and continuum mechanisms, and decomposition methods are necessary for addressing scale translations from the pore to the porous medium. These advances also are needed to integrate molecular biogeochemical process information into pore-scale descriptions of reactivity. Because subsurface systems may not exhibit distinct scale separations but rather gradations, new methods or scaling approaches are required to account for a continuum of evolving heterogeneity within or across scales. A variety of complex systems science tools and methods holds promise for this research (see sidebar 3B, Applying Complexity Science Tools, p. 14).

Research Opportunity 3: Integrated System Behavior

Research Opportunities 1 and 2 focus on scales ranging from submicrons to the multimeter-field scale, the latter of which generally represents a small fraction of the aerial extent of many plumes, aquifers, or watersheds of concern (e.g., compare Fig. 3.3, p. 12, and Appendix B, Fig. B.1. The 300 A Uranium Plume at the Hanford Site, p. 32). Within DOE energy and environmental mission areas, an acute need involves understanding and predicting the temporal and spatial dynamics of larger-scale subsurface systems as a whole and describing, with reasonable accuracy, their interactions with other linked environmental systems (e.g., surface waters and uncontaminated zones), ecosystems, climate, and human populations (see Appendix B, p. 29). These systems pose great challenges for understanding and prediction because of large, up-front data and monitoring demands requiring both time and resources to acquire. Complex systems science methods may provide an effective means for system conceptualization to optimize characterization and data collection efforts, thereby maximizing scientific and predictive impact.

Research Opportunity 3 seeks to move beyond our current mode of subsurface investigation and prediction to explicitly characterize and simulate subsurface hydrological, geochemical, and microbiological properties and processes with as much detail as possible. New strategies are needed for studying the integrated behavior of poorly described but extremely important large-scale systems, such as dynamic and static groundwater plumes. This Research Opportunity focuses on the three challenges described below.

A. Identification of Field-Scale Emergent Phenomena Using Numerical Modeling

Both bottom-up and top-down strategies exist for modeling the integrated response of complex, hierarchical systems (Murray 2007). Modelers using bottom-up numerical approaches strive to mechanistically represent processes on scales as small as practical. Reactive transport models integrating geochemical and microbiologically driven reactions as well as advection, dispersion, and diffusion (e.g., Bethke 2008; Regnier et al. 2003; Steefel et al. 2005) are now essential components of many subsurface flow and transport investigations. These models can vary markedly in sophistication, but all calculate temporal and spatial concentrations of solid and aqueous chemical components resulting from equilibrium or kinetic reactions as well as from microbial growth and decay occurring within a representative elementary volume of the modeled system (e.g., Fang et al. 2009; Yabusaki et al. 2007). Most reactive transport simulations are performed at a single scale of prediction, and relationships are invoked to compensate for the effects of heterogeneity and process uncertainties across scales. Modelers using a top-down approach typically ignore the mechanistic details of lower-scale processes and are interested most in describing the effects of smaller-scale processes on larger-scale system behavior. Recent theoretical and numerical studies have illustrated that watersheds indeed exhibit complex behavior (e.g., Bloomfield et al. 2008; Kirchner et al. 2001; Kollet and Maxwell 2008a). However, explicit consideration of complexity in reactive subsurface transport modeling has not been attempted yet.

Innovative modeling approaches are needed for numerically identifying emergent system behavior at the field scale. A needed first step is the explicit coupling of bottom-up, mechanistic submodels across scales. This might include loose coupling of microbial community dynamic and pore-scale flow models (Scheibe et al. 2008) with subsurface reactive transport models or linking subsurface reactive transport with land-surface and climate simulators. To determine where mechanistic model predictions deviate from observations, evaluation is needed of the nested and coupled model predictions relative to systems-level measurements (e.g., changes in the composition and functioning of a microbial community in response to field-scale perturbation or a time-series of solution chemistry at receiving waters). Rather than the common practice of refining or further calibrating the mechanistic model to improve the match between simulations and observations, this research challenge will emphasize using deviation points to identify and quantify emergent or other complex system behaviors. Numerical sensitivity analysis is needed to identify which variables and couplings have the most influence on integrated, complex subsurface system behavior. Once identified, these key variables and couplings can be investigated more thoroughly and models can be developed that seek to identify, explore, and predict the behavioral patterns that they control.

B. Strategies for Interrogating Large-Scale Behavior

New research strategies are necessary for interrogating large-scale properties and quantifying diagnostic measures of system function and response. This approach contrasts with the common practice of collecting subsurface data at increasingly higher resolution and precision. Important needs include developing new sensors, acquiring different data forms and types, and deploying observational networks—all specifically designed to characterize critical aspects of system behavior or large-scale system control. For example, rather than a detailed characterization of potentially influential variations in subsurface hydraulic conductivity, emphasis is needed on assessing the degree of flow connectivity or on measuring the responses of subsurface reactive constituents to natural forcings (e.g., hydrological and storm events) over various diagnostic time scales. Research is needed to identify response patterns that are repeatedly observed for one system and generalized patterns common to many systems. Such patterns should become predictable if an adequate number of natural complex systems are understood sufficiently.

Large-scale field manipulations are needed to perturb key system components (e.g., microbial community structure or redox state), as illustrated at the smaller field scale in sidebar 3A, p. 11. The response to intentional perturbation will provide a basis for understanding the linkages and function of internal processes and their roles in overall system regulation and control. New techniques, including different types of innovative research monitoring, are required to discover and quantify space-time patterns that might indicate integrated, emergent, or self-organizational behavior within a particular system or between similar systems. Critical to advancing subsurface complex systems science are systematic learning and model development that must progress concurrently with system interrogation. This topic forms the basis of the following challenge.

C. Phenomenological Models for Prediction

Phenomenological models are needed to understand and eventually describe large-scale system dynamics through systematic learning. Such learning is promoted by integrating collected data, using complexity methods for analysis, and establishing and testing falsifiable models (e.g., Harte 2002) developed to explain large-scale behavior relevant to subsurface flow and transport. Envisioning the form of these models is difficult. They may invoke accepted complex system modeling formalisms, such as cellular automata, network models, or agent-based models (see sidebar 3B, p. 14). They also could entail the development of hybrid approaches conforming to general principles observed at the larger scale while honoring mechanistic processes characterized at smaller scales. Numerous described models offer potential starting points for this effort (e.g., Boccara 2004). Research needs include developing models that predict key parameters of interest (i.e., not just those of expedience), testing model predictive power (e.g., accuracy and uncertainty) at relevant DOE sites, and identifying the organizing principles that might underlie the complexity and heterogeneity of complex subsurface systems sharing common characteristics.

4. Summary of Workshop Findings

Field-scale subsurface systems and their smaller-scale component processes can be extremely complicated. In many cases, they demonstrate accepted characteristics of complex systems (see Appendix A, Complex Systems Science and Subsurface Complexity, p. 21), such as emergence, nonlinearity and feedback, and memory (see Appendix B, Complex Subsurface Systems and Merit of Approach, p. 29). Other characteristics of subsurface systems that have long challenged the scientific community include inaccessibility, widespread heterogeneity at multiple scales, and hierarchical coupled processes. These difficult characteristics, when combined with society's critical need to understand and predict subsurface environments, mandate that all reasonable scientific approaches to investigate and understand such systems be carefully considered and applied where and when appropriate. To date, the complex systems science approach has not been explicitly incorporated into BER's Subsurface Biogeochemical Research but appears to have significant merit, given insights provided by this approach to other areas of the Earth and biological sciences (see Appendices A and B). Moreover, the approach has high potential to advance subsurface science regardless of whether the particular systems studied are formally considered complicated or complex.

Complexity science tells us the holistic behavior of a complex system cannot be fully understood or predicted from knowledge of its smaller-scale features or processes. This does not mean that studies of component processes are unnecessary or useless or that upscaling research on how smaller-scale processes influence or control aspects of higher-level behavior is futile. Given the current state of science, each activity promises major future scientific advances for subsurface science. Indeed, both are needed as components of complexity-based research to document emergence when it occurs and to understand the nature and outcomes of fundamental, multiscale process interactions leading to complex behavior.

The overall research objectives of both reductionism and complexity science may be similar (e.g., systems-level predictions), albeit with distinctions related to the intermediate scientific outcomes and impacts sought. Variants of both approaches intersect and preserve select strengths of each, as desired for the scientific application of interest or to meet program science goals. In some cases, a combination of reductionistic and complexity science approaches may provide critical insight into the workings of systems that are intractable using either approach alone. The most beneficial overall approach will be one that maximizes program goals for scientific understanding of system-scale behavior while providing valuable and transferrable scientifically based tools for prediction of meaningful and useful variables.

The terms *understanding* and *prediction* are nuanced and relate to a research approach through the types of models employed (i.e., the "toolkit" associated with the approach). *Understanding* involves the mechanisms, processes, and interactions within a system that collectively define dynamic behavior in response to environmental variables. Models are fundamental to understanding because they integrate different forms of data and knowledge and encapsulate our belief about the way a system operates. As such, they are essential for hypothesis definition and evaluation. *Prediction* involves many levels ranging from qualitative assessments of system behavior (based on conceptual models and heuristic principles) to quantitative forecasts of dynamic system response. Clearly, the need to improve our predictive understanding of subsurface systems is great. Reductionistic, bottom-up approaches have recognized limitations, and simplified top-down models characteristic of complex systems science are unlikely to independently predict the spatial and temporal distributions of chemical components in groundwaters. As each of these approaches reveals and quantifies different but important aspects of the system, a worthy avenue of pursuit lies in pragmatically applying a combination of top-down and bottom-up approaches through iterative experimentation and modeling. Systems-level understanding can be iteratively tested and advanced by comparing qualitative and quantitative model predictions to carefully designed experiments.

The following research gaps and needs were identified after evaluating the current state of understanding and predictive capability for complex subsurface systems.

1. A hybrid research approach combining complementary bottom-up reductionism with top-down complexity concepts is needed to reveal the inner workings of complex hierarchical subsurface systems. This approach will help identify and quantify emergent properties and behaviors when they occur and provide new means for robust and verifiable system-scale predictions.

   The melding of reductionism and complexity approaches will identify mechanisms and interactions defining system behavior at different scales and will support development of new types of models (both theory based and pragmatic) with the predictive power needed to effectively manage subsurface systems. Groundbreaking scientific outcomes with a new perspective are expected.

2. Three interdisciplinary Research Opportunities and their associated challenges have been identified as major gaps in understanding and predicting complex subsurface systems: (1) fundamental process coupling, (2) scale transitions in hierarchical systems, and (3) integrated system behavior. Their resolution holds high potential for the impact and advancement of subsurface science.

   Well-conceived, hybrid research efforts are needed on relevant field study sites and representative laboratory model systems to develop an understanding of fundamental interactions between microbiological, geochemical, and hydrological processes and their impact on overall system behavior. The linkage of iterative experimental and modeling activities is required at all scales to accomplish both heuristic and simulation goals.

3. Complex systems science approaches are required to provide the scientific basis for effective DOE management of Earth systems involving interactions between water, solutes, microorganisms, and mineral solids in heterogeneous subsurface environments.

   Interdisciplinary, collaborative research is needed to transfer new BER-developed system characterization, observation, and modeling strategies to key DOE mission sites for broader impact on critical national needs.

Pursuing the three Research Opportunities and resolving their scientific gaps will improve the understanding of complex subsurface systems at different scales and the process interactions controlling or distinguishing them. By melding reductionism and complexity concepts, the merits of both bottom-up and top-down modeling concepts will become clear, revealing essential insights on the best approaches for achieving predictive capability. Emphasizing the quantitative understanding of fundamental process interactions as a primary control on system complexity will produce transferable scientific concepts applicable to different subsurface systems. The research will provide (1) new concepts for transitioning essential information between scales; (2) appreciation for systems in which complex system concepts will and will not work; (3) higher-level knowledge of natural laws governing the behaviors of complex systems; and (4) new modeling approaches to address such systems at all scales, from the kilometer and above. This fourth contribution will give important scientific support to multiple DOE mission areas focused on the subsurface environment.

Appendix A

Complex Systems Science and Subsurface Complexity

A. Complex Systems Science

Complex systems science has evolved from the need to describe and predict the holistic behaviors of natural and human systems containing myriad interacting or interwoven parts. Occurring at virtually any scale, these systems are difficult to analyze and understand, and all exhibit higher-scale features or behaviors not readily derived from the sum of their parts (Murray and Fonstad 2007; Watkins and Freeman 2008). Key to this is the concept of emergence—behavior or features that do not clearly or cleanly derive from the attributes or function of internal components but do arise at higher scale from their multiple interactions (Baas and Emmeche 1997; Manson 2001). The field of complex systems science is well described in recent Wikipedia texts (e.g., Bar-Yam 1997) and on websites of academic research centers espousing this approach (e.g., Santa Fe Institute, CSIRO Centre for Complex Systems Science, and the University of Michigan Center for the Study of Complex Systems). Fundamentally an interdisciplinary and integrative science, the complex systems approach seeks to understand the primary interactions that determine emergence and overall system behavior at the prediction scale. The goals of this approach are (1) identifying broadly operative macroscopic laws applicable to different systems and (2) predicting systems-scale behaviors using phenomenological rather than mechanistic models.

Complexity and complex systems have become terms of our time, partly because of recognized global climate change issues; the extreme complexity of Earth-scale systems; and the need to forecast future conditions for effective resource management, mitigation, and societal protection. Complex systems science has distinct and evolving analytical (Shalizi 2006) and modeling approaches (Boccara 2004; Grimm et al. 2005; Murray 2007) and theoretical concepts (Manson 2001). Modeling often uses a top-down approach based on empirical descriptions of emergent variables, features, patterns, or behaviors rather than mechanistic descriptions of smaller-scale processes (e.g., Murray 2007; Werner 1999). However, approaches to explicitly deal with complexity from the bottom up also exist (Grimm et al. 2005). Various modeling strategies continue to be debated for different applications. The complexity approach is increasingly applied in ecology (Bousquet and Le Page 2004; Kreft et al. 2001; Wooton 2001), geomorphology (Fonstad 2006; Murray 2003; Murray 2007; Werner 1999; Werner 2003), and catchment hydrology (Kirchner et al. 2000; Kirchner et al. 2001; McDonnell et al. 2007; Sivapalan 2005). To date, application of this approach to subsurface systems has been only limited (Bloomfield et al. 2008). Complex systems science is recognized as a potential integrative strategy in environmental science, a tool for pragmatic systems-level explanation and prediction, and a functional means for linkage with the social sciences. As such, it is a recommended component of high-level nuclear waste assessment (Ewing 2004) and future research by national science agencies from the United States and abroad (NERC 2007a; NERC 2007b), even while the merit of such approaches is debated (Sardar and Ravetz 1994).

B. Characteristics of Complex Systems

There are no widely accepted formal definitions for *complexity* or *complex system* (see, for example, *Science* 1999). However, characteristics associated with both terms include complex behavior (deterministic chaos, intermittency, and oscillation) in simple systems, particularly nonlinear ones. Other attributes include extreme sensitivity to initial conditions, perturbations, or ambient conditions (experimental control parameters or theoretical model parameters) and the formation of spatial and temporal patterns by the collective behavior of many components, also referred to as emergent behavior. Complexity often is associated with nonlinear and far-from-equilibrium systems, but neither is an essential characteristic of complex system behaviors. Formation of spatial and temporal fractals and the processes associated with them generally are considered part of complexity science, as is the study of networks, their properties, and processes taking place within them.

In emergent systems, interactions between many components—which themselves may be simple or complex—result in the self-organized formation of distinctive collective structures and behaviors much different than those associated with the individual components or with systems consisting of only a few components. Summarized by the often quoted statement, “More is different” (Anderson 1972), this characteristic is where the greatest intersection between complexity science and subsurface science is likely to be found. While applicable in theory, a reductionistic approach may be impractical when numerous components act together and with their environment to generate distinctive structures and behaviors. In this context, understanding the difference between complex and complicated systems is important. Like complex systems, complicated systems consist of many interacting parts that often are quite different, yet these systems lack self-organization and emergent behavior. Compared to complex systems, complicated systems contain relatively few parts, and fully understanding them is possible, at least in principle, based on a bottom-up approach. An automobile usually would be considered a complicated system (however, the turbulent combustion process in cylinders is an example of complexity, as is the dynamic behavior associated with coupled vibrations). In contrast, the intermittent and quasi-periodic behavior of heavy traffic on a freeway is an example of complexity and can be understood and modeled without understanding the internal workings of an automobile or driver. Importantly, there are no uniform criteria to distinguish complicated and complex systems. Some people further argue that complicated systems are so specialized, few general insights can be learned from studying them.

A simple example of collective behavior is the formation of hexagonal Rayleigh-Bénard convection cells (see Fig. A.1. Hexagonal Convection Cells in SF_6 near Its Critical Point, this page). As the temperature gradient is increased across a thin horizontal layer of fluid heated from below, a simple convection pattern, like that shown in Fig. A.1, emerges spontaneously because of the collective behavior of myriad fluid molecules when a critical Rayleigh number[1] is exceeded. In Rayleigh-Bénard convection experiments, as the Rayleigh number is raised by increasing the temperature difference across the fluid layer, a variety of more-complex behaviors is observed, including intermittent and chaotic behaviors. These patterns could, in principle, be simulated using molecular dynamics. However, simulating so many molecules would be cost prohibitive (each convection cell in Fig. A.1 consists of about 10^{15} molecules, and the number of molecules in the field of view is on the order of 10^{18}). Instead, the simulation of Rayleigh-Bénard convection patterns is based on continuum computational fluid dynamics (see Fig. A.2. Simulation of Spiral Defect Chaos in Rayleigh-Bénard Convection, p. 23) or lattice Boltzmann simulations, which do not include molecular details.

Cooperative, self-organized pattern formation is common in biological systems. For example, Fig. A.3. Self-Organized Bacterial Cell Colonies, p. 24, shows dendritic colonies of the bacterium *Paenibacillus dendritiformis* grown on a nutrient substrate in a Petri dish. In this case, many millions of bacteria act cooperatively to form a structure beneficial to the whole

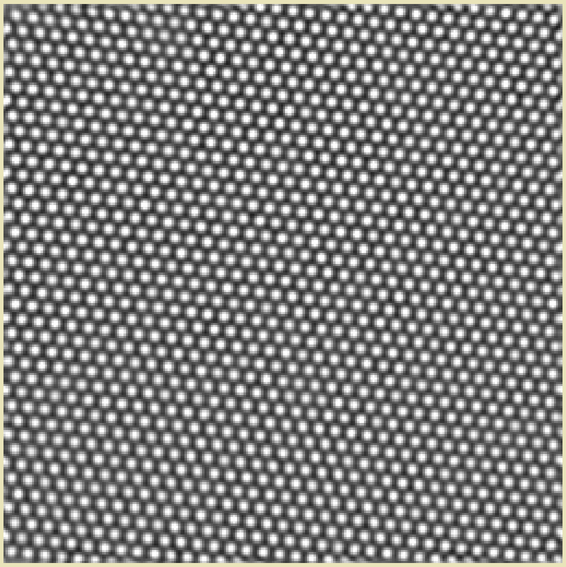


Fig. A.1. Hexagonal Convection Cells in SF_6 near Its Critical Point. A thin layer of compressed SF_6, confined between two parallel transparent sheets, is heated from below. The collective behavior of myriad fluid molecules forms a simple convection pattern when the Raleigh number is exceeded. [From G. Ahlers, “Experiments with Rayleigh-Bénard Convection” (www.nls.physics.ucsb.edu/papers/Ah_Benard_03.pdf) and from J. Oh and G. Ahlers, unpublished]

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[1] The Rayleigh number is defined as $Ra = (ag\Delta t b^3 \rho)/(D_T \eta)$, where a is the thermal expansion coefficient, g is the acceleration due to gravity, Δt is the temperature difference imposed across the horizontal cell ($\Delta t = T_L - T_U$, where T_L is the temperature of the lower wall and T_U is the temperature of the upper wall), b is the width of the fluid-filled gap, D_T is the thermal diffusivity, and η is the fluid viscosity.

Fig. A.2. Simulation of Spiral Defect Chaos in Rayleigh-Bénard Convection. [From Egolf et al. 2000. Reprinted by permission from Macmillan Publishers Ltd: *Nature*]

colony. The individual microorganisms are complex, self-organized systems interacting with each other (via chemotaxis) and with their substrate. In this example, the bacteria collectively secrete a lubricant enabling them to move on hard surfaces. The internal chemical "machinery" in each bacterial cell is not well understood. Nevertheless, high-level models based on simple concepts about the ways individual bacterial cells interact with each other can be used to simulate patterns remarkably similar to those formed in a Petri dish (see Fig. A.3, p. 24). This provides an understanding of how the cell colonies work and "adapt" to changes in their environment. This understanding is achieved despite the fact that the number of cells in the model system is much smaller than the number of cells in the experimental system (by a factor of almost a million) and that only a few simplified interaction mechanisms are included in the model. The hierarchical complexity in bacterial cell colonies is found in many other complex systems. In mammals, for example, small molecules and macromolecules interact to form products such as membranes, vesicles, chromosomes, and a nucleus (or nuclei in some cases). These products in turn form cells, organs, individuals, and groups (e.g., packs and herds) that interact with each other and their environment. At each level in the hierarchy, the behavior can be described and at least partially understood in terms of the properties of and interactions between the components constituting the immediate underlying level in the hierarchy.

An important note is that if Rayleigh-Bénard experiments were to be repeated under conditions that generate patterns similar to the one shown in Fig. A.2, this page, the results could be completely different because of sensitivity to control parameters. Many complex systems have numerous distinct "states," and in simple numerical models, the number of states often is infinite. In practice, it often is impossible to control experimental complex systems precisely enough to prevent switching between different states during an experiment or to guarantee the system will be in the same state if an experiment is repeated. This has a profound impact on quantifying the uncertainty of numerical simulations of complex systems because standard statistical approaches cannot be used. Even if experimental conditions did not change, sensitivity to initial conditions and perturbations (exponential amplification of perturbations in nonlinear systems) could lead to different results. For example, the cell colonies illustrated in Fig. A.3, p. 24, are not subject to large transitions when conditions change slightly. However, if one of the experiments were to be repeated, some patterns would be quite different, such as the locations of the branches and their side branches. Nevertheless, the human eye and brain instantly would recognize the pattern and associate it with the appropriate one shown on the right-hand side of Fig. A.3. In addition, all statistical measures associated with the two patterns would be the same. This is similar to the problem of weather forecasting. Because the weather system's dominant Lyapunov time (the time constant associated with the exponential growth of perturbations) is on the order of days, long-term weather prediction (beyond one to two weeks) is fundamentally impossible. However, predicting climate (weather statistics) is possible, at least in principle.

Although using first-principles molecular models to simulate typical complex systems is futile, higher-level modeling and simulation approaches can provide important understanding. They also can enable prediction of expected behavior and the quantitative generic characteristics (often expressed in terms of statistical measures) associated with this behavior (Boccara

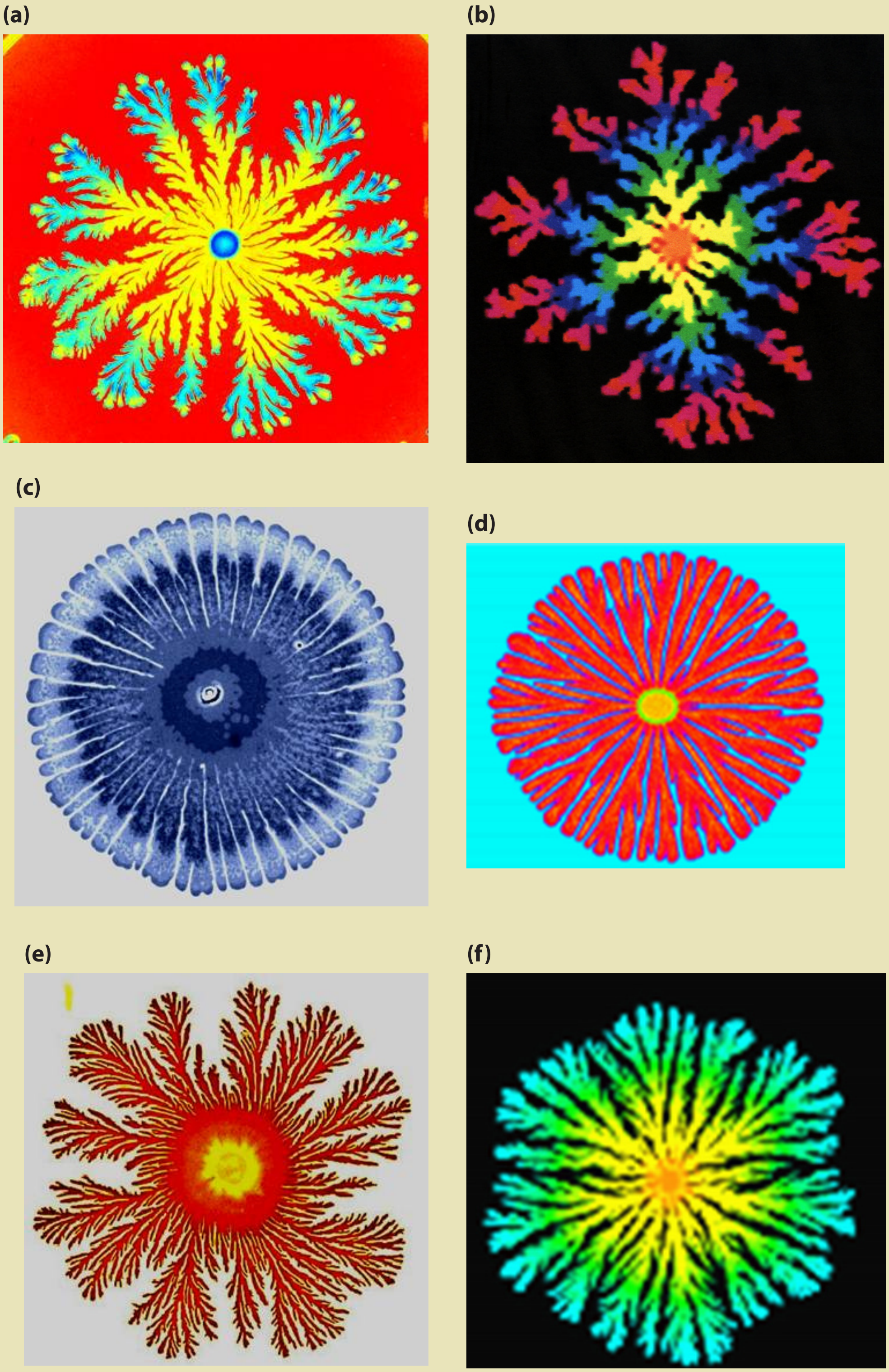

Fig. A.3. Self-Organized Bacterial Cell Colonies. Parts **a**, **c**, and **e** show colonies of the bacterium *Paenibacillus dendritiformis* grown under medium (**a**), high (**c**), and low (**e**) nutrient level conditions. Parts **b**, **d**, and **f** show corresponding patterns generated by a simple computer model. For the experiments, color is added according to the density of bacterial cells; for the simulations, colors indicate growth time. [From Ben-Jacob and Levine 2006]

2004). Examples of such models include those developed to simulate the spread of disease (Grais et al. 2003), animal and plant territories (Grimm et al. 2005; Letcher et al. 1998), and the behavior of a school of fish or flock of birds (Reynolds 1987). In most cases, complex behavior emerges from simple interactions between otherwise independent agents. This often requires the numerical development and implementation of systems-level models (Shalizi 2006) that may be phenomenological and of largely empirical origin. In the case of Rayleigh-Bénard convection, a direct numerical simulation approach based on continuum fluid dynamics and thermal physics can be used, and model parameters can be accurately measured or obtained from molecular simulations. However, similar reductionistic approaches are not applicable to most complex systems. In many cases, the level of reduction is minimal. For example, in simulations of the behavior of a school of fish, individual fish are the interacting components or agents, and further reduction (such as the mechanisms allowing one fish to detect and respond to its neighbors) is not sought.

In the Earth sciences, geomorphology and landscapes of different types have been evaluated from the perspective of complexity (Murray and Fonstad 2007; Werner 1999). Rivers and streams form a variety of spectacular self-organized patterns (see Fig. A.4. Complex Patterns Created by Fluvial Systems, this page), including

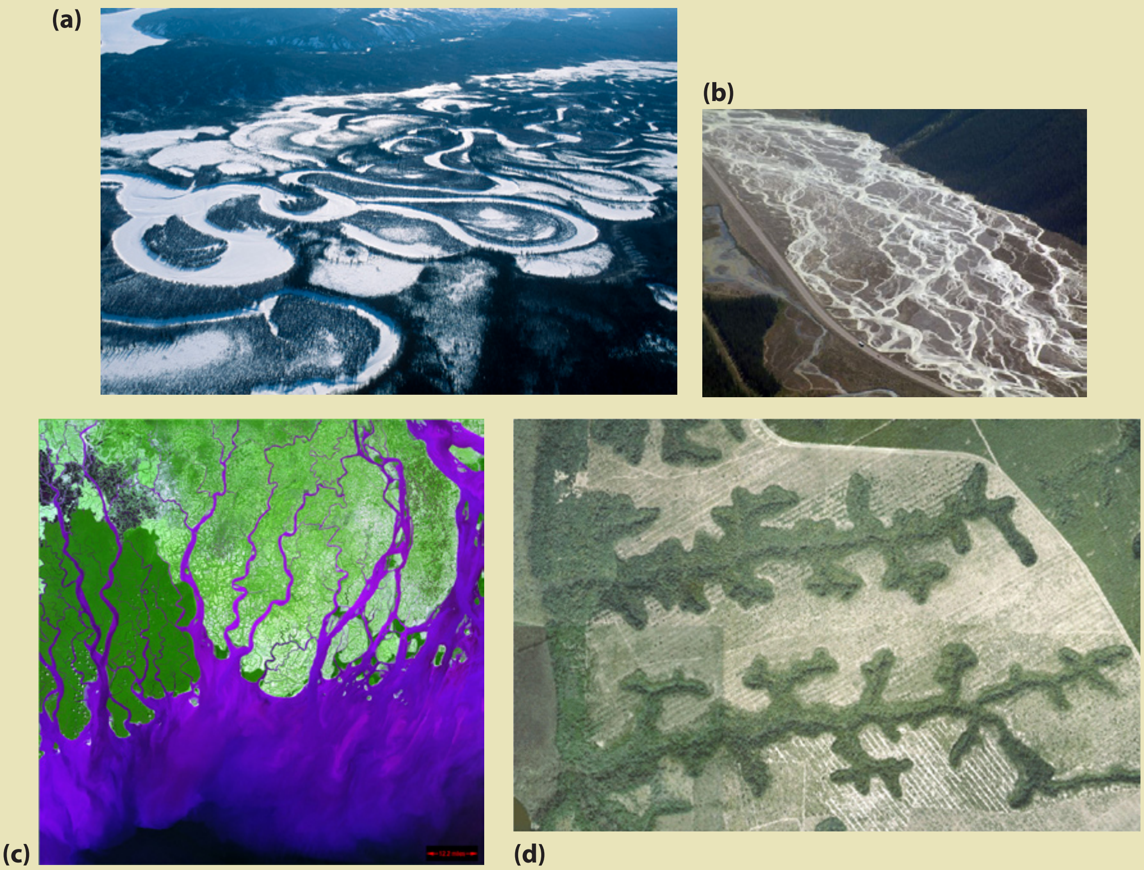

Fig. A.4. Complex Patterns Created by Fluvial Systems. **(a)** Meandering river in Alaska. [© AccentAlaska.com] **(b)** Braided pattern of the Sunwapta River in Alberta, Canada. [Reproduced with permission of Natural Resources Canada 2010, courtesy of the Geological Survey of Canada (Photo 2002-597 by R. Couture and G. B. Fasani)] **(c)** River delta, Ganges River, Bangladesh. [Courtesy of USGS National Center for EROS and NASA Landsat Project Science Office] **(d)** Branched channels in Florida formed primarily by groundwater outflow (Abrams et al. 2009; Howard 2009). [Published in Howard 2009 courtesy of the Florida Department of Revenue (FDOR). Reprinted by permission from FDOR and Macmillan Publishers Ltd: *Nature Geoscience*] Patterns shown in **a–c** are highly dynamic; the one in **d** may develop further by headward growth, but the channels change slowly once established.

meandering and braided channels, deltas, branched networks, and anastomotic channels (branched and interconnecting rivers and networks). However, morphology varies widely within these general classes, and "transitional" patterns also occur. This variability arises from several sources: the nature of sediment load, slope of the land surface, erodibility, the rate at which sediment is transported into a river, tectonic effects, climate, large-scale geological heterogeneity, vegetation, and other influences. Transitions, for example between meandering and braided and between straight (low sinuosity) and meandering (high sinuosity) patterns, also may result (Schumm 1985) from changing conditions. In the United States, rapid transitions between various river patterns have occurred due to water diversion and farming that influence sediment load and type (Hickin 1985; Schumm 1985).

Simple models developed to simulate these and other complex fluvial patterns and features provide important insight into how rivers transport sediment and solutes (e.g., Abrams et al. 2009; Murray and Paola 1994; Rinaldo et al. 1993; Sun et al. 1996; Sun et al. 2002). In the case of branched rivers, braided rivers, and the basin boundaries of branched rivers, several general power-law (fractal) relationships have been observed and are consistent with complex behavior. Simple models mimicking these complex systems have been created (e.g., Dodds and Rothman 1999; Rinaldo et al. 1993; Tarboton 1999).

C. Complexity and Subsurface Science

In the subsurface, heterogeneity will complicate research efforts. Recognizing and measuring self-organization in subsurface geological media will be much more difficult than in bacterial colonies grown on a homogeneous substrate (e.g., see Fig. A.3, p. 24). Moreover, unlike the land systems shown in Fig. A.4, 25, that are readily observed at almost all scales and easily by air, the subsurface poses tremendous observational and characterization challenges for both spatial and temporal features and behaviors. The subsurface is fundamentally inaccessible, and *in situ* observations often are made by boreholes and wells. With limited vertical and spatial resolution, these techniques do not easily capture lateral continuity and three-dimensional distributions and may not allow resolution of emergent behavior even if it exists. For many subsurface systems, devising monitoring systems or characterization strategies that successfully define the statistical character of key or determining properties or behaviors may be difficult. This situation differs somewhat for watershed studies in which stream-flow monitoring provides access to integrated system response. Owing in part to these characterization and monitoring challenges, subsurface science still is at the stage of process discovery for its key workings.

However, the same mechanisms controlling formation of the microbiological patterns shown in Fig. A.3 (e.g., cell motion, growth, and division in response to the concentrations and concentration gradients of nutrients, metabolic products, and chemical signaling agents) still can be expected to operate in the subsurface. Yet they operate in this environment for different reasons and in response to different local drivers. Vastly more complicated, the subsurface contains a great diversity of organisms with different functions and activities residing in varied and distributed physical settings including biofilms and colonies. These organisms interact synergistically and antagonistically, yielding a community with collective behaviors that reflect past and current environmental conditions and that dynamically respond to perturbations. This system has all the hallmarks of complexity.

The subsurface is characterized by coupled microbial, geochemical, and hydrological processes operating in a heterogeneous physical framework. Even one of these processes alone can exhibit complex behavior. For example, fluid-fluid displacement processes are well known for their ability to generate fractal patterns in homogeneous porous media under some circumstances (see Fig. A.5. Fractal Patterns in Fluid Displacement, p. 27). These complex fluid-fluid displacement patterns and their three-dimensional counterparts can be simulated using simple models, such as the diffusion-limited aggregation model (Witten and Sander 1981) and the invasion percolation model (Wilkinson and Willemsen 1983).

While these models pre-date modern complexity approaches, their strategies in describing the higher-level aspects of behavior are similar to those now used in complex systems science (Shalizi 2006). The coupling of multiple processes can lead to complex feedback mechanisms and phenomena, different types of memory effects (e.g., biomineral phases and organism microniches), and nonlinear behavior at multiple scales. Consequently, collective behavior and self-organization are expected to be common in the subsurface, with emergent features evolving at different scales.

At a much larger scale, the coupling between groundwater and surface water systems is a challenging domain in hydrology (Cardenas 2007; Freeze and Harlan 1969; Kollet and Maxwell 2008a; Sudicky et al. 2008) that plays a key role in the dissemination of contaminants to ecosystems (Ford 2005). Using time-series data analysis techniques, Kirchner et al. (2000) observed power-law distributions of travel times for nonreactive tracer (Cl^-) elution from multiple watersheds (see Fig. A.6. Analysis of Long-Term Stream Chemistry Data, this page). These distributions indicated "memory" of

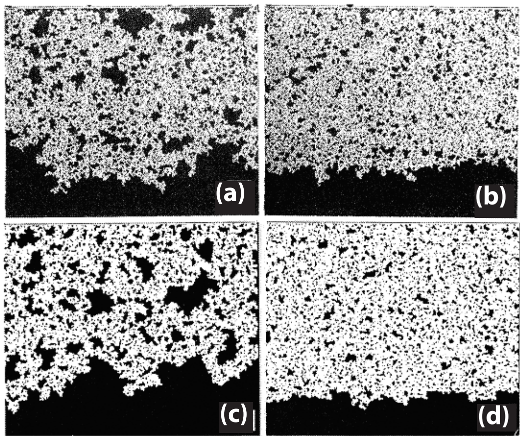

Fig. A.5. Fractal Patterns in Fluid Displacement. These develop during slow (capillary- and gravity force–dominated) displacement of a wetting fluid by a nonwetting fluid in an inclined quasi-two-dimensional porous medium. Top row: Experiments in which air displaces a water-glycerol mixture. Bottom row: Computer simulations using a gradient invasion percolation model. On the left-hand side, the Bond number (Bo is the ratio between gravitational and capillary forces, which can be varied by changing the inclination) is 0.005, and on the right-hand side, Bo = 0.018. In the Bo⟶ 0 limit, the pattern is a self-similar fractal. In the non-zero Bond number case, illustrated here, the structure is fractal on short length scales and uniform on long length scales, with a Bond number–dependent crossover length. [From Birovljev et al. 1991. Copyright (1991) by The American Physical Society and used with permission from APS and authors]

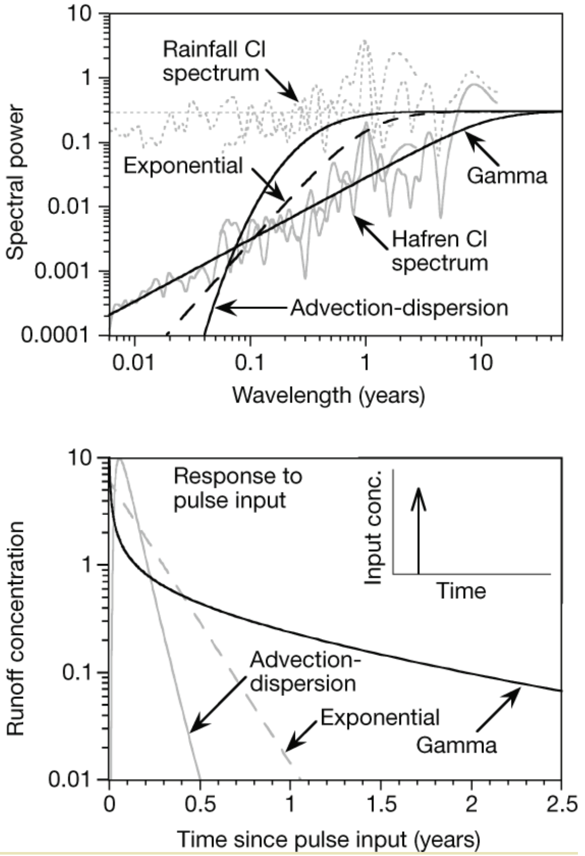

Fig. A.6. Analysis of Long-Term Stream Chemistry Data. The observed catchment response (modeled by a gamma function) is distinctly different from what would be expected with the use of an exponential distribution (commonly used to model travel times in catchments considered to be well-mixed reservoirs) or the advection-dispersion equation (which assumes that solutes reach the stream by transport and dispersion along a single flow path) for prediction. [From Kirchner, Feng, and Neal 2000. Reprinted by permission from Macmillan Publishers Ltd: *Nature*.] This and other studies illustrate the potential for complex systems science approaches to identify hydrological system behaviors that may be similar across different catchments.

past events, a characteristic of complex systems. More importantly, generalized catchment-scale phenomenological relationships were developed for these emergent phenomena and later were used to provide constraints for robust hypotheses testing of systems-scale interactions controlling stream tracer concentrations at multiple locations (Kirchner et al. 2001). Similarly, the flow paths and travel time distribution obtained from a three-dimensional simulation of Oklahoma's Little Washita watershed (with an area of ~ 1000 km^2) were well described with a particle-tracking model constrained by a power-law (fractal) distribution (Kollet and Maxwell 2008b; see Fig. A.7. Flow Paths and Travel Times Obtained from a Three-Dimensional Model that Couples Surface Flow with Variably Saturated Subsurface Flow, this page). Model results also indicated long-range correlations. These studies point to commonality in watershed elution behavior over a range of watershed types and phenomenological behavior differing from current concepts and models.

These and other related observations have led to a new view of watershed hydrology based on concepts of complexity science (Sivapalan 2005). Such studies of natural environments from the perspective of complexity science are in their infancy. An increase in their number is expected to reveal a high frequency of complex systems at different scales in human-significant settings and insights on general principles and laws governing system behavior.

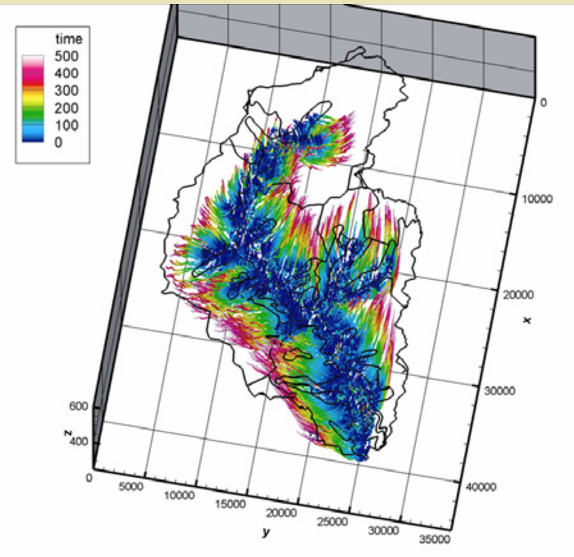

Fig. A.7. Flow Paths and Travel Times Obtained from a Three-Dimensional Model that Couples Surface Flow with Variably Saturated Subsurface Flow. The travel times were obtained using a backward-in-time Lagrangian particle-tracking algorithm after the three-dimensional velocity field was calculated. The color scale indicates the travel times in years, and the solid black line denotes the watershed boundary. The flow simulation was based on the Little Washita watershed in central Oklahoma. [From Kollet and Maxwell 2008b. Used with permission from the American Geophysical Union]

Appendix B
Complex Subsurface Systems and Merit of Approach

A. The Subsurface Environment as a Complex System

Subsurface systems usually are not characterized or evaluated from the perspective of complex systems science. The subsurface includes various types of soil-sediment-water systems, such as the vadose zone, aquifers, coupled groundwater-river systems, and the hyporheic and riparian zones. To a certain extent, their scale is arbitrary—generally exceeding a meter but ranging up to hundreds of kilometers in the case of a regional groundwater aquifer. All exhibit water flux; are populated by microorganisms; and display chemical reactions between water, mineral phases, microbes, and contaminants. Most hydrobiogeochemical systems display significant physical and geochemical heterogeneity resulting from geological depositional events, inherited geological structures, or *in situ* biogeochemical processes. Heterogeneity may be random, ordered, or fractal. In turn, heterogeneous physical and chemical features as well as water and nutrient fluxes propagate microbiological heterogeneity through the physicochemical environment.

A hierarchy of different interactive subcomponents and subsystems is present over a wide range of scales in subsurface systems. For microbiology, different features, behaviors, and processes occur when moving downscale from the ecosystem, to community, to population, to individual organism, and finally to the suborganism scale. A similar geochemical hierarchy exists in which reaction type, kinetic nature and rate, and reactive components change across scales. This hierarchy is evident when moving downscale from an assemblage of hydrogeological facies (e.g., a sediment layer with common macroscopic properties), to the pore scale within a particular facies, to a specific mineral surface, and finally to nanometer internal pores or specific crystal faces on a reactive mineral phase. Likewise, for hydrology, dominant transport pathways change from meter-scale or larger preferential flow channels (at the longest scale), to meter-scale interfacies advective and diffusive transport, to pore-scale preferential advection pathways between rock fragments and mineral grains, to intragrain diffusion in particle coatings and internal pore and fracture space. Different interactions affecting overall system behavior occur at each scale. Some components are more significant at one scale than another, yet others important at smaller scales may propagate to or even be magnified in the field. Each subsystem itself also may exhibit complex behavior, producing emergent behaviors at different scales. Subcomponent interactions may lead to fully predictable behavior at higher scales (emergent simplicity) or even more complex behavior (emergent complexity; see Bar-Yam 1997).

Workshop participants evaluated several subsurface systems and their important subcomponents (both microbiological and geochemical) from the perspective of systems complexity using criteria noted by Bloomfield et al. (2008) and others (see Table B.1. Criteria Used in Judging Whether a Subsurface System or Its Subcomponents Exhibit Complexity, p. 30). This evaluation was not exhaustive. Some systems met the criteria of complexity; others did not. With additional emphasis and experience, other criteria diagnostic of complex subsurface systems might be found in the future.

Subcomponents of subsurface systems can exhibit complex behavior. In biological systems, interactions between parts as well as influences from the environment are well recognized as often giving rise to new or emergent behavior (Alm and Arkin 2003; Morange 2001; Van Regenmortel 2004). Biological systems also can exhibit the complex systems attribute of robustness (Kitano 2002), a trait which may enable adaptation to changes in environmental conditions to occur through the presence of redundant components that compensate if primary components fail. In particular, microorganisms possess many characteristics of complex systems. These include (1) system properties (i.e., phenotype) not fully explained by an understanding of component parts (i.e., genotype), (2) coupled processes resulting from myriad interacting components (e.g., genetic regulatory elements, protein-protein interactions, allelopathic and quorum-sensing compounds, and syntrophic and parasitic relationships), and (3) dynamic interacting components and processes capable of adapting as they are subject to evolutionary forces (e.g., via lateral gene transfer, spontaneous mutation, and natural selection).

Table B.1. Criteria Used in Judging Whether a Subsurface System or Its Subcomponents Exhibit Complexity*

Feature	Description
System is open	Complex systems exist in a thermodynamic gradient, dissipate energy, and typically are far from an energetic equilibrium. Despite this, they may show dynamically stable local patterns or phenomena.
System boundaries	Defining or locating the boundaries of a complex system is difficult and may require relatively arbitrary decisions by the observer. Complex systems often are nested, a trait which also may lead to difficulties in defining boundaries. Components of complex systems may themselves exhibit complex characteristics.
Interactions between objects	Interactions between many linked objects or agents lead to a network that can share information. The rules of interaction are important and can lead to phenomena such as system memory and emergent behavior.
Feedback and adaptation	Dynamics of interactions at small scales shape macroscopic system dynamics that in turn feed back to influence the smaller scale. Potential exists for multiple outcomes or regime shifts due to exogenous or endogenous influences.
Memory and learning	Regularly occurring external relationships reinforce growth of the same set of components and subsystems in a complex system. This reinforcement can cause the system to appear to have a memory through the persistence of internal structures.
Nonlinear behavior and relationships	Defining a linear sum of independent components to solve for a nonlinear variable is impossible for a complex system. Complex nonlinear systems are inherently unpredictable, in that small perturbations in the system may cause large effects, a proportional effect, or no effect at all (Phillips 2006).
Emergence	Emergent phenomena arise out of nonlinear behavior and simple interactions between numerous agents or objects.
Self-organization	Some complex systems evolve toward a dynamically stable condition known as self-organized criticality (Bak 1996; Frigg 2003) that permits the system to more effectively interact with the environment.
Broad distribution of events or scales	Diagnostic system variables, features, or behaviors can show spatial and temporal scale invariance represented by a power law.

*Modified from Bloomfield et al. 2008. Copyright British Hydrological Society.

Also demonstrating complex behavior are various biogeochemical subcomponents, such as the mineral-microbe interface (emergence), coupled abiotic and biotic kinetic reaction networks with multiple components (nonlinearity and feedbacks), and certain types of biomineralization processes (memory and self-organization). Subcomponents often are studied in laboratory model systems under controlled, frequently homogeneous conditions in which robust spatial and temporal measurements and system characterization can be performed. Consequently, emergent behavior and other complex system characteristics are easier to recognize when they occur.

Workshop participants concluded that many field-scale subsurface systems display characteristics of a complex system. These characteristics include nonlinearities and feedbacks from process coupling and geochemical gradients; numerous process and property interactions at different scales; and the presence of memory effects resulting from past contamination and waste disposal (e.g., high-low pH excursions), hydrological events (rising and falling water tables), or seasonal biogeochemical regimes (e.g., redox stratification). For some subsurface systems, emergent or collective behavior may be identified through data analysis for watershed studies (as described in Appendix A. Complex Systems Science and Subsurface Complexity, p. 21). However, demonstrating such criteria for other cases could prove more difficult because of two fundamental problems. First, few subsurface systems have been studied with sufficient detail to make these evaluations. Second, the criteria themselves are ambiguous and thus challenge the development of a transparent definition for subsurface systems. Moreover, documenting emergence—behavior not readily predictable from its parts—in some cases requires that the parts (e.g., processes, subcomponents, or subsystems) be understood and described and that their controlling properties be sufficiently characterized. Accomplishing this is especially problematic for the subsurface, where multiscale processes and their interactions only now are being studied in detail and where collective behavior (if it exists) may be obscured because of difficulties in observing subsurface phenomena. Consequently, upscaling lower-level process information or models to document or evaluate emergence is a research challenge in its own right with significant data and knowledge requirements.

Given the characterization challenges posed by many subsurface systems, considering certain field sites as *de facto* complex systems may be useful. For these sites, significant heterogeneity and difficulties in sampling and characterization may prevent clear identification of emergence, self-organization, or other key complex system attributes. Such system types also greatly challenge a bottom-up modeling strategy because properties controlling the rate and extent of small-scale processes are virtually indeterminate over the spatial scale of interest and show large variability or high uncertainty. Still others in this category may have many interactive processes defying accurate quantification and description. The upscaling of small-scale process information or models for *de facto* complex systems is unlikely to satisfactorily describe the system as a whole, regardless of whether it is complicated or complex. An appropriate descriptor for such systems is reductionistic intractability. For these, a top-down analysis and modeling strategy may be the only option for adequate system description and prediction.

B. Examples of Complex Subsurface Systems and Components

Recognizing the hierarchies of scales and associated processes discussed previously, the following cases provide examples of subsurface complexity at three distinct scales discussed at the workshop. Complexity may exist from the kilometer to the molecular scale in subsurface systems, and many field-scale systems contain embedded levels of complexity in which lower-level systems exert strong influence on higher-level behaviors. These examples are presented because of the unresolved discussions that ensued at the workshop on the distinctions between complex and complicated subsurface systems. Evaluating these particular cases from the perspective of complex systems is enabled by the relatively large knowledge and research base existing for each.

1. A Complex Field System: The 300 A Uranium Plume

Contaminated field-scale systems are complicated because of source-term history and conditions, variable geological structures and facies, multiple processes and interactions, heterogeneity at different scales, and impacts of weather and seasonality. These characteristics challenge the understanding and prediction of contaminant behavior for all but the simplest field systems. But the question is, do these systems conform to the criteria of complexity, and is our understanding of them likely to be improved by a complexity approach? Can a general understanding of complex systems behavior and the identification of common governing laws be derived from studying field sites with often unique, site-specific attributes?

The 300 A uranium (U) plume at the Hanford site is a subsurface system representative of the Columbia River corridor where groundwaters strongly interact with surface waters. The 2-km^2 groundwater plume containing dilute dissolved U ($< 100\ \mu g/L$) as the primary contaminant has been monitored for over 40 years (Peterson et al. 2005; Peterson et al. 2008). The plume resides within a coarse-textured, 8-m aquifer zone containing preferential flow paths and meter-sized, silt-textured clasts. It discharges discontinuously to the Columbia River along its eastern boundary (see Fig. B.1. The 300 A Uranium (U) Plume at the Hanford Site, p. 32) through the hyporheic zone and a series of seeps. Plume hydrology including water level, flow direction, and velocity is influenced strongly by Columbia River stage, which varies both seasonally and daily (see Fig. B.2. Columbia River Discharge by Month and Year, p. 32). Uranium concentrations in the plume (see Fig. B.1) and fluxes to the Columbia River also vary seasonally in a complicated manner that has

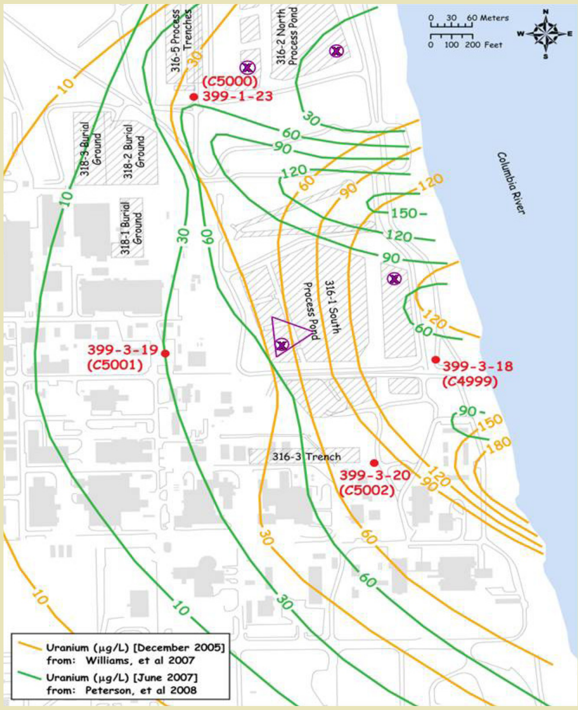

Fig. B.1. The 300 A Uranium (U) Plume at the Hanford Site. Depicted are U concentration contours (in parts per billion, µg/L) measured in December 2007 (gold) and June 2007 (green). These seasonal variations are different each year and are not predictable with existing models. The regulated concentration is 30 parts per billion. The DOE BER Hanford Integrated Field Research Challenge site is shown as the magenta triangle. Other locations represent excavations and other boreholes studied previously by DOE's Subsurface Biogeochemical Research activity. [From Um et al. 2010, in press. Copyright Elsevier]

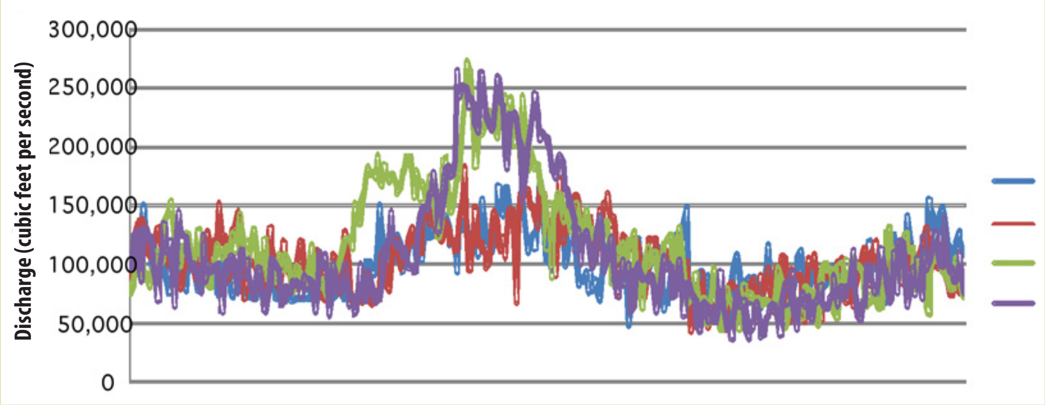

Fig. B.2. Columbia River Discharge by Month and Year. Large seasonal variations exist and are dominated by spring snowmelt. Short-term fluctuations represent dam manipulations for fish passage and power generation. The near-shore groundwater system and the Columbia River are in close hydrological communication. The groundwater water table rises in early spring and falls during the summer, strongly influencing dissolved uranium concentrations in the plume.

not been well described with any modeling approach. The plume has not dissipated due to groundwater flushing as projected by earlier modeling. The contours shown in Fig. B.1 are average saturated-zone concentrations that mask the true and significant heterogeneity in vertical and spatial U concentrations resulting from incomplete mixing and complex hydrogeology.

The geochemistry of the site has been studied extensively with samples from select locations, emphasizing the microscale to macroscale transition. Precipitated phases exist in the upper vadose zone, and adsorbed chemical species are present at moderate concentration in the deep vadose zone and at low concentration in the aquifer (Arai et al. 2007; Catalano et al. 2006; Singer et al. 2009; Stubbs et al. 2009). Rising and falling water table events driven by river stage fluctuations desorb U from the lower vadose zone and resupply the plume. The desorption behavior of sorbed contaminant U shows strong kinetic behavior at all scales studied (see Fig. B.3. Desorption Profile of Contaminant U from a Core of Field-Textured, Deep Sediment in the Vadose Zone p. 33), with release rates approximated by power-law functions with scale-dependent statistical parameters (Bond et al. 2008; Liu et al. 2009; Liu et al. 2008; Qafoku et al. 2005). These behaviors result from the coupling of geochemical and transport

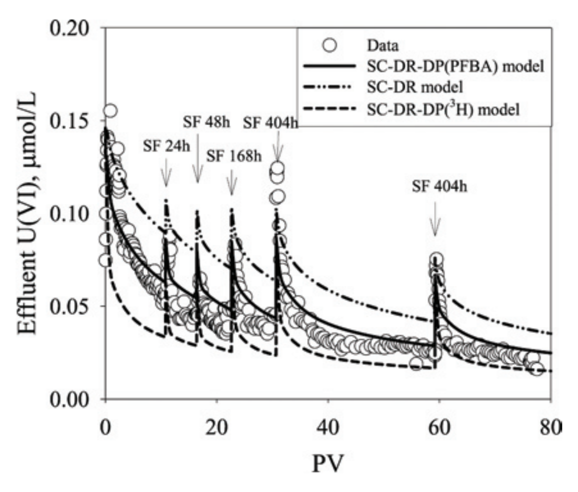

Fig. B.3. Desorption Profile of Contaminant U from a Core of Field-Textured, Deep Sediment in the Vadose Zone. Concentration spikes result from stop-flow events that were performed to evaluate *in situ* diffusion rates. Significant kinetic behavior was observed and is approximated by a power-law function. The scaling of reaction parameters from smaller-scale studies to this one is difficult. The desorption behavior is best described by a distributed rate (DR)–dual porosity (DP)–surface complexation (SC) model with microscopic transport parameters derived from pentafluorobenzoic acid (PFBA) tracer. [From Liu et al. 2008. Reprinted with permission from the American Geophysical Union]

(diffusion and advection) processes at a hierarchy of scales (intragrain, pore, and facies). Seasonally varying time scales of water residence in the aquifer effect power function shapes. Reaction reversals from desorption to adsorption, and back again, occur as groundwater flow vectors and water compositions change in response to river stage variations (Yabusaki et al. 2008).

Larger-scale geological features influence the overall behavior of the plume at different scales. Buried channels of coarse sediments cut across the plume in several locations, providing conduits for rapid water exchange between the groundwater and river. These channels strongly influence reaction time scales in nearby sediments and cause mass transfer and other physical effects at multiple scales.

The 300 A uranium plume conforms to many criteria of complex systems. The current distribution of U is influenced strongly by the "memory" of past disposal operations, historical events of high water table that redistributed chemical species, and yearly water table rise and fall cycles. The geochemical behavior of U is kinetically controlled by different processes and phenomena at each hierarchical scale. The presence of domains with highly variable reaction time scales and directions controlled by river stage fluctuations promotes nonlinear chemical interactions and responses. The seasonal and spatial distribution of U concentrations within the groundwater plume and the consequent flux of U to the Columbia River appear as emergent variables. Though currently unpredictable, these variables are determined by geological structures, multiple process interactions, memory effects, distributions of unknown properties, and seasonal details that vary by year. Extended periods of high river stage increase U inventory in the plume through vadose zone solubilization, which then is subject to forward geochemical reaction (adsorption). In contrast, extended periods of low river stage decrease U plume inventories by discharge to the river, which in turn promotes backward reaction (desorption). The number of interactive and coupled multiscale processes—combined with the large spatial range, presence of geological structures, significant heterogeneity, and complex patterns of controlling properties—makes using a reductionistic approach to study plume-scale behavior expensive and impractical and thus intractable.

The site has a long history of inadequate predictions. To understand multiscale coupled processes operating in the plume and to develop simplified but robust field-scale process models, research currently is under way at a 1300-m^2 site within the plume footprint [see Hanford Integrated Field Research Challenge (IFRC), magenta triangle, in Fig. B.1, p. 32]. The overall approach entails calibrating simple, linked surface complexation and mass transfer models in the laboratory and upscaling parameters to the 1300-m^2 study domain. Predictions from the resulting upscaled models that incorporate three-dimensional geostatistical distributions of reaction and transport properties will be compared to outcomes of field experiments assessing the rates and extent of *in situ* adsorption and desorption.

However, the only viable approach for forecasting plume-scale (e.g., 10^6 m^2) behavior without and with engineered remediation may be to conceptualize the entire plume and its associated groundwater-river hydrological domain as a complex system. This is an important Hanford site need with great financial implications. A higher-level approach to identify key factors controlling overall plume behavior and emergent features would involve comprehensive monitoring activities designed with the consideration of complex system characteristics. Taking such an approach might assure that the collective effects of smaller-scale processes are accurately and efficiently captured and properly represented in a systems-scale predictive model. Moreover, a top-down predictive model based on scales not much smaller than that of interest might avoid the pitfalls of a bottom-up approach in which unavoidable inaccuracies in small-scale process models can add up to predicted large-scale behaviors that are unrealistic (Murray 2007).

2. A Complex Intermediate-Scale Subsurface System with Coupled Biogeochemical Processes

In the previous field-scale example, complex behavior is caused by a hierarchy of interactive geochemical and transport processes operating largely above the meter scale in a hydrologically dynamic and heterogeneous environment. Emergence in the form of unpredictable groundwater U concentrations and fluxes was observed at this level of observation. Complex behavior also can occur at the intermediate scale (millimeters to meters), where interdependent and dynamic physical, geochemical, and biological processes interact to control system chemistry and contaminant mobility.

The ability of subsurface microbial communities to respond to changing environmental variables is an inherent but unpredictable property of natural and engineered systems. For example, natural attenuation and environmental remediation strategies depend on specialized microorganisms and the supporting microbial community to catalyze contaminant transformation reactions of interest. However, numerous environmental parameters can impact the activity, stability, resilience, and propensity for adaptation of the key players and microbial community as a whole. Current tools and knowledge fall short of being able to predict microbial responses to natural and engineered perturbations. Heterogeneous fluctuations in environmental variables—such as pH, temperature, electron donor and acceptor availability, and presence of inhibitors or predators—induce changes in microbial behavior and microbial community composition that prove difficult to mechanistically describe and predict in the subsurface. Fluctuating redox conditions (e.g., aerobic versus anaerobic) can alter substantially the structural (mineral dissolution and precipitation), geochemical (redox poising), and microbiological (community composition and activity) character of the local environment. These changes directly can affect flow conditions and contaminant mobility in desirable or deleterious ways. Microbial community responses, including their consequences on the local physical and chemical environment, meet all the requirements of a complex system and exhibit emergent character.

As an example of an intermediate-scale system exhibiting complex behavior, consider the response of a subsurface system to the introduction of an electron donor in the form of a degradable substrate, either via natural nutrient input or an environmental remediation strategy. Field studies of substrate addition have been performed at DOE BER's Oak Ridge and Rifle IFRC sites to enhance U remediation. These field experiments have documented the capability to lower dissolved U concentrations to acceptable values through biostimulation. However, the two studies were largely empirical, and important questions cannot be answered *a priori*, including where, when, and for how long microbial activity will be stimulated in the subsurface.

The pattern of stimulated growth and activity induced through environmental remediation will be heterogeneous because spatial variations in hydraulic and geochemical properties (e.g., solid-phase electron acceptors) impact the distribution of injected amendments. Figure B.4. Plan View, Model-Computed Map of Acetate and Bromide Transport, p. 35, is a model simulation of acetate (an electron donor) and bromide (a conservative tracer) transport from an injection well gallery (on the left side of each panel) through a 20-m monitoring array at the Rifle IFRC. The simulation demonstrates the effects of subsurface heterogeneity (e.g., hydraulic conductivity and bioavailable Fe(III) oxide distribution) on bromide and acetate dispersal and transport. Microbial activity, stimulated in areas where acetate is available, modulates local chemical and physical environments that affect pore-scale permeability and contaminant transport. Substrate utilization and depletion by microorganisms give rise to biogeochemical reaction products that evolve heterogeneously over space and time, as shown by the simulation in Fig. B.5. Plan View Map of Simulated, Heterogeneous Patterns of Mineral Distribution and Biomass, p. 36. The evolution of precipitates and biofilms can, in turn, impact aquifer permeability (e.g., Fig. 3.4, p. 15), which influences the effectiveness and sustainability of the treatment.

Understanding these feedbacks between biogeochemical transformations and flow in the presence of heterogeneity requires hierarchical studies of controlling processes at multiple observation scales. Detailed metabolic studies of environmentally relevant microbes and simplified communities, combined with geochemical studies, are beginning to unravel the complex mechanistic couplings involved in biogeochemical processes impacting contaminant transport and fate. Integral to these studies is the iteration between observation, experiment, and modeling. Genome-enabled simulations at the cellular and population levels are beginning to provide mechanistic information on cell metabolism, growth, and activity in a form that can be coupled to reactive transport codes. These codes then can be used to predict the impact of microbial activity on local geochemical and hydrological parameters (Scheibe et al. 2009). Such models ultimately will be

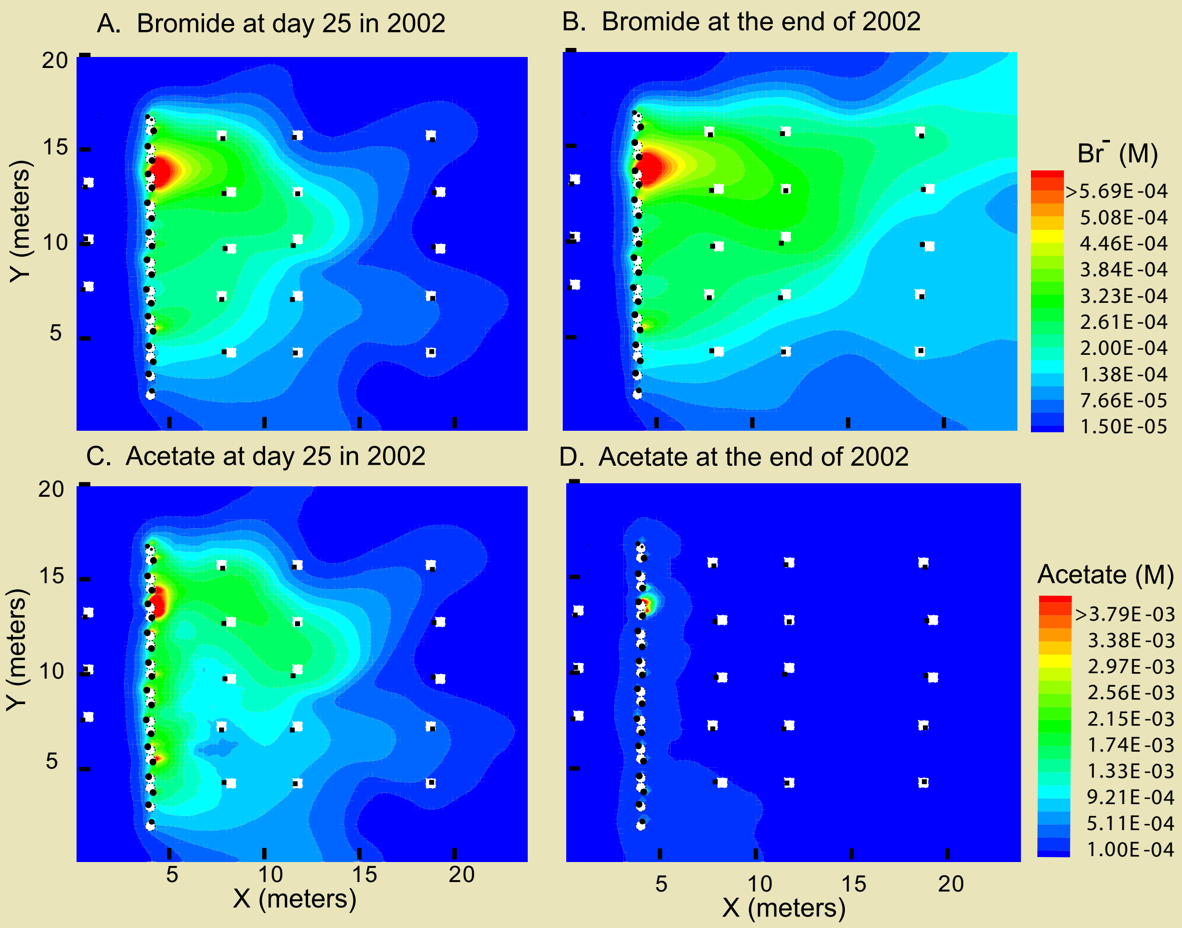

Fig. B.4. Plan View, Model-Computed Map of Acetate and Bromide Transport. The solutes were injected into a heterogeneous 20-m domain of the uranium-contaminated Rifle aquifer. Computed patterns of solute migration are shown at early (left) and later (right) times. Flow is from left to right. Concentration decreases from red to green to blue. [Adapted and reprinted from Li et al. 2010 with permission from Elsevier]

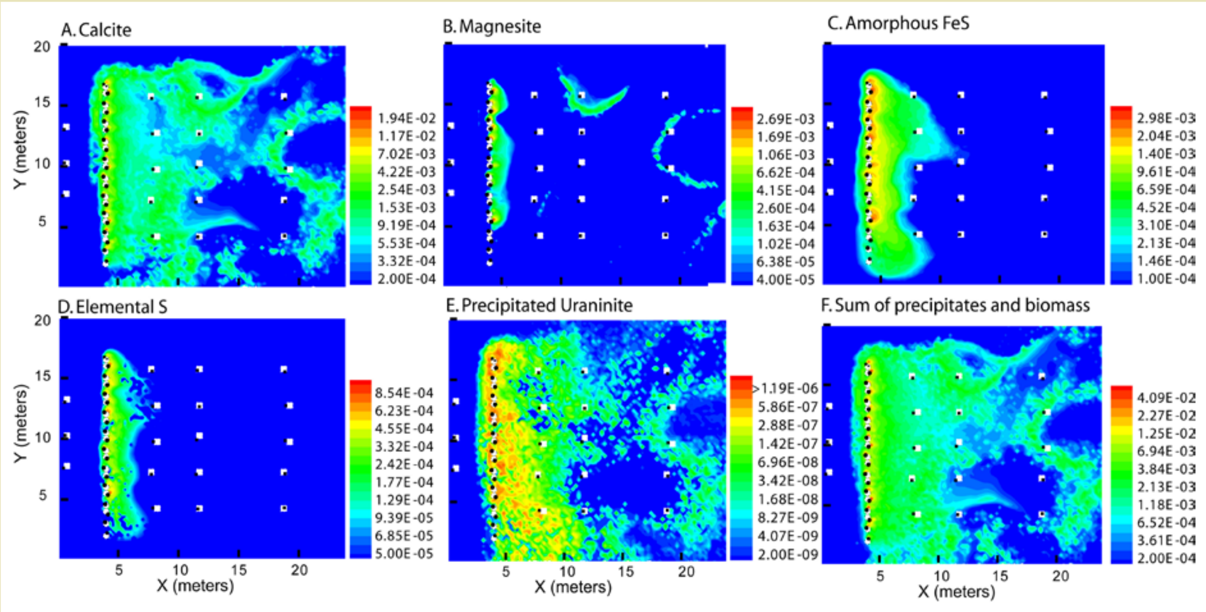

Fig. B.5. Plan View Map of Simulated, Heterogeneous Patterns of Mineral Distribution and Biomass. The simulated patterns of mineral distribution were a consequence of acetate injection into the subsurface to immobilize dissolved uranium as uraninite (UO_2) through microbiological action. Simulation results are given for only one time point after injection. The complex patterns result from heterogeneities in hydraulic conductivity and Fe(III) oxide distribution and their attendant coupled effects on system biogeochemistry. [Adapted and reprinted from Li et al. 2010 with permission from Elsevier]

able to incorporate new information on regulatory processes governing cell metabolism that will provide crucial insight into how environmental variables impact metabolic processes that direct cell growth and activity. Metaomics studies integrating genomic, transcriptomic, and proteomic information expand findings made at the single-cell and population levels to those of consortia (defined mixed communities) and natural subsurface communities. Information generated by these tools will provide the foundation for understanding the key couplings between microbial, geochemical, and hydrological processes at the pore scale that drive complex and emergent behavior at larger scales.

The patterns of microbial activity and the effects on local geochemical and hydraulic conditions illustrated in Fig. B.5, this page, provide a visual example of the complex nature of coupled biogeochemical processes in the subsurface. While the simulation models used embody the current state of the science in understanding the coupling of biogeochemical processes and how these processes may change and evolve in the subsurface over time, significant improvements are both necessary and possible. Measurements at the pore and intermediate scales are critical data inputs to generate systems-level understanding. However, the ultimate goal of predicting landscape-scale system behavior requires methods that measure the integrated effects of hierarchically structured subsystems at the larger scale. Steps in this direction have been taken. Several geophysical and sensing techniques are being developed to track—over field-relevant scales—the systems-level changes in subsurface biogeochemistry (see Fig. B.6. Remediation-Induced, Time-Lapse Changes in Electrical Induced Polarization Phase Responses, p. 37, and Fig. 3.4, p. 15). These techniques also could track other system properties resulting from the remediation-induced activity of microbial communities. (See, for example, Druhan et al. 2008; Hubbard et al. 2008; Williams et al. 2009.)

These and other imaging techniques offer opportunities to link pore-scale properties and processes with intermediate- and larger-scale diagnostic signatures of systems-level behavior. Obtaining and integrating information from multiple scales are expected to advance our ability to predict the functioning of subsurface systems over meaningful temporal and spatial domains.

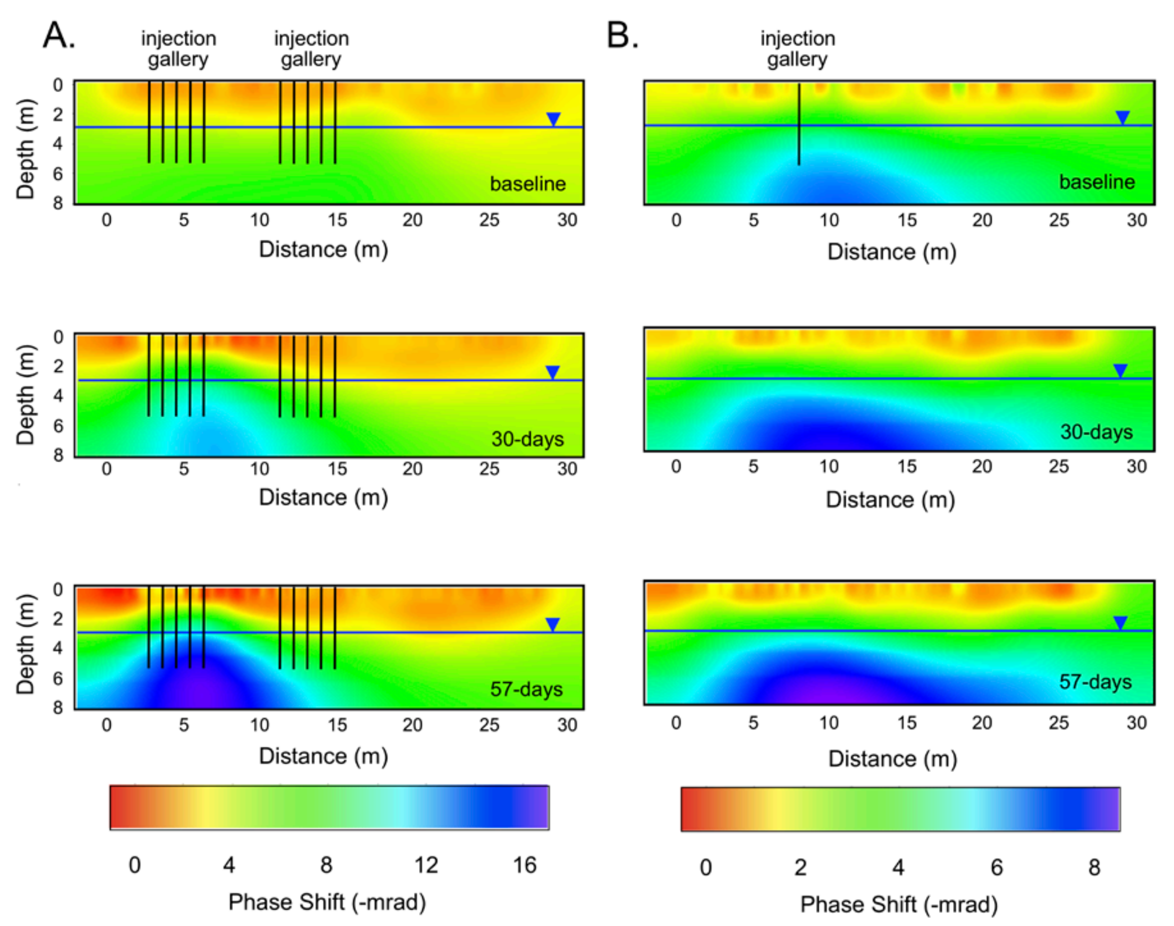

Fig. B.6. Remediation-Induced, Time-Lapse Changes in Electrical Induced Polarization Phase Responses (at 0.25 Hz). Surface Spectral Induced Polarization datasets were collected over time along surface transects oriented orthogonal (A) and parallel (B) to groundwater flow direction during a biostimulation experiment conducted at the Rifle IFRC site. In agreement with behavior elucidated through laboratory biostimulation experiments (Williams et al. 2005), these figures show the development of a phase response that corresponded with changes in groundwater geochemistry accompanying stimulated iron and sulfate reduction and sulfide mineral precipitation. The accumulation of mineral precipitates and electroactive ions are interpreted to have altered the ability of the pore fluids to conduct electric charges, thus leading to the development of the phase response shown here. This example indicates the potential of geophysical methods for tracking biogeochemical transformations over field-relevant scales. [Adapted with permission from Williams et al. 2009. Copyright 2009 American Chemical Society]. Note that related research (see Fig. 3.4., p. 15) has shown the utility of using this type of geophysical information for quantifying the volume of evolved precipitates and associated permeability reduction associated with the same remediation treatment.

3. A Microscale Biogeochemical Subcomponent as a Complex System: The Mineral-Microbe Interface

Moving down to the molecular and microscopic scale, this final example discusses an important microscopic reactive domain in many subsurface systems: the mineral-microbe interface. The Rifle IFRC is investigating field-scale bacterial metal reduction as a means of immobilizing contaminant uranium (see sidebar 3A, BER's Rifle IFRC Site, p. 11, and previous intermediate-scale example, Section 2, p. 34). The mineral-microbe interface is a crucial subcomponent of this overall system where microorganisms attach to existing mineral surfaces or facilitate the formation of new ones. The interface is where subsequent interfacial electron transfer is mediated between microorganisms, solid-phase electron acceptors, and polyvalent solutes (e.g., uranium) when appropriate electron donors (e.g., acetate) are present. This microscopic biogeochemical process ultimately determines whether contaminant uranium is immobilized at the groundwater plume scale. Although many other factors and processes also are important, reactions at the mineral-microbe interface define the Rifle groundwater system, as they do at numerous locations nationwide. Moreover, mineral-microbe interactions are fundamental to the fate and migration of many contaminant types, to carbon cycling and sequestration, and to bioenergy.

The interplay between microorganisms and their surrounding environment is a dynamic process that has impacted the planet for nearly its entire history. Because of their small size and high ratio of surface area to volume, microorganisms exert a tremendous influence on the geosphere. As agents of weathering for rocks and minerals, microbes also are catalysts for their formation and influence subsurface water quality through such interactions. The interfacial region between microorganisms and reactive solids is dynamic, with chemistry and structure determined by adaptive interplay, response, and feedback. Microenvironments are generated with unique chemical and structural attributes that enhance microbe survivability. The mineral-microbe interface can be considered a complex system for many reasons but primarily because the behavior of the assembled biochemical system is dramatically distinct from the sum of its components.

The mineral-cell interface is characterized by steep concentration gradients that may not reflect bulk properties in either the solid or solution phase. With even the most sophisticated modern instrumentation, investigating it is difficult. The properties of the mineral-microbe interface are dynamic, reflecting time-variable biosynthetic and biogeochemical reactions occurring at small spatial scales (i.e., < 1 nm). Our understanding of the complexity of microbial cells is improving. This progress includes insights into how microbes sense and respond to each other and to their environment and how they modify their immediate surroundings via secretion of extracellular polymers to form biofilms, proteins for catalyzing reactions with solids and substrates not accessible to intracellular compartments, and signaling molecules for communicating with other cells. In a colloquium sponsored by the American Academy of Microbiology (Nealson and Ghiorse 2001), participants concluded that significant and critical events in geobiology happen at the level of individual cells or groups of cells and that the details of such processes are best revealed by observations and measurements made at small scales.

Complex systems behavior also can be found in molecular-scale aspects of microbe-mineral interfaces. An important example being studied is operation of the transmembrane electron-transport chain in the cell envelope of metal-reducing bacteria (Fredrickson and Zachara 2008). This chain is composed of a series of structurally complex mono- and multiheme redox proteins (i.e., *c*-type cytochromes; Shi et al. 2007) that transport electrons more than 8 nm from the inner membrane, across the periplasmic space, through the outer membrane, and to bioavailable forms of Fe(III), Mn(III,IV), or contaminant metals such as U(VI) and Tc(VII) (see Fig. B.7. Roles of MtrC and OmcA in *Shewanella oneidensis* MR-1-Mediated Extracellular Reduction of Fe(III) Oxides, p. 39). The architecture of the chain entails several linkages between water-soluble and membrane-bound proteins in which structured multiheme cytochromes interface in a specific molecular fashion to create a functional wire of heme cofactors capable of electron transfer over nm distances (Hartshorne et al. 2007; Hartshorne et al. 2009; Shi et al. 2009). The rate of electron transfer from cofactor to cofactor within a protein is strongly coupled to local and tertiary protein structures and their fluctuation dynamics (Pascher et al. 1996; Smith et al. 2006); these component molecules also display complex behavior.

Occurring within the mineral-microbe interface are hierarchies of biochemical and biogeochemical interactions that determine overall system behavior. The efficiencies of the interfacial protein-protein electron transfer and the terminal protein-metal electron transfer to the mineral interface depend on the lifetimes of protein-protein and protein-metal interactions (Kerisit et al. 2007; Rosso and Dupuis 2006). Dynamics in the cofactor structure, solvation, and distance of separation at the molecular scale involve

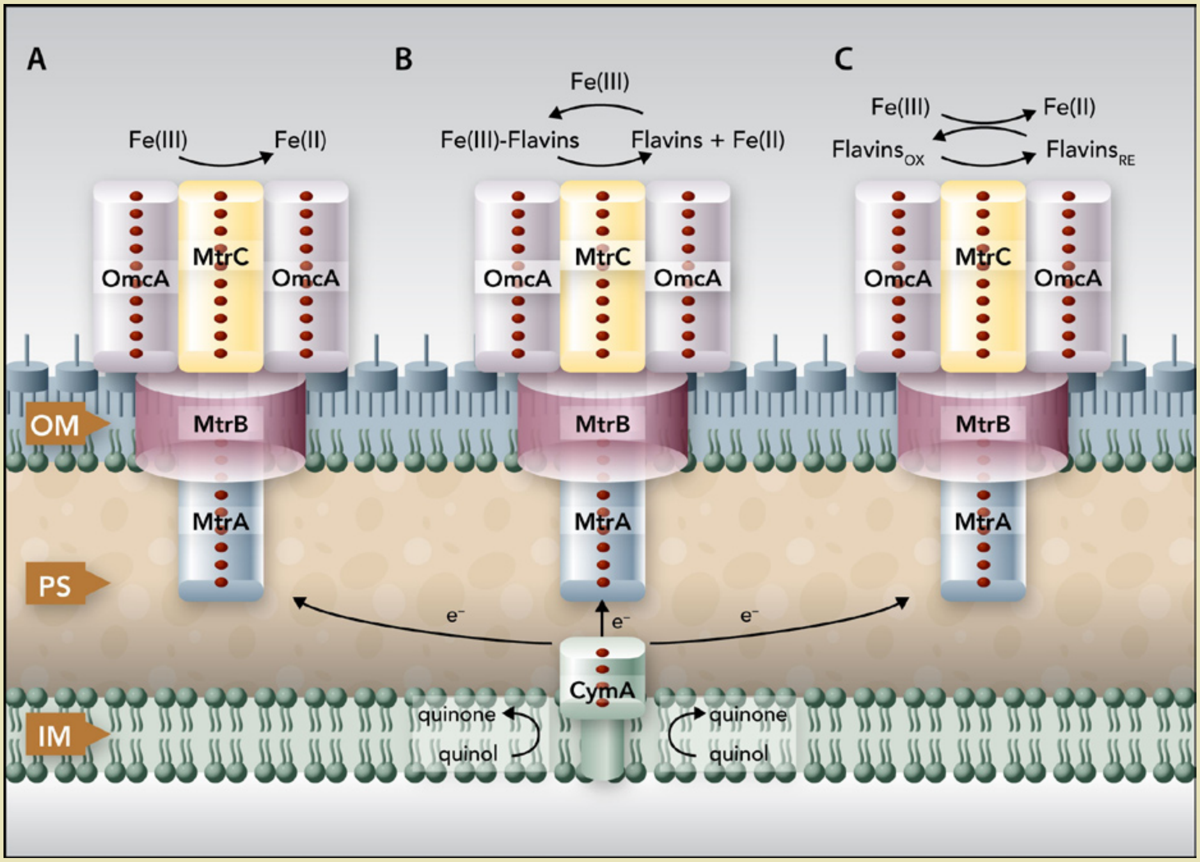

Fig. B.7. Roles of MtrC and OmcA in *Shewanella oneidensis* MR-1-Mediated Extracellular Reduction of Fe(III) Oxides. Proteins known to be directly involved in the reduction include (1) the inner membrane (IM) tetrahaem c-Cyt CymA that is a homologue of NapC/NirT family of quinol dehydrogenases, (2) the periplasmic decahaem c-Cyt MtrA, (3) the outer membrane (OM) protein MtrB, and (4) the OM decahaem c-Cyts MtrC and OmcA. (**A**) Together, they form a pathway for transferring electrons from the quinone and quinol pool in the IM to the periplasm (PS) and then to the OM where MtrC and OmcA can transfer electrons directly to the surface of solid Fe(III) oxides. (**B**) MtrC and OmcA also might reduce Fe(III) oxides indirectly by transferring electrons to either flavin-chelated Fe(III) or (**C**) oxidized flavins. [From Shi et al. 2009]

picosecond to nanosecond fluctuations (Kerisit et al. 2007; Wang et al. 2008). At the biomolecule scale, tertiary fluctuations operate at micro- to millisecond time scales. Many key protein structures, protein-protein super-complex structures, and interaction lifetimes are unknown, complicating the understanding of key component interactions. Furthermore, the structure and dynamics at the protein-metal or protein-mineral interface are elusive and difficult to probe directly. At a higher level, the transmembrane electron-transport system is dynamically coupled to other metabolic systems in a living cell that itself is responsive and adaptive to environmental conditions. The collective behavior of the electron-transport system cannot be quantitatively examined by separating individual biomolecular components, nor can the boundaries of the system (e.g., any ancillary components that constrain interaction distances to optimal values) be easily identified. Consequently, the system behavior is unpredictable, with the overall cellular electron-transfer rate an emergent property. This system therefore is complex, requiring a systems-level approach to understand and model key interactions determining electron-transfer rate.

This is just one of many reaction- and process-specific examples that could be chosen because the mineral-microbe interface is a dynamic region fundamental to biogeochemistry. An important aspect of these small-scale complex systems is that they are one of several primary controls on field-scale behavior. The mineral-microbe interface also is a domain suitable to complex systems science approaches and models (Kreft et al. 2001; Pennisi 1999; Weng et al. 1999) in which extremely complex molecular interactions may be described using more simple rules. Consequently, integrating systems biology–based models of microbial metabolism and gene regulation into complexity models of the mineral-microbe interface is envisioned. Their subsequent incorporation into higher-level models (e.g., macroscopic or field scale) of biogeochemical systems would eliminate the need for complex upscaling relationships. Such an approach could yield new insights on common microscopic functional relationships occurring at all mineral-microbe interfaces.

C. Application of Complexity Approaches and Merit of Concept

Despite uncertainties in categorizing representative subsurface systems as complex in terms of accepted criteria, many workshop participants believe there is merit in conceptualizing the subsurface as such and applying tools of complex systems science as part of a comprehensive research strategy to understand and predict subsurface behavior. Understanding how processes (e.g., system subcomponents) acting on different scales and hierarchal levels are bound to one another is an important goal of interdisciplinary subsurface research, regardless of whether a reductionistic or systems approach is taken. However, there are major differences in carrying out these two approaches, with consequent implications for the types of data collected and the nature of conceptual and numerical models developed.

In the reductionistic approach, *ad hoc* decisions often are made about which components or processes of the real system to include or ignore based on preconceived beliefs, biases, and observations at limited or convenient scales. Sometimes these choices are representative of important processes controlling system behavior at the higher scale, and sometimes they are not. Often, reactive transport models with associated lower-scale parameters are developed and upscaled in an attempt to describe larger-scale system behavior. These "mechanistic" models integrate geochemical and microbiologically driven reactions along with advection, dispersion, and diffusion (e.g., Bethke 2008; Regnier et al. 2003; Steefel et al. 2005). Varying markedly in sophistication, reactive transport models calculate temporal and spatial concentrations of solid and aqueous chemical components resulting from equilibrium or kinetic reactions and diffusive or advective transport. They also calculate microbial growth and decay occurring within a representative elementary volume of the modeled system (see, for example, Fang et al. 2009 and Yabusaki et al. 2007). Considerable current research is focused on how reaction parameters and models upscale and on which higher-level system interactions, characteristics, or attributes (often related to undescribed effects of heterogeneity, complex hydrological flow fields, or microbial ecology) to include for adequate system understanding and description.

In a systems approach, the system is looked at holistically to identify (1) patterns characterizing it and its dynamic behavior (Kirchner et al. 2000) and (2) the key variables, processes, and their interactions that appear to define emergent or otherwise complex behavior (e.g., Kirchner et al. 2001; Kollet and Maxwell 2008b). Emphasis may be placed on longer-term monitoring of the studied system to provide time-series data for observational constraints on models (Kirchner et al. 2000) or to identify hierarchal interactions controlling the system-scale features to be predicted and their description by phenomenological means (e.g., Werner 1999; Werner 2003). The resulting model is tied to the internal, functional organization of the real system as it controls behavior at some targeted scale (Grimm et al. 2005) and thus can be used for explanation and generally coarse-scale prediction (Kreft et al. 2001; Murray 2007; Werner 1999). However, since the complexity approach has not yet been applied to subsurface systems, several things are unclear, including how models common to complexity [e.g., particle dynamics, cellular automata, agent based, or pattern oriented (Grimm et al. 2005; Shalizi 2006)] would be applied or formulated for the subsurface or their subcomponent processes. Also unclear are which system variables these models are likely to describe and to what level of uncertainty and spatial specificity. Thus, the true promise (or lack thereof) of the complex systems science approach as currently practiced cannot be easily ascertained. Beyond that, applying this approach to subsurface science likely will require new perspectives and modeling strategies, given that systems have different characteristics, constraints, and prediction needs.

The philosophy and approaches for investigating and modeling subsurface systems vary depending on whether a reductionistic or complex systems approach is adopted (see Table B.2. Characteristics of Reductionistic and Complexity Approaches, this page). A reductionistic approach provides motivation to study previously chosen system subcomponents in great detail and to drive programmatic scientific accomplishments at more mechanistic and fundamental levels. Because of various uncertainties, this approach typically places less emphasis on upscaling and on documenting that the chosen subprocesses and characteristic properties describe real system behavior. In contrast, a complex systems approach identifies and characterizes (presumably without bias) the subcomponent interactions and drivers responsible for emergent behaviors and yields the integrative, higher-scale scientific findings better suited for predicting systems behavior. As research and understanding progress, both approaches support the development of sequential scientific hypotheses on the interactions of subcomponents or subprocesses controlling system-scale behavior. However, the nature of hypotheses, the scientific footprint, and the resulting models describing these interactions may be quite different.

In the past, most scientific investigations have relied almost entirely on either bottom-up or top-down approaches and methods. Employing a broader

Table B.2. Characteristics of Reductionistic and Complexity Approaches

	Reductionism	Complexity
Philosophy	Most systems are too complex to study in their natural state. They must be deconstructed into more-fundamental units or smaller-scale parts for comprehension. Understanding the detailed specificity of a given problem is key. Fundamental process understanding is a desired objective because it is transferrable between different systems. Higher-scale behavior results from interactions of smaller-scale processes and is predictable from detailed models of them.	A complex natural system should be studied as a whole because its behavior does not result from the sum of its smaller-scale parts. Higher-scale behavior exhibits emergence resulting from unexpected interactions of processes or the effects of other properties at different scales. Complex systems exhibit common, underlying macroscale laws that are applicable elsewhere. Understanding pervasive commonalities between systems and their relationships to more simple systems is key.
Strategy	Quantify lower-scale fundamental mechanisms, processes, and their interactions in detail as a primary goal. Working upward, understand and model system behavior as some permutation of the sum of its lower-scale parts (e.g., processes) and their interactions. Blame heterogeneity for shortcomings.	Identify diagnostic variables and common patterns of emergence defining high-level system behavior. Working downward, identify, understand, and model critical subscale interactions and environmental tensors that control diagnostic variable dynamics and behavioral patterns. Identify transferrable macroscale laws as a primary goal.
Research Approach	Investigate underlying mechanisms at multiple scales below the prediction scale, often using model or abstract systems with hypothesis-based research. Develop robust generalized models at the subscale for simulating process interactions and detailed responses. Ascertain how heterogeneity in properties controls process manifestations at the prediction scale.	Collect significant databases on target system(s) over time, or with perturbation, to define characteristic behavior. Apply data analysis tools to identify diagnostic emergent system variables, controlling properties, and macroscopic laws to constrain models. Develop transparent models that explain system operation and simulate emergent variable responses.
Modeling	Mechanistic details of lower-scale processes are preserved but streamlined in upscaling. Relationships are developed that link fundamental process models and their parameters to the prediction scale. Lower-scale models are calibrated at the prediction scale because of characterization uncertainties and the effects of heterogeneities.	Mechanistic details of lower-scale processes are ignored. Phenomenological models are used to explain and describe key process contributions, interactions, and properties controlling characteristic system behavior at the prediction scale. Add more-complete theory as needed for improved explanation and prediction.

arsenal of techniques and approaches is now necessary because the focus of scientific research is shifting from narrowly defined topics requiring in-depth specialized knowledge and understanding to more-complex, multicomponent applications requiring a much broader multidisciplinary approach (without losing sight of the importance of in-depth understanding). Society faces challenges at the nexus between sufficient energy to support a thriving economy, adequate high-quality water to provide food for a growing population and for industry, and the need for a high-quality environment so that all can enjoy a healthy and rewarding lifestyle. These challenges can be met only through a holistic approach that takes advantage of the full spectrum of scientific methods and capabilities. In this context, the relative weight placed on reductionistic or complexity approaches, and the ways in which they are combined to solve important problems, will be driven by programmatic science and modeling goals. The choice ultimately depends on the particular aspects of a system for which understanding and simulation are desired and what degrees of uncertainty are acceptable (Beven 2001; Murray 2003).

Workshop discussions supported the need for a new research strategy to investigate subsurface systems. In this strategy, complexity and reductionistic approaches could be melded to (1) identify common behavioral patterns for different types of complex subsurface systems, (2) understand and describe the workings of representative complex systems at relevant scales, and (3) yield new modeling strategies for improved system understanding and prediction. Complex systems selected for research could include those at the field scale and the key subcomponents and subprocesses at lower scales known to control field-scale behavior and that have potential for high scientific impact. Critical overall needs are research to emphasize hierarchical subsurface systems containing coupled processes and the characterization of inter- and cross-scale process interactions and feedback mechanisms that can lead to emergent behavior or other complex system characteristics.

A hybrid approach is needed for integrating complementary top-down and bottom-up research. Combined with robust system characterization and modeling, this approach would allow the comprehensive understanding and prediction of complex subsurface system behavior. Two primary elements are needed in this approach:

- Multidisciplinary investigations of important subsurface systems to identify common behavioral patterns observed at different scales, regardless of exact system characteristics, and the variables controlling these patterns. This includes identifying features diagnostic of complexity, determining emergent behaviors and controlling interactions that constrain models, and developing and evaluating systems models and their predictive power.
- Experimental, theoretical, or field studies of key components, interactions, controlling variables, and hierarchies of subsurface systems. In these studies, (1) interactions and key processes and mechanisms are quantified and modeled at lower scales, (2) simplified process abstractions are developed and their transitions to larger scales and their roles in emergent and collective behavior investigated, and (3)systems-scale predictions are made using upscaled models of primary processes believed to be responsible for system response.

Such melding of perspectives is necessary to simultaneously develop robust understandings of key underlying mechanisms and interactions and the importance of scale transitions and to provide insights into common macroscopic laws governing complex system behavior at the prediction scale. Changes to traditional research strategies are required to enable comprehensive investigations of complex subsurface systems with their characteristic multitude of processes at different scales, significant heterogeneity, and ever-present measurement and observational constraints. Integrating fundamental information derived from multiple perspectives is essential to achieve the level of in-depth understanding and quantitative system predictability needed for complex subsurface systems.

Appendix C

Workshop Program

BER Workshop on Subsurface Complex System Science Relevant to Contaminant Fate and Transport

Workshop Co-Chairs: Susan Hubbard, Frank Loeffler, and John Zachara

Sunday, August 2, 2009 – EVENING

Pre-meeting: Workshop organizers and panel leads

6:00 p.m. – 6:15 p.m.	Welcome and purpose of meeting
6:15 p.m. – 6:30 p.m.	Overview of agenda
6:30 p.m. – 7:00 p.m.	Discussion of breakout sessions
7:00 p.m. – 8:00 p.m.	Working dinner: Workshop report and discussion

Monday, August 3, 2009 – MORNING

7:00 a.m. – 8:00 a.m.	Registration and continental breakfast

Plenary Opening Session

Session 1: Introduction

8:00 a.m. – 8:10 a.m.	Introductory remarks	Anna Palmisano
8:10 a.m. – 8:25 a.m.	ERSP strategic planning	David Lesmes
8:25 a.m. – 8:50 a.m.	Workshop structure and agenda	Co-Chairs
8:50 a.m. – 9:20 a.m.	Summary of DOE-BES Workshop: Basic Research Needs in the Geosciences	Donald DePaolo
9:20 a.m. – 9:45 a.m.	Break	

Session 2: Complex Systems Science – Perspectives from the Field

9:45 a.m. – 10:30 a.m.	Scaling, Universality and Geomorphology	Peter Dodds
10:30 a.m. – 11:15 a.m.	Mercury Cycling in the Environment	Scott Brooks
11:15 a.m. – 12:00 p.m.	Microbial Oceanography	Mick Follows

Monday, August 3, 2009 – AFTERNOON

Breakout Session 1: Complex Subsurface Subsystems at Different Scales

12:00 p.m. – 1:00 p.m.	Working lunch – describe breakout agenda/format
1:00 p.m. – 3:30 p.m.	Series of presentations by panelists: My Favorite Things…
3:30 p.m. – 4:00 p.m.	Break
4:00 p.m. – 6:00 p.m.	Discuss, identify, and prioritize *key* complex systems at different scales for breakout session

Monday, August 3, 2009 – EVENING

6:00 p.m. – 7:30 p.m.	Working dinner
7:30 p.m. – 9:00 p.m.	Draft slides describing system attributes, scientific challenges, scientific impacts, and interdisciplinary research approaches for 3 to 5 “high-priority” complex systems for breakout session

Tuesday, August 4, 2009 – MORNING and AFTERNOON

7:30 a.m. – 8:30 a.m.	Continental breakfast

Plenary Session

8:30 a.m. – 10:00 a.m.	Presentation of *Complex Subsurface Subsystems at Different Scales* (three 30-minute blocks of time for presentations and discussion).

Breakout Session 2: Disciplinary Research to Understand Complex Systems

10:00 a.m. – 11:00 a.m.	Review the *key* complex systems at different scales and suggest refinements to be presented at the plenary session.
11:00 a.m. – 12:00 p.m.	Determine major disciplinary research goals that advance our ability to characterize, monitor, understand, and predict the dynamic behaviors of key complex subsurface systems and their functional components. Develop a Logic Model to summarize the near-term, mid-term and long-term research goals and the potential scientific impacts of these advances.
12:00 p.m. – 1:00 p.m.	Working lunch
1:00 p.m. – 2:30 p.m.	Continue working in disciplinary groups and preparing Logic Models for presentation at the plenary session.

Plenary Session

2:30 p.m. – 4:00 p.m.	Feedback by disciplinary groups about proposed *key* complex systems at different scales.
	Presentation of Logic Models by Transport, Geochemistry, and Microbiology breakout groups for *Disciplinary Research to Understand Complex Systems.*

Breakout Session 3: Complex Systems Across Scales

4:00 p.m. – 6:00 p.m.	The objective of this exercise is to identify research needed to connect and integrate knowledge and models of complex systems across scales as is needed to make accurate predictions of contaminant fate and transport in naturally complex subsurface systems. A hierarchical approach, involving interdisciplinary groups, will be used to develop two alternate ("competing") Integrated Logic Models for *Complex Systems across Scales.*

Tuesday, August 4, 2009 – EVENING

7:00 p.m.	Dinner with your assigned group at a local restaurant (6 small interdisciplinary groups with 5 to 6 people/group)

Wednesday, August 5, 2009 – MORNING

7:30 a.m. – 8:30 a.m.	Continental breakfast

Breakout Session 3: Complex Systems Across Scales (continued)

8:30 a.m. – 12:00 p.m.	Group 1 and Group 2 each merge inputs from three scale-based and interdisciplinary subgroups to independently develop alternate ("competing") Integrated Logic Models for *Complex Systems Across Scales*

Wednesday, August 5, 2009 – AFTERNOON

Plenary Closing Session

12:00 p.m. – 2:00 p.m.	Working lunch
12:00 p.m. – 12:30 p.m.	Presentation of *Complex Subsurface Subsystems at Different Scales*
12:30 p.m. – 1:00 p.m.	*Disciplinary Research to Understand Complex Systems* – Presentation of Logic Models by Transport, Geochemistry, and Microbiology breakout panels
1:00 p.m. – 1:15 p.m.	*Complex Systems Across Scales* – Presentation of Integrated Logic Model by Group1
1:15 p.m. – 1:30 p.m.	*Complex Systems Across Scales* – Presentation of Integrated Logic Model by Group 2
1:30 p.m. – 1:45 p.m.	Closing Remarks

Begin Writing Workshop Report

2:00 p.m. – 6:00 p.m.	Workshop co-chairs and writing team begin organizing and writing the first draft of the workshop report.

Appendix D
Workshop Participants and Observers

Participants

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Appendix E

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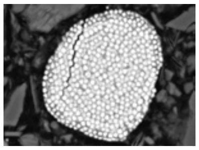
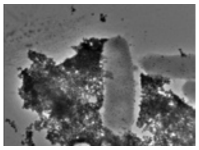


Framboidal pyrite from a naturally bioreduced alluvial sediment, Rifle, Colorado. [From Qafoku, N. P., R. K. Kukkadapu, J. P. McKinley, B. W. Arey, S. D. Kelly, C. T. Resch, C. M. Wang, and P. E. Long. 2009. "Mineralogical Control on U(VI) Attenuation in the Contaminated Sediments from Rifle, Colorado." American Chemical Society Spring Annual Meeting, Salt Lake City, Utah. March 24, 2009. See also Qafoku, N. P., R. K. Kukkadapu, J. P. McKinley, B. W. Arey, S. D. Kelly, C. Wang, C. T. Resch, and P. E. Long. 2009. "Uranium in Framboidal Pyrite from a Naturally Bioreduced Alluvial Sediment," *Environmental Science & Technology* **43**(22), 8528–34]



***Shewanella oneidensis* MR-1 with associated biogenic uraninite (UO_2).** [Modified from supporting materials of Marshall, M. J., A. E. Plymale, D. W. Kennedy, L. Shi, Z. Wang, S. B. Reed. A. C. Dohnalkova, C. J. Simonson, C. Liu, D. A. Saffarini, M. F. Romine, J. M. Zachara, A. S. Beliaev, and J. K. Fredrickson. 2008. "Hydrogenase- and Outer Membrane *C*-Type Cytochrome–Facilitated Reduction of Technetium(VII) by *Shewanella oneidensis* MR-1," *Environmental Microbiology* **10**(1), 125–36. Copyright 2008 John Wiley and Sons]

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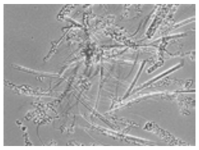

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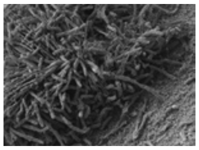

Colony of metal-reducing bacteria and iron phosphate bioprecipitate. [From Peretyazhko, T. S., J. M. Zachara, D. W. Kennedy, J. K. Fredrickson, B. W. Arey, J. P. McKinley, C. M. Wang, A. C. Dohnalkova, and Y. Xia. 2010. "Ferrous Phosphate Surface Precipitates Resulting from the Reduction of Intragrain 6-Line Ferrihydrite by *Shewanella oneidensis* MR-1," *Geochimica et Cosmochimica Acta*, in review. Copyright Elsevier]

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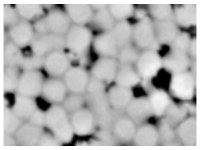
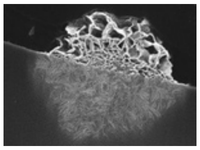


Scanning electron microscopy (SEM) backscattered image of framboidal pyrite from a naturally bioreduced alluvial sediment, Rifle, Colorado. [Reprinted with permission from Qafoku et al. 2009 *Environmental Science & Technology* paper. Copyright 2009 American Chemical Society. Also from Qafoku et al. March 2009 presentation at the ACS Spring Annual Meeting. See related image in Column 1]



Iron phosphate bioprecipitate in cross-section with bottom extending into internal pores of silica. [From Peretyazhko et al. 2010. Copyright Elsevier. See related image in Column 3]

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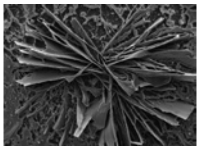

Cryo-SEM image of a bioprecipitate formed during incubation of *S. oneidensis* MR-1 with ferrihydrite (magnification = 1500 ×) [From Reardon, C. L., A. C. Dohnalkova, P. Nachimuthu, D. W. Kennedy, D. A. Saffarini, B. W. Arey, L. Shi, Z. Wang, D. Moore, J. S. McLean, D. Moyles, M. J. Marshall, J. M. Zachara, J. K. Fredrickson, and A. S. Beliaev. 2009. "Role of Outer-Membrane Cytochromes MtrC and OmcA in the Biomineralization of Ferrihydrite by *Shewanella oneidensis* MR-1," *Geobiology* **8**(1), 56–68. Copyright 2009 John Wiley and Sons]

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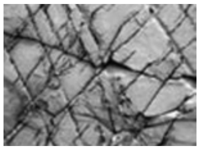

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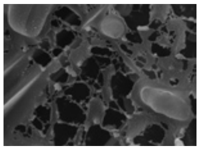

Bacterial dissolution of ferrous phosphate (magnification = 20,000 ×). [Courtesy C. Reardon, J. Fredrickson, A. Dohnalkova, and J. Zachara; Pacific Northwest National Laboratory]

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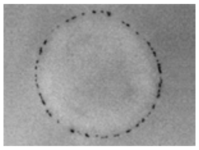
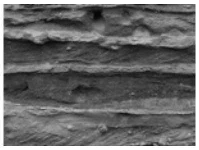


$Tc(IV)O_2$ precipitates on the surface of *S. oneidensis* MR-1 mutant, with MR-1 shown in cross-section. [From Marshall et al. 2008. Copyright 2008 John Wiley and Sons. See related image in Column 1]



Physically heterogeneous sediment layers. [Courtesy Andy Ward, Pacific Northwest National Laboratory]

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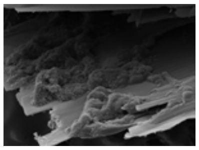
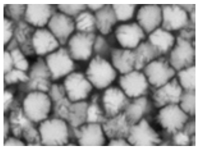


Metal-reducing bacteria on a ferrous phosphate growth plane; bioprecipitation or biodissolution? [Courtesy C. Reardon, J. Fredrickson, A. Dohnalkova, and J. Zachara; Pacific Northwest National Laboratory]

Branched river channels in Florida [From Howard, A. D. 2009. "Hydrology: Forming Valleys from Below," *Nature Geoscience* **2**, 165–66. Published in Howard 2009 courtesy of the Florida Department of Revenue (FDOR). Reprinted by permission from FDOR and Macmillan Publishers Ltd: *Nature Geoscience*]



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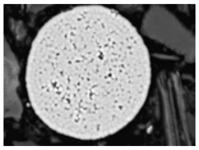

Framboidal pyrite from a naturally bioreduced alluvial sediment, Rifle, Colorado. [From Qafoku et al. March 2009 presentation at the ACS Spring Annual Meeting. See also Qafoku et al. 2009 *Environmental Science & Technology* paper (Copyright 2009 American Chemical Society) and related images in Columns 1, 4, and 8]

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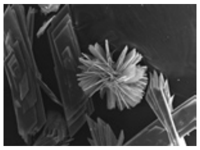
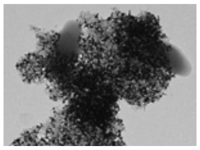
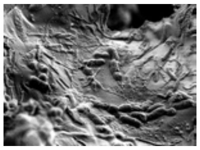


Two morphologically distinct phases of ferrous phosphate (50–100 µm florets and plates) formed during incubation of *S. oneidensis* MR-1 with ferrihydrite. [From Reardon et al. 2009. Copyright 2009 John Wiley and Sons. See related image in Column 5]



***Shewanella oneidensis* MR-1 cells engulfed in goethite (FeOOH) resulting from the biologically induced recrystallization of ferrihydrite.** [Courtesy C. Reardon, J. Fredrickson, A. Dohnalkova, and J. Zachara; Pacific Northwest National Laboratory]



SEM image of a sulfate-reducing biofilm obtained from a borehole used for long-term (100+ days) acetate injection during biostimulation activities at DOE's Integrated Field Research Challenge site near Rifle, Colorado. The outer surface of the biofilm was stabilized with ruthenium red prior to SEM analysis. [Image courtesy A. Dohnalkova, Pacific Northwest National Laboratory. Biofilm material courtesy K. H. Williams, Lawrence Berkeley National Laboratory]

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