

Controlling Subsurface Fractures and Fluid Flow: A Basic Research Agenda



DOE Roundtable Report

May 22, 2015
Germantown, MD



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Controlling Subsurface Fractures and Fluid Flow: A Basic Research Agenda

Report of a Roundtable Convened to Consider Foundational Research Relevant to Subsurface Technology and Engineering RD&D

May 22, 2015
Germantown, MD

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Cover:

Upper Left: Color SEM-cathodoluminescence image showing quartz-filled micro-fractures cutting quartz grains in sandstone from Rangely Field, Piceance Basin, Colorado (Courtesy of Rob Reed). Lower Left: Parallel fractures oriented perpendicular to the sedimentary strata in Mosaic Canyon, Death Valley National Park, California (Courtesy of Siyi Shao). Upper right: Carbonate minerals (white) filling fractures formed from mechanical response to chemical reactions in olivine-rich rocks (Courtesy of Peter Kelemen). Lower Right: Localized geochemical alteration of rock matrix due to fluid flow and reactions along fractures (Source of image unknown).

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Executive Summary

From beneath the surface of the earth, we currently obtain about 80-percent of the energy our nation consumes each year. In the future we have the potential to generate billions of watts of electrical power from clean, green, geothermal energy sources. Our planet's subsurface can also serve as a reservoir for storing energy produced from intermittent sources such as wind and solar, and it could provide safe, long-term storage of excess carbon dioxide, energy waste products and other hazardous materials. However, it is impossible to underestimate the complexities of the subsurface world. These complexities challenge our ability to acquire the scientific knowledge needed for the efficient and safe exploitation of its resources.

To more effectively harness subsurface resources while mitigating the impacts of developing and using these resources, the U.S. Department of Energy established SubTER – the Subsurface Technology and Engineering RD&D Crosscut team. This DOE multi-office team engaged scientists and engineers from the national laboratories to assess and make recommendations for improving energy-related subsurface engineering. The SubTER team produced a plan with the overall objective of “adaptive control of subsurface fractures and fluid flow.” This plan revolved around four core technological pillars—**Intelligent Wellbore Systems** that sustain the integrity of the wellbore environment; **Subsurface Stress and Induced Seismicity** programs that guide and optimize sustainable energy strategies while reducing the risks associated with subsurface injections; **Permeability Manipulation** studies that improve methods of enhancing, impeding and eliminating fluid flow; and **New Subsurface Signals** that transform our ability to see into and characterize subsurface systems.

The SubTER team developed an extensive R&D plan for advancing technologies within these four core pillars and also identified several areas where new technologies would require additional basic research. In response, the Office of Science, through its Office of Basic Energy Science (BES), convened a roundtable consisting of 15 national lab, university and industry geoscience experts to brainstorm basic research areas that underpin the SubTER goals but are currently underrepresented in the BES research portfolio. Held in Germantown, Maryland on May 22, 2015, the roundtable participants developed a basic research agenda that is detailed in this report.

Highlights include the following:

- A grand challenge calling for advanced imaging of stress and geological processes to help understand how stresses and chemical substances are distributed in the subsurface—knowledge that is critical to all aspects of subsurface engineering;
- A priority research direction aimed at achieving control of fluid flow through fractured media;
- A priority research direction aimed at better understanding how mechanical and geochemical perturbations to subsurface rock systems are coupled through fluid and mineral interactions;
- A priority research direction aimed at studying the structure, permeability, reactivity and other properties of nanoporous rocks, like shale, which have become critical energy materials and exhibit important hallmarks of mesoscale materials;
- A cross-cutting theme that would accelerate development of advanced computational methods to describe heterogeneous time-dependent geologic systems that could, among other potential benefits, provide new and vastly improved models of hydraulic fracturing and its environmental impacts;
- A cross-cutting theme that would lead to the creation of “geo-architected materials” with controlled repeatable heterogeneity and structure that can be tested under a variety of thermal, hydraulic, chemical and mechanical conditions relevant to subsurface systems;
- A cross-cutting theme calling for new laboratory studies on both natural and geo-architected subsurface materials that deploy advanced high-resolution 3D imaging and chemical analysis methods to determine the rates and mechanisms of fluid-rock processes, and to test predictive models of such phenomena.

Many of the key energy challenges of the future demand a greater understanding of the subsurface world in all of its complexity. This greater understanding will improve the ability to control and manipulate the subsurface world in ways that will benefit both the economy and the environment. This report provides specific basic research pathways to address some of the most fundamental issues of energy-related subsurface engineering.

Introduction

The future of the world's energy supply and the ability to deal with associated carbon emissions are closely tied to our capabilities in subsurface or geological engineering. Developments over the past ten years, including the growth of natural gas and petroleum extraction from fine-grained or "tight" sedimentary geologic formations, the desire to expand geothermal energy generation, and the expectation that subsurface storage of enormous quantities of CO₂ is necessary, have heightened expectations for improvements in the efficiency of energy-related subsurface engineering. While such improvements are continually being made by industry, there remains a large technology gap between current capabilities and those that can be imagined. Petroleum and natural gas extraction efficiency is generally low, environmental impacts are substantial, engineered geothermal systems are still an aspiration, and issues with the security of long term CO₂ storage persist.

In recognition of the key role that subsurface engineering plays in our nation's energy future, the Department of Energy established a multi-office crosscutting technology team to assess and make recommendations about how to accelerate improvements in subsurface engineering for energy purposes. The DOE technology team engaged a group of National Laboratory scientists and engineers to help define a prospective R&D agenda, and this overall effort, referred to as SubTER (Subsurface Technology and Engineering RD&D Crosscutting Team) has yielded a four-component plan around the overall objective of "adaptive control of subsurface fractures and fluid flow," as shown in **Figure 1**.

The SubTER team has developed an extensive R&D plan for advancing the technologies, but also identified several areas where new technologies would require

basic research. To extend this part of the process the DOE Office of Science, through the office of Basic Energy Science convened a roundtable consisting of 15 national lab, university and industry experts in the Geosciences to brainstorm basic research areas that underpin the goals of the broader SubTER Technology Team efforts, and are currently underrepresented in the BES research portfolio. This Roundtable was held in Germantown, MD, on May 22, 2015, and resulted in this report.

The Roundtable participants developed a basic research agenda that is inspired by the goals of SubTER, and can be broken down into one overall Grand Challenge, three Priority Research Directions, and three crosscutting research themes and approaches that are described in detail below in the remainder of the report (**Figure 2**).

Grand Challenge: Imaging Stress and Geochemical Processes

Priority Research Directions

- (1) Reactive multiphase flow in fractured systems
- (2) Chemical-mechanical coupling in stressed rocks
- (3) Nanoporous rock structure, permeability and reactivity

Crosscutting Research Themes

- (1) Advanced computational methods for heterogeneous time dependent geologic systems
- (2) Capturing heterogeneity and scale through geo-architected materials
- (3) Laboratory studies of subsurface processes

Figure 2. Summary of the results of the BES Roundtable on Foundational research that underpins the SubTER initiative goal of adaptive control of subsurface fractures and fluid flow.



Figure 1. Schematic of the four R&D "pillars" of the SubTER initiative.

Context of Fundamental Earth Science Research

The materials, chemical and Earth sciences share many research goals and challenges, especially those associated with identifying, monitoring and predicting the mechanisms of chemical and material evolution. However, achieving progress in fundamental Earth sciences that is relevant to real-world systems requires particular attentiveness to the complexity and context of geologic materials.

Modern materials science is largely focused on designing and creating (“architecting”) new materials with special properties (cf. Fleming and Ratner, 2008). These properties arise from the physical arrangement of the chemical constituents and structural units, and the dynamics of electrons, phonons, plasmons, and other interacting units that determine the character of the material at different time and length scales. Modern chemical science emphasizes reactions, especially between units in the liquid or gas state, but also at interfaces between phases. To understand materials and chemical processes, it is beneficial to study systems that are as simple as possible, and where the physical state of the reacting constituents is well characterized. To achieve this generally means using ideal crystals or even single crystal faces, and nearly pure liquids and gases. Even with these simplifications, chemical processes can be complicated.

However, since almost all Earth materials – minerals, rocks, fluids and gases – originate naturally, they tend never to be chemically pure or structurally perfect. Solids, liquids, and gases are virtually always composed of a few major constituents plus some amount of almost every other element in the periodic table. Overlaid on the chemical complexity are structural defects, internal surfaces, and adsorbed species that tend to decorate the surfaces. Such complexities are essential characteristics of most Earth materials and for many such materials it is not clear whether they are intrinsically irreducible, or will require new creative leaps (cf. Crabtree and Ratner, 2012; DePaolo and Orr, 2007, 2008).

A further key aspect of Earth materials is that they occur in a larger geologic context. Understanding the origin of that context, and appreciating its significance, requires forms of knowledge, training and expertise that are distinct from those that are taught in the other physical sciences. For example, sedimentary rocks have different features (from cm to km scale) and mineralogical composition depending on the geological environment in which they formed. They also can have different

post-depositional histories, which can determine their rheological properties, porosity, and permeability, and can add a predictable set of secondary minerals to the assemblage. While many key properties of geological materials cannot be replicated or even studied in the laboratory, these properties nevertheless follow established rules of causality that can add vital information to models of remote formations, and inform expectations about their evolution to a given perturbation. Many of the key energy challenges of the future will require not only that we can understand and manipulate complex materials in the laboratory, but also in their geologic context, typically at elevated temperatures and pressures and large length and time scales, and commonly in remote locations kilometers below the Earth’s surface. This is indeed a challenge; one that we must become increasingly better at addressing, and one for which we must continue to train scientists with the appropriate range of expertise.

Grand Challenge: Imaging Stress and Geochemical Processes

The knowledge of the distribution of stress and reactive chemical substances in the subsurface is critical to subsurface engineering. All subsurface activities perturb the natural stress states of rocks and the geochemical equilibria of rocks and fluids, causing changes in rock mineralogy, integrity and rheology, and altering permeability, over many length and time scales. For example, inducing fractures in the subsurface to enhance energy production requires the injection of engineered fluids with pressures that exceed the minimum stress condition in the rock and chemical compositions that are far from equilibrium with the rock. The engineered fluids interact with formation fluids and minerals resulting in chemical alteration of fractures and rock properties along induced and natural connected flow paths. In addition, fluid and pore pressures are perturbed, leading to additional deformation, fracturing, damage and micro-seismicity that can alter stress even at locations not reached by the injected fluids. The grand challenge for subsurface science is to map out and monitor the state of stress and geochemical alteration in the subsurface before, during, and after engineering activities.

If the state of stress and geochemical reactivity were known, subsurface engineering strategies could be designed to enhance productivity or isolation and avoid failure by working within the framework of the known and evolving stress field; and by engineering fluids and fluid flow pathways to reduce or enhance chemical reactivity.

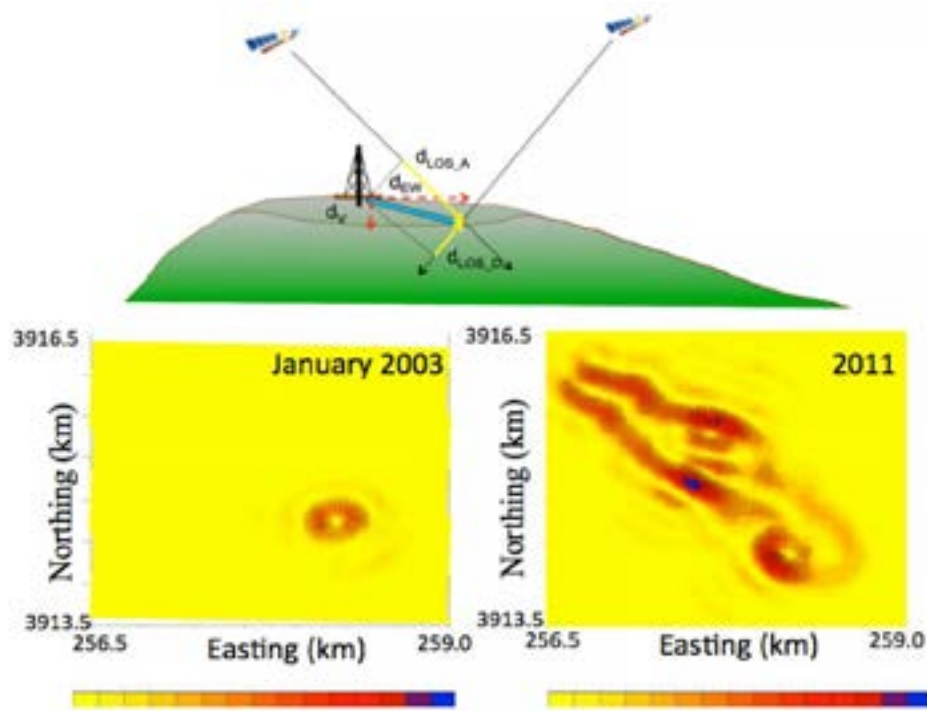


Figure 3. Comparison of overburden stress at 100 m depth over a 3 km x 3 km region from an oil field in central California from (a) InSAR (Interferometric synthetic aperture radar) measurements of surface displacements from (b) January 2003 and (c) 2011. Color scale represents the interpreted stress magnitude based on estimates of changes in reservoir volume from the displacement data. Improvement in interpretation requires information on the subsurface geological structure, properties of overburden and rock, three-dimension geomechanical models and joint inversion with other data sets (courtesy of Don Vasco).

1. Imaging Subsurface Stress

Current technology is unable to *directly* measure the stress state in subsurface reservoirs. Instead, measuring stress involves the use of “proxies” that reflect the state of stress. Typically these proxies are strain, micro-seismicity or a failure response, and from those observations stress is inferred. Examples of proxy measurements are those in boreholes from over-coring, strain-meters or hydraulic fracturing, from earthquake mechanisms and locations, or from displacements measured at the Earth’s surface (**Figure 3**). The accuracy of stress estimates from proxy measurements depends on (1) the initial state of stress (2) the constitutive relationship that describes how the observed deformation is related to the applied stress, which in turn depends on (3) the presence of fractures, faults and other mechanical discontinuities that can initiate, reactivate, propagate or close in response to changes in stress. Some rheological properties can be obtained from geophysical signals (e.g. seismic or electromagnetic signals). The speed at which seismic waves travel through rock depends on the Young’s and shear moduli

of the rock. However, rock masses are rarely isotropic, can deform through elastic, plastic, or visco-elastic modes, and contain faults and fractures with heterogeneous stiffness and frictional properties. Fluids exert pore pressure and can chemically alter the rock, both of which can vary with time and affect the responses to stress. The moduli and fracture and fault properties depend on the mineralogy, pore structure, fabric, fluid content, fluid saturation, and microcracks in the rock, and also on the deformation rate and the thermal, chemical, and stress history.

Significant advances in our ability to quantify subsurface stress require improvements in the process for establishing rock properties, estimating initial stress, verifying constitutive and friction/failure relationships and monitoring subsurface proxies for the evolution of stress. The outcome of this effort could be an integrated predictive model of stress that incorporates observations of deformation, geology, and natural and engineered sources of deformation. Progress toward this goal implies the following research needs.

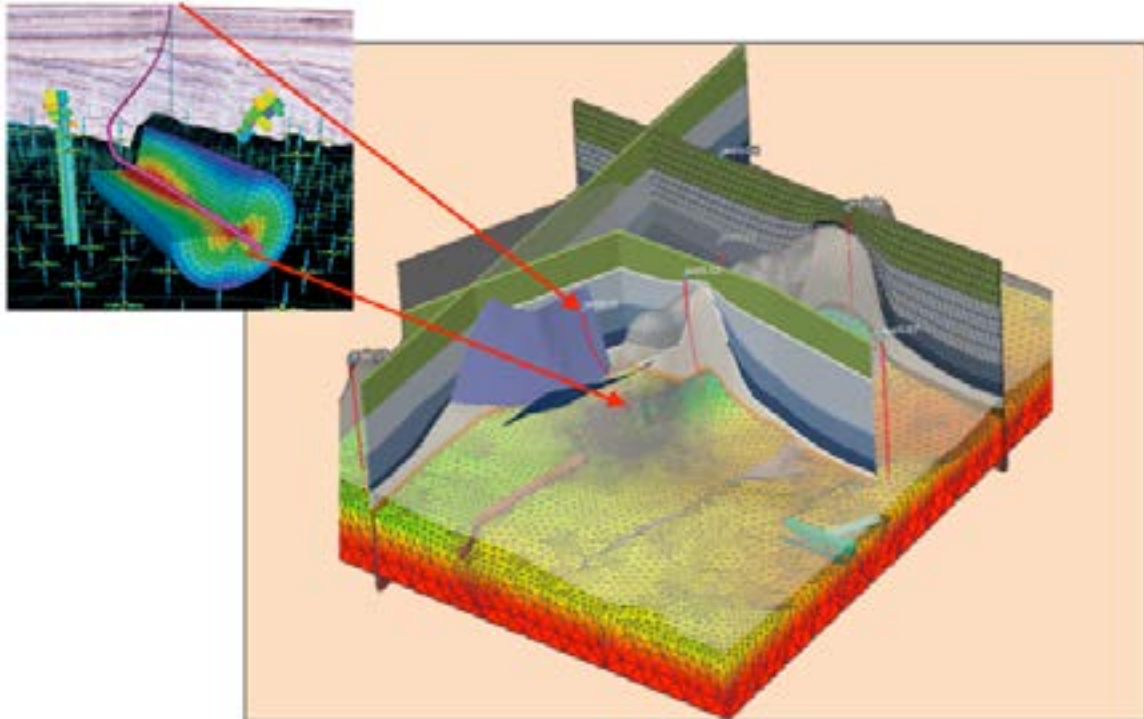


Figure 4. Borehole techniques enable measurements of stress near the well bore (pink line) along the length of the borehole (inset upper left) but do not provide information between or away from wells at depth in the reservoir. Interpretation of stress away from the borehole requires integration of geologic and geophysical datasets from multiple length scales over time frames of a project. Red arrows indicate location of borehole in the reservoir. Image schematics adapted from Baker Hughes JewelSuite Manual.

Rheological Properties of Rocks in Subsurface Systems

Rheological properties of rock are used in constitutive equations that allow the state or change in state of stress to be inferred from deformation or strain measurements. New or improved constitutive relationships are needed that account for heterogeneity, depth-dependent properties, and the presence of engineered fluids. For example, no constitutive relationship incorporating fluid pore pressure currently exists for rocks like shale that are anisotropic from layering on multiple length scales, have little connected porosity, contain thin films of water, clays, variable geochemical reactivity, mixed wettability and mechanical discontinuities. Currently, the main access to rheological information is from laboratory studies of retrieved cores and from borehole measurements (**Figure 4**). However, boreholes sample a narrow cylindrical volume along the borehole and provide little information on the lateral extent of rock type or rock properties.

The scientific challenges are:

- (1) Accurate measurement, accounting and representation of the effect of geometry, lateral extent, location and thickness of layering, and mechanical discontinuities, on the rheological properties of rock under subsurface geochemical, thermal, stress, hydraulic and pressure conditions;
- (2) Development of new well logging tools and interpretation methods that collect and analyze data at appropriate time and spatial intervals;
- (3) Development of mathematical, statistical and numerical frameworks to extend rheological parameters obtained from core and borehole logging, to locations away from the borehole and between boreholes using statistical approaches that are constrained by geological environment, and using joint inversion of geophysical data from surface deformations (tiltmeters, InSAR, GPS, repeat LiDAR), seismic and electromagnetic tomography, hydraulic tests, and other existing or new techniques;
- (4) Development of constitutive relationships with tunable length and time scales constrained by field and laboratory data to match the multiple spatial and temporal scales of field observations, borehole observations, and core experiments;
- (5) Definition and mathematical description of the suite of relaxation phenomena that control the timescales and pathways by which a disturbed subsurface system relaxes to a new steady state, or a meta-stable or near-equilibrium state.

The Effect of Mechanical Discontinuities on the State of Stress

The presence of faults, joints, fractures and other mechanical discontinuities affect the state of stress. Perturbations can lead to slip along existing faults, reactivation of dormant faults, and accumulation of damage from the initiation, propagation, and coalescence of mechanical discontinuities that range in scale from micro-cracks (micrometers) to fractures (10s-100s of meters) to faults (100s meters to km). Opening, closing, or generating fractures and slip along faults can alter the flow paths for injection or withdrawal of fluids, and can result in trapped fluids and non-uniform pore pressure distributions. Imaging stress and geochemistry in the subsurface has the potential to improve the prediction of imminent subsurface failure that may hinder or halt geo-engineering projects. Some induced damage or slip is often desired (e.g., fractures that enhance permeability), while some is undesirable (e.g., earthquakes on pre-existing faults). A challenge is to identify signatures of fracture and fault behavior that enable prediction of the state of stress along mechanical discontinuities.

The scientific challenges are:

- (1) Accurate friction and failure laws for time-dependent heterogeneity (e.g. structural, frictional and fluid pressure) along faults, fractures and other slip surfaces under subsurface conditions;
- (2) Quantitative laboratory and field data, and mathematical relationships for mechanical discontinuities that connect mechanical heterogeneity, stress/thermal/hydraulic/geochemical gradients, non-uniform fluid distributions, and other scale-relevant data to the geophysical signatures used to interpret stress;
- (3) Mathematical and computational frameworks to capture crack, fracture and fault opening, closing or failure, across time and spatial scales with geochemical, geomechanical, hydraulic and thermal feedback mechanisms that affect mechanical stability;
- (4) Geophysical approaches with spatial resolution needed to delineate potentially catastrophic changes in stress from modest alterations along mechanical discontinuities;
- (5) Mathematical approaches to capture the behavior of mechanical discontinuities that exist on multiple and overlapping scales in subsurface systems, and to determine when the properties of discontinuities at various scales can be averaged or must be treated discretely.

The Initial and Evolving State of Stress

Most estimates of the initial stress state of rock formations derive from measurements of breakouts

and tensile fractures that develop in borehole walls as a well is drilled (**Figure 4**). Those borehole observations, when combined with laboratory mini-hydraulic-fracture experiments, yield estimates of the stress tensor along the boreholes. The evolving state of stress is obtained through active and passive time-lapse methods that ideally incorporate a range of complementary geophysical signals. In all cases, new and improved geophysical methods are required for determining stress away from the borehole.

The scientific challenges are:

- (1) Design and development of new high-resolution, broadband, time-lapse imaging techniques that take advantage of joint inversion of several active and passive monitoring techniques to determine changes in the state of stress;
- (2) Development of computational and mathematical methods for big data and machine learning approaches to extract relevant signal components from geophysical monitoring data that link temporal and spatial variations to the physical evolution of the rheology and fracture/fault systems;
- (3) Development of robust inverse and forward elastic full-waveform modeling approaches based on new constitutive equations, friction laws, and geologically constrained site descriptions to interpret and link the temporal and spatial variations in seismic scattering to physical and chemical evolution.

2. Measuring Geochemical Characteristics and Processes

Subsurface geochemistry can have a strong influence on the rheological properties of rock, the condition of mechanical discontinuities, stress and strain fields, and permeability. Dissolution, dissolution and precipitation processes along fractures can change flow pathways and permeability, and in some cases can cause rock deformation (**Figure 5**). The presence of even small amounts of water can substantially lower the effective viscosity of rocks at high temperature. The composition of fluids collected from wells provides the main window into subsurface geochemistry, but typically the chemistry can be altered on the way to the surface. Nevertheless, the extraction of information on subsurface processes from the chemical and isotopic composition of fluid samples is poorly developed. The goal of imaging geochemical reactions in the subsurface—to perform dynamic “geochemical tomography”—is an important aspect of this grand challenge. Advances in this field could revolutionize our ability to recognize and predict the geochemical consequences of subsurface manipulation.

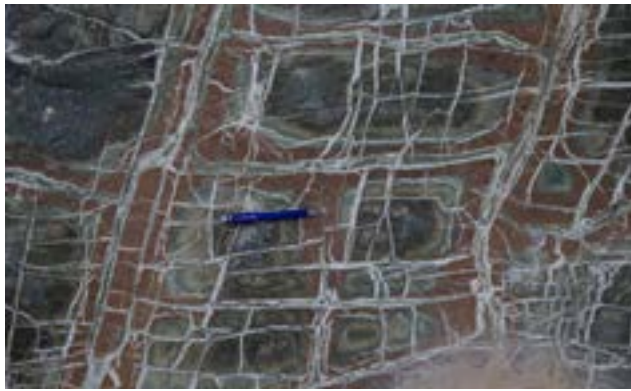


Figure 5. Natural example of fracturing driven by mineral-fluid chemical reactions. These olivine-rich rocks from the Earth's mantle were exposed to seawater-like fluids after having been brought up near the surface from depths of more than 20 km by tectonic processes. The rocks have been hydrated (green areas), carbonated (white veins) and oxidized (red zones). Volume changes associated with these alteration processes produced the grid of fractures filled by white carbonate veins (Kelemen and Hirth, 2012), in a positive feedback process that maintained or enhanced permeability and reactive surface area. (Photo courtesy P. Kelemen)

Ultimately, it would be desirable to be able to infer at least some aspects of subsurface geochemical processes remotely from geophysical signals. Geophysical signals like seismic and electromagnetic (EM) waves can propagate long distances and effectively monitor large volumes of rock. However, much subsurface chemistry takes place at small scales, particularly interfaces and pores, and many chemical changes do not couple strongly to seismic or EM probes. Consequently, expertise in imaging subsurface geochemistry is much less well established than imaging subsurface rock mechanics. Moreover, most available studies are in porous media rather than fractured systems, where coupling to flow and transport is different.

Imaging Subsurface Fluid Flow

The current state of the art for subsurface geochemical monitoring lies in the realm of imaging the flow of subsurface fluids. Electromagnetic signals are influenced by the dielectric properties of fluids within pores and by the pore space interconnectivity. Seismic wave propagation is influenced by fluid and rock elasticity and density. By using one or more of these signals, subsurface fluid processes such as changes in salinity or the replacement of brine with supercritical CO_2 can be recorded. **Figure 6** shows a comparison of deep subsurface monitoring of the same supercritical CO_2 plume using alternative crosswell geophysical signals and inversion algorithms. While seismic and electromagnetic methods achieve convergence on the same mean CO_2 saturation state, there are notable differences in predicted fluid distribution.

The scientific challenges are:

- (1) Development of techniques to quantify and image changes in fluid properties and fluid distributions at smaller spatial scales, greater depth, and improved sensitivity to small changes in fluid chemistry;
- (2) Achievement of fluid imaging in the deep subsurface with surface sensors or combined well-bore and surface sensor arrays without the need for monitoring wells;
- (3) Improvements of the quantification of uncertainty associated with signal quality, rock and fluid properties, and rock/fluid physical models;
- (4) Improvement of the prediction of fluid distributions by joint inversion of complementary signals;
- (5) Development of improved understanding of geophysical signatures of geochemical processes of interest in the context of fractured rocks.

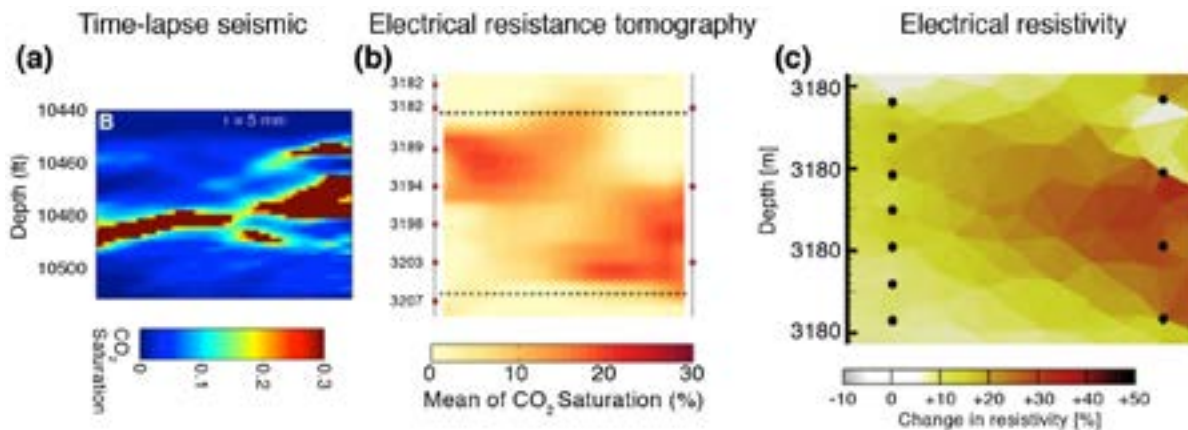


Figure 6. Characterization of a CO_2 plume at the Cranfield Site using three cross-well geophysical methods at the same location and time after injection. (a) Estimated CO_2 saturation obtained using seismic tomography. (b) Estimated CO_2 saturation using electrical resistance tomography. (c) 2D electrical resistivity map. Data from Ajo-Franklin et al. (2013), Yang et al. (2014) and Doetsch et al (2013).

New Tracers of Subsurface Geochemical Species and Processes

Certain subsurface activities allow occasional or regular sampling of the natural subsurface fluid, an injected fluid, or a production fluid. There are several aspects of the chemistry of subsurface fluids that could be useful for understanding the reactive transport that is occurring during an engineered process. For example, where flow is mainly through fractures, often there are additional diffusive or other transport mechanisms to and from the fractures. Chemical and isotopic signals can be used to determine the extent to which diffusion is an important transport process. Diffusive transport through a vapor phase or aqueous fluids can separate isotopes and dissolved chemical elements, and concurrent processes like mineral precipitation can cause further isotopic and chemical effects. Thermal gradients and redox processes can also generate isotopic and chemical effects. Although some of these effects have been demonstrated in laboratory experiments under controlled conditions, further research is needed to understand how they develop in more realistic geologic materials, and to develop appropriate models to interpret such chemical signals for information on transport or chemical transformations.

The scientific challenges are:

- (1) Development of accurate and robust representation and models to interpret changes in the chemistry of natural, injected or produced fluids that enable delineation of transport or reaction mechanisms;
- (2) Establishment of new stable isotope proxies for subsurface growth, dissolution or redox reactions and verification of their applicability to relevant subsurface systems.

Priority Research Directions

The response of rock formations to pressurized fluid injection and withdrawal involves deformation that occurs at different rates and spatial scales, and that can be elastic, poro-elastic, plastic, viscoelastic, or brittle, and either distributed or localized along fractures and faults. The additional stress, especially any associated damage, changes rock properties and the response to further perturbations. Multiphase fluids present additional complications because they have different properties and distribute themselves non-uniformly in the pore space. Chemical reactions among fluids and minerals, and temperature contrasts between injected and ambient fluids give the system properties additional time dependence.

The Roundtable discussion identified the following research directions as being critical for making progress on the Grand Challenge, for which there are particular opportunities for advances that are not adequately pursued through current BES activities.

1. Reactive Multiphase Flow in Fractured Systems

The transport of fluids in the subsurface must occur either through interconnected pores or through a network of natural pre-existing or induced rock fractures. Achieving control of fluid flow through fractured media is of increasing importance for new subsurface technologies but is far less well understood than flow in porous media. There are numerous challenges for modeling and predicting the flow of single and especially multiphase fluids through fractured porous rock, particularly in the presence of rock-fluid reactions that can change the dimensions, topology and wettability of flow pathways. Reactive fluids can also alter rock rheology, and the resultant couplings between flow, reaction and rock deformation are considered in a subsequent section.

Advances in our understanding of reactive multiphase flow in fractured porous media will require the development of time-lapse 3D imaging with improved spatial and temporal resolution to reveal fluid and mineral phase distributions, fluid flow rates and pathways, and the wetting angles for fluid-rock interactions. All efforts described here will also benefit from the development of geo-architected fracture systems with known spatial distributions of reactive minerals and geometric apertures to perform controlled experiments on specific aspects of multiphase reactive transport. The fundamental understanding provided by the following research is of key importance for the development of more accurate computational models that capture the physical and chemical processes of fluid-rock interaction in subsurface reservoirs.

Reactive Multiphase Fluid Flow in Mixed Wettability Systems

For nonreactive fluids in fractured mono-mineralic rock, the distribution of immiscible fluids and the mixing of miscible fluids is well understood and known to be controlled by interfacial tension (*i.e.*, wetting angles), fluid composition and viscosity, pressure and the geometry of the connected flow paths. Pore-scale modeling performs well in predicting such flow under controlled conditions. However, in heterogeneous rock, the distinct tendency of different fluid phases to wet accessible mineral surfaces can strongly alter

fluid phase distributions and fluid flow in response to pressure gradients (**Figure 7**). Moreover, reactive fluids can alter mineral saturation states, surface properties and wetting, or colloidal mobility, leading to coupling between flow, reaction, fracture geometry and stress.

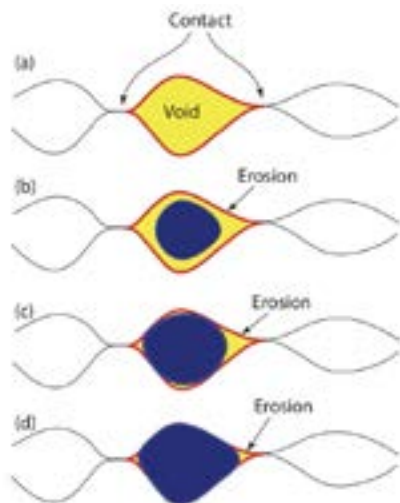


Figure 7. Two rough surfaces in contact. If reactive fluid (yellow) fills the entire void space (a), both voids and contact area can be potentially eroded (red regions). In the presence of a second non-wetting, non-reactive, immiscible fluid (blue), the erosion of voids or contact area is controlled by the relative saturation of each phase (b-d). For case (d), preferential erosion of contact area while subjected to an ambient stress field could result in closure of the fracture and degradation of the permeability. For a fracture with patchy mineralization, whether contact area or voids is composed of erodible minerals leads to additional unknowns in fracture evolution. (courtesy of L. J. Pyrak-Nolte,)

Experimental, theoretical and numerical research is needed to :

- (1) Determine the effect of elevated temperature and pressure on wettability and contact angles of relevant minerals for natural and engineered subsurface fluids;
- (2) Quantify the influences of mineral grain size and wettability, and fracture void geometry, on fluid phase distribution and flow of non-reactive, immiscible fluids in poly-mineralic, mixed wettability fractures;
- (3) Determine how reactive fluids and common solutes including organic molecules affect mineral wettability to enable prediction of the evolution of fluid phase distribution and flow in poly-mineralic fractures;
- (4) Determine the role of fracture-matrix fluid interactions on the evolution of wettability and hence flow in poly-mineralic fractures;
- (5) Develop methods to accelerate relevant reactions at the laboratory scale to enable confident extrapolation to the long timescales consistent with subsurface activities;

- (6) Develop new averaging and upscaling approaches for reactive multiphase flow in fracture systems that include heterogeneous rock properties.

While the above research topic encompasses a large range of subsurface processes involving reactive multiphase fluids, two important scenarios are likely to exhibit strong, non-linear coupling between reaction and flow, with major impacts on permeability evolution.

Evolution of Permeability in Stressed Fractures Exposed to Reactive Fluids

The flow of a reactive fluid through a natural or induced fracture could strongly increase or decrease fracture permeability. For example, mineral dissolution coupled to flow within the fracture can lead to dissolution fronts and changes to fluid chemistry, especially mineral saturation state, within the fracture. Reactive fluids can also generate, mobilize, or dissolve colloidal particles. Moreover, reactive fluids could alter the stability of stressed fractures by eroding or mineralizing contact areas between opposing surfaces. In general, highly non-uniform processes could result from the interplay of transport and reaction, especially in the presence of highly heterogeneous natural or re-mineralized fracture surfaces. Even in the absence of net changes to fluid flow within the fracture, surface reactions may alter the fluid or molecular transport characteristics, or rheological properties, of the rock matrix away from the fracture surface.

Quantifying and predicting the evolution of permeability in reactive subsurface systems can be achieved through a combination of experimental, theoretical and numerical research that includes:

- (1) Determination of how coupled flow and dissolution/precipitation lead to changes in fracture geometry and fracture network connectivity for homogeneous rock, or heterogeneous rocks with alternative distributions of reactive minerals and geoarchitected chemical surfaces;
- (2) Determination of how multiphase flow and dissolution/precipitation alter the geomechanical stability of fractures and fracture networks, particularly for cases in which reactive minerals are located in fracture void spaces or regions of contact or fracture intersections;
- (3) Establishment of the effects of reactive fluid flow within fractures on the porosity and rheological properties of the rock matrix away from the fracture surface;

- (4) Development of numerical approaches that couple geochemical models of reactive multiphase flow to geomechanical models of fracture deformation, propagation and slip under stress;
- (5) Determination of the effect of fracture-filling materials, including proppants, clay particles, and organic material, on flow within, deformation of and slip along fractures;
- (6) Development of real-time monitoring techniques to identify rheological changes that indicate imminent geochemically driven failure.

Reactive Nanoscale Wetting Films

There is evidence that thin (nanoscale) wetting films may play decisive roles in the evolution of certain subsurface systems exposed to reactive fluids. For example, water-bearing supercritical CO₂ fluids can cause surprisingly fast mineral carbonation reactions that are mediated by nm-thick adsorbed H₂O films that condense from the scCO₂ (supercritical carbon dioxide) phase onto largely hydrophilic mineral surfaces. It is anticipated that such thin fluid layers will exhibit high reactivity, due to chemical characteristics such as low water activity, extremes of redox potential, and high ionic strength. However, there is little current knowledge as to the unique properties of such fluid layers, their effective reactivity when constraints on reagent transport are considered, or their chemo-mechanical impacts upon fracture permeability.

To address these questions, experimental research is needed to:

- (1) Establish the physical, chemical and solute transport properties of nanoscale thin wetting films on mineral surfaces;
- (2) Measure the rate of interfacial chemical processes, and of mass transport, in thin wetting films on mineral surfaces;
- (3) Determine the role of nano-scale alterations on macroscopic properties that affect deformation, flow and geophysical signals.

Reactive wetting films can alter the local or spatially averaged rheological properties of the underlying rock. These processes, and the consequences for rock deformation, are addressed in the next section.

2. Chemical-Mechanical Coupling in Stressed Rocks

While mechanical and geochemical perturbations to subsurface rock systems may act independently, these processes are often coupled through fluid and mineral

interactions. For example, geochemical reactions can affect the rates of crack initiation and propagation; enhance or reduce fracture opening, closing and healing; lead to major volume changes and rock deformation; and alter rock rheological properties. At the same time, geochemical reactions are affected by mechanical processes that generate new highly reactive surfaces, and control flow path connectivity, fluid distributions, and local stress concentrations. Improved models of chemical-mechanical coupling in stressed rocks are critical in order to predict and monitor dynamic changes to the state of subsurface stress. The necessary models cannot be developed without a fundamental understanding of the temporal and spatial extent of positive and negative feedbacks between geochemical and mechanical alterations that affect rheological behavior. Recent numerical and experimental research on geochemical dissolution along fractures shows that the resulting altered flow paths depend on relative rates of chemical reactivity, mass transport, and advective and diffusive transport. However, these studies neglect the role of stress on opening/closing flow paths and creating/reducing contact area during dissolution and precipitation of minerals.

Geochemically Driven Deformation

Geochemically driven deformation arises from volume changes caused by hydration, carbonation, oxidation, precipitation and dissolution of minerals in rock that is confined under stress (**Figure 5**). Several research efforts have begun to define the conditions that lead to stable systems or nonlinear feedback mechanisms between geochemical reactions and the mechanical response of a rock. Key scenarios are summarized below:

Two classes of process are not self-sustaining. (1) The rock maintains a constant volume because volume expansion caused by open-system reactions (*e.g.*, hydration, carbonation and/or oxidation) is balanced by dissolution and export of other components such that no significant deformation occurs. (2) A volume change is accommodated by irreversible, viscous relaxation of the rock that results in a return to mechanical equilibrium.

Other volume changes may be sufficiently large and fast to cause fractures that, in turn, maintain or enhance permeability and reactive surface area to repeat the process such that fractures continue to propagate over time, weakening the rock. (3) An increase in volume results in the generation of tensile forces that drive crack propagation and can lead to failure. (4) A reduction in volume can result in pore and fracture collapse, fluid and stress redistribution. In all cases of new volume change in closed systems, (5) pore

fluid pressure changes can affect integrity of the rock through crack initiation, coalescence and propagation.

Identifying which feedback mechanisms are likely for specific subsurface engineering applications requires theoretical, numerical and experimental research to determine:

- (1) The reaction rates of minerals that are relevant to subsurface activities under the temperature and pressure conditions experienced in the subsurface;
- (2) The effects of positive and negative feedback mechanisms on deformation, slip and rheological properties;
- (3) The rate and spatial extent of these feedback mechanisms in the presence of chemical, temperature and stress gradients such as those commonly found between injection and withdrawal boreholes;
- (4) How chemical reaction kinetics compare to and affect mechanical reaction and relaxation rates under confined conditions;
- (5) The rates at which rheological and fracture properties evolve under different feedback mechanisms;
- (6) If microbial-rock-fluid interactions can drive crack growth.

Geochemically Enhanced or Reduced Deformation

Numerous geochemical processes can alter the rheological properties of rock, and thereby alter its deformation or fracture evolution. As described above, the flow of a reactive fluid can either strengthen or weaken a fracture and thereby change its resistance to closure or slip under stress. Geochemical processes can increase the mechanical strength of granular rock through cementation. The rate of propagation of cracks in minerals under stress can be highly dependent on solution composition. Highly reactive nanoscale wetting films (introduced above) may be particularly important for controlling the evolution of subcritical cracks. In all cases, there are major challenges for determining the effect of geochemical processes on fracture deformation, elastic wave propagation and macroscopic rheological properties.

It is particularly important to improve understanding of the spatial extent of geochemical reactions that arise from fluid-rock interactions and can alter rock properties. For example, as illustrated by **Figure 8**, fluid-rock interactions will be highly localized around fractures in tight rocks or may be distributed far into the rock matrix for a fracture in a well-connected highly porous medium. The spatial extent of such reaction halos will have large consequences for the transport of desirable or contaminant substances into fractures, and for long-term fracture stability. *In situ* X-ray micro-computed

tomography and *ex situ* scanning electron microscopy have provided some information as to the extent of reaction halos around fractures, but higher resolution and chemically sensitive *in situ* imaging approaches will be required.

Establishing geochemical controls and effects on rock rheology and deformation requires:

- (1) Accurate measurement and theoretical representation of the fluid-mineral and fluid-rock interactions that affect crack initiation, coalescence and propagation;
- (2) Determination of the time-scales associated with geochemical alteration induced deformation of the fracture versus inelastic rock behavior;
- (3) Determination of the material (mineralogy, porosity, etc.) and geometric (aperture, contact area, fracture-matrix interface) controls on the location and extent of reaction halos along fractures, fracture networks and fracture intersections;
- (4) Determination of the spatial extent of changes in the stress and geochemical reactivity distributions from natural or engineered fluids and pore-filling materials;

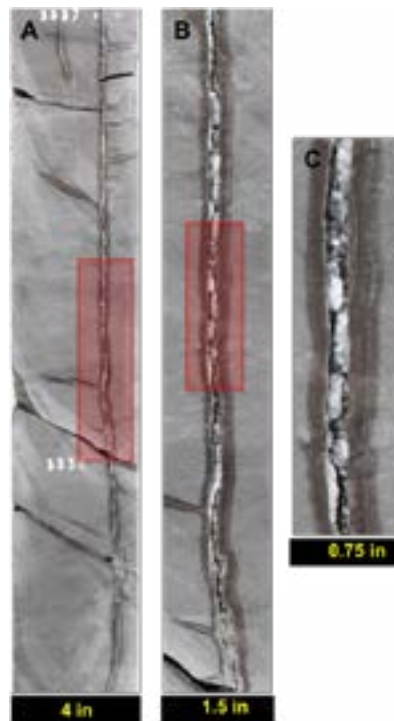


Figure 8. Optical micrographs of a dolomite core exhibiting fracture occlusion by precipitates (calcite) and a near-fracture geochemical weathering zone. The core was obtained from a section the Duperow Formation (Kevin, MT) exposed to migration of supercritical CO₂ from a deep natural source. (Courtesy of Jonathan Ajo-Franklin (LBNL) and the Kevin Dome Phase 3 geological carbon sequestration project – Big Sky Carbon Sequestration Partnership).

- (5) Development of statistical approaches for averaging or scaling the mechanical response of pore reaction halos that are non-uniformly distributed throughout the matrix.

Mechanical Control on Geochemical Reactivity

Mechanical controls on geochemical reactivity arise when the magnitude and direction of stress affects the porosity and permeability of rock, thereby altering the area of interaction between fluids and the rock along connected flow paths. Mechanically induced fractures provide additional reactive surface areas. The opening and closing of existing pores and fractures under stress affect flow path connectivity. Deformation of natural fractures in shale can lead to compression of pores in clay-rich regions at the fracture surfaces and a major drop in local porosity and permeability. High stress concentrations can lead to pressure solution along grain boundary contacts.

Theoretical, numerical and experimental research is needed to:

- (1) Determine the effect of stress and stress gradients on chemical alteration of flow paths through fractures and across the fracture-matrix interface;
- (2) Develop numerical codes to predict how the interplay of mechanical deformation and geochemical reactions alter fluid flow paths in fractures, fracture networks and through the matrix;
- (3) Determine the effect of cyclic or step-function stress, thermal and chemical loading, similar to that used at field sites, on the geomechanical, geophysical and geochemical behavior of fractured porous media;
- (4) Determine if the macroscopic properties used to monitor stress can differentiate between mechanically-induced alterations versus geochemically-induced alterations.

3. Nanoporous Rock Structure, Permeability and Reactivity

Many common subsurface rock types, and most mineral coatings on rock surfaces exhibit porosity with nanoscale dimensions (**Figure 9**). These nanoporous materials can strongly attenuate fluid flow and ion transport, enabling their use as caprocks for CO₂ storage or as natural barriers to radionuclide migration. Nanoporous rocks also serve as reservoirs of hydrocarbons, water, contaminant metals, and many critical elements.

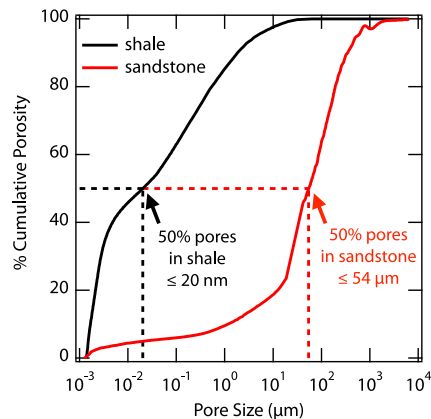


Figure 9. Advanced techniques, including neutron and X-ray scattering and X-ray or electron imaging, can provide quantification of pore size distributions over many orders of magnitude when used in combination. Porosity distributions of representative rock samples measured with small-angle neutron scattering and scanning electron microscopy. The sandstone has 50% of its pores smaller than 54 μm (St. Peter Formation; (Anovitz et al., 2013). In contrast, the shale has 50% of its pores smaller than 20 nm (Photo courtesy L. Anovitz)

The properties of nanoporous rocks differ in fundamental ways from those of more familiar coarser-grained rocks with larger pores. For example, the mechanical properties of nanoporous rocks cannot be predicted only from knowledge of their constituents, and thus exhibit an important hallmark of mesoscale materials (Crabtree and Sarrao, 2012). With a high surface area-to-volume ratio, nanopores can dominate the total surface area, but may or may not be the primary sites of chemical interaction due to transport limitations and differences in surface and interfacial properties. Changes in mineral-fluid interface properties in nanopores alter the electrical double layer structure, pore wall reactivity and thus mineral and adsorbate reactions. Moreover, confinement of fluid into either hydrophilic or hydrophobic nanopores alters the fluid structure and properties, and hence speciation and transport of dissolved ions and molecules.

Below, we describe two important sets of subsurface processes that may be strongly altered within nanoporous relative to macroporous materials. Obtaining a better understanding of chemical processes in nanoporous materials is a crosscutting challenge in many areas of chemical sciences. Progress in these topics will particularly benefit from study of synthetic analogs of natural nanoporous media.

Transport of Ions and Neutral Molecules through Nanopores

Prior research has established distinct conceptual models for the transport of charged and neutral species through saturated nanoporous networks.

However, there is a need to verify experimentally the dominant modes of transport of both gases and dissolved solutes. For example, the transport of methane through organic-rich nanopores must occur over relatively large distances to account for observed release into fractures. However, it is difficult to establish whether transport is dominated by fluid flow or by the diffusion of neutral molecules (Amann-Hildenbrand et al., 2012). Moreover, ion transport through nanopores in the presence of charged mineral surfaces, as found in packed clay-rich shales, leads to strong effects including anion exclusion. These phenomena can strongly affect contaminant release into production water through ion exchange, or prevent the migration of radionuclides. Here too, macroscopic models of ion transport typically fail to predict molecular or nanoscale controls on transport.

Theoretical, numerical and experimental research is needed to:

- (1) Obtain improved characterization of nanoporosity associated with mineral and organic phases in model and natural rocks including pore size distributions, 3D imaging of pore connectivity, and fluid, mineral and interfacial chemistry;
- (2) Quantify and model neutral molecule transport through architected nanoporous media and through heterogeneous nanoporous rocks;
- (3) Quantify and model dissolved ion transport through architected nanoporous media and through heterogeneous nanoporous rocks;
- (4) Develop chemical or stable isotope tracers that can serve as signatures of subsurface transport pathways in nanoporous rocks.

Mineral Precipitation and Dissolution in Spatial Confinement

The introduction of new fluids into the subsurface alters native conditions and creates conditions that stimulate new chemical reactions. Although mineral precipitation and dissolution reactions are thought to be influenced by pore size, there is no agreement regarding the extent to which nucleation, growth or dissolution are enhanced or suppressed by nanoscopic pore size. There is evidence that the chemical interaction of the precipitating phase and the substrate play a role (Stack, 2015). These nanoscale effects influence the response of macroscopic phenomena such as porosity and permeability (Borgia et al., 2012) and geomechanical strain (Pontbriand et al., 2014) to engineering perturbations.

Theoretical, numerical and experimental research is needed to:

- (1) Determine the influence of spatial confinement on solvent structure and properties within hydrophobic or hydrophilic nanopores;
- (2) Determine the influence of spatial confinement on the molecular speciation of geochemical reagents, including solutes and sorbates, and the structure of newly formed precipitates;
- (3) Develop new conceptual and quantitative models for the rates of mineral nucleation within nanopores and the relationships between mineral dissolution – precipitation and transport properties.

Crosscutting Themes and Approaches

1. Advanced Computational Methods for Heterogeneous Time-dependent Geologic Systems

Advanced computational methods lie at the heart of all solutions to the grand challenge, and to all of the foundational research required to get there (cf. Crabtree et al., 2010). The ability to model and forecast coupled processes caused by fluid injection into the subsurface is an inherently multi-scale (spatial and temporal) modeling challenge that requires concurrent treatment of thermal, hydrological, mechanical and chemical (THMC) processes, augmented for certain environments with descriptions of biological activity. Moreover, such THMC models must be designed from the outset to integrate closely with a range of field-scale geophysical and geochemical monitoring and imaging tools. Most of the commonly used codes were developed to tackle specific engineering challenges and only consider a subset of the coupled processes. Advanced computation will require coordinated development of algorithms and computational strategies to accurately account for and to integrate improved representations of rock systems at all relevant length scales. Three specific areas for fundamental computational and mathematical research are described below that cross-cut the Grand Challenge and the Priority Research Directions

Representation and Simulation of Evolving Fracture Systems

A challenge in modeling significant volumes of the subsurface is how to account for the effects of millions to many billions of mechanical discontinuities that vary from sub-millimeter to kilometer scale. Fractures

can be modeled either discretely (i.e., with grid points at the scale of the fracture aperture) or as a continuum using averaged properties or behavior. The time scale of fracture generation and growth is far different from that of fluid flow or geochemical reaction rates. This contrast adds an additional level of computational complexity because of the range of time scales that must be considered.

Fundamental research is needed to:

- (1) Develop the mathematical framework for numerical homogenization methods for finite fracture systems to enable accurate representation of mechanical discontinuities on multiple spatial scales in computational models;
- (2) Develop mathematical and computational methods to simulate emergent and accumulating damage, deformation, slip, fracture opening and closing, crack propagation and coalescence in response to changes in stress, chemistry, temperature and fluid pressure that occur on multiple spatial and temporal scales.

Seismic Wave Interaction with Evolving Fracture Systems

Seismic waves that pass through evolving fracture systems are expected to be high-resolution probes for assessing and monitoring subsurface alteration because different waves are highly sensitive to different elements of the subsurface. Evolving mechanical discontinuities and fluid redistribution in fault/damage zones and other geodynamically-driven systems pose serious challenges for detection and modeling because mechanical discontinuities span many orders of magnitude in size, are structurally/topologically complex and are subjected to complicated stress fields. Seismic monitoring has the potential to be immune to this problem because seismic arrays can be designed and tuned appropriately to achieve maximum recovery of the scattered wave-field, if the data can be appropriately interpreted to identify the state/condition of the zone.

Research is required to:

- (1) Develop computational models of elastic wave scattering that capture the averaged and discrete effects of mechanical discontinuities on the wave field, and that enable the connection between the scattered-wave field and the dynamic evolution of fracture systems from stress gradients, geochemical reactions, temperature and fluids;
- (2) Compare wave scattering from controlled simple laboratory fracture systems to models that include the fundamental topology of stressed fracture systems with and without fluids to ground-truth simulated behavior;

- (3) Determine the relevant signal components (compressional and shear wave velocity ratio, coda wave analysis and shear-wave splitting, i.e. anisotropy, P-to-S conversions, guided modes) linked to fracture evolution and to develop the mathematical framework for using machine learning techniques to identify these signals.

Pore-Scale Simulations of Transport, Reaction and Rock Deformation

High performance computing provides an important opportunity to use our understanding of pore-scale physical and chemical rock-fluid interaction processes as the basic building block for descriptions of THMC processes in rock at larger scales (**Figure 10**). Flow and reaction in the intricate geometry of subsurface pores and fractures can lead to non-linear or emergent phenomena that can now be predicted and verified in the laboratory with advanced *in situ* imaging approaches described below. However, direct pore-scale simulations cannot yet be applied to many types of subsurface materials, especially those containing extensive nanoporosity and microfractures such as shale. Pore scale studies and simulations represent a scale that can link molecular species and processes to continuum scale averages, providing a quantitative basis for upscaling to macroscopic quantities like permeability, diffusivity and reactivity.

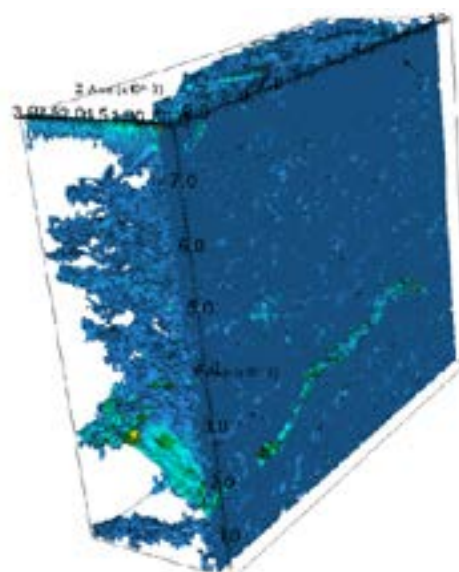


Figure 10. (a) Simulation of flow in a previously imaged sample of fractured Marcellus shale using 60,000 cores of NERSC Hopper and the software package Chombo-Crunch. Fluid velocity shown with 48-nm resolution. The foundation of Chombo-Crunch is a flow and transport algorithm based on the embedded boundary method in which finite volume approximations are used to discretize the solution in cut cells that result from intersecting microscopic pore space with a structured Cartesian grid. The algorithm is also capable of block structured adaptive mesh refinement (AMR) to increase spatial resolution dynamically in regions of interest. [Trebotich and Graves, 2015]

Research directions should include efforts to:

- (1) Develop computational approaches to handle the small but important scale of nanoporosity and micro-cracks which require extreme computations to transition to larger scales;
- (2) Develop next generation models that couple geomechanics with pore scale multiphase, reactive flow in a multiscale, multimodel framework to manage the complex THMC interactions;
- (3) Develop the underlying software of these new simulation tools so that they can adapt to next generation computing hardware and balance heterogeneous problems, memory management, resiliency and fault tolerance, and even bigger data requirements.

Atomistic Simulations of Subsurface Processes

Classical and quantum chemical simulations of minerals, fluids, solutes and adsorbates have attained the accuracy and scale to provide unrivaled insight into the molecular-scale structure of many important geological systems. Such detailed depictions can be crucial for understanding processes that can exert a major impact on subsurface operations. Major challenges for molecular simulation are the incorporation of chemical reactivity and locating pathways for rare events such as chemical reaction or mineral nucleation. However, advanced simulations are becoming accessible to all research communities including hybrid molecular mechanics/quantum mechanics methods, and metadynamic schemes designed to explore reaction pathways. These simulations also offer the ability to predict the effects of high temperature and pressure, conditions that are always challenging to recreate in the laboratory.

Thus there are many valuable opportunities for using atomistic simulations to inform models of subsurface processes including:

- (1) Predicting the mechanism and rates of ion or molecule diffusion in bulk fluids or in the vicinity of mineral interfaces;
- (2) Identifying the short- and long-range interactions that control the distribution of immiscible fluids at mineral interfaces;
- (3) Predicting temperature effects on solute and adsorbate speciation and mobility;
- (4) Determining how mineral strain affects the rate of interfacial chemical processes, and how surface reactions can facilitate subcritical crack propagation.

2. Capturing Heterogeneity and Scale through Geo-architected Materials

Rock is a scientifically fascinating material because of the non-uniformity and heterogeneity of the compositional, textural and structural components. Such heterogeneity occurs on multiple length scales (nanometer to kilometer) and is altered over a range of time scales (microseconds to years) by natural and induced processes. A goal of laboratory research is to provide insight on the effect of compositional and structural heterogeneity on chemical and physical processes to help reduce the significant challenges that heterogeneity introduces in modeling, design and monitoring of subsurface processes. Although there is extensive research done on “representative” rock samples, any given rock core or sample provides either a limited view of the structural complexity observed in the field or non-repeatable compositional heterogeneity that prevents accurate delineation of chemical kinetics and thermodynamics. Recent advances in 3D printing, laser writing, mineral synthesis, and structured and functionalized surface patterning provide a new opportunity to create “geo-architected materials” with controlled repeatable heterogeneity and structure that can be tested under a range of thermal, hydraulic, chemical and mechanical conditions.

Architected Nanoporous Geomaterials

The development of synthetic geo-architected materials with tailored pore-size distributions and substrate reactivity will enable delineation of the effects of particular pore sizes and interfacial composition on the properties of nanoporous rocks. Natural rock samples often contain complicated mineralogies, widely varying impurity contents, and a continuously variable distribution of pore sizes. Architected porous media with salient physical and chemical properties of natural rock samples, but with a simplified mineralogy and well-defined pore size distribution, will provide enhanced hypothesis testing of different processes related to transport and reactivity.

While increasingly well known for applications such as energy storage, there are only a few nanoporous materials readily available that are relevant to the geosciences (**Figure 11**). Geo-architected materials relevant to large classes of subsurface rock, comprising crystalline mineral phases and other materials present in the subsurface such as organic matter, are either lacking or have not been applied to geoscience problems.

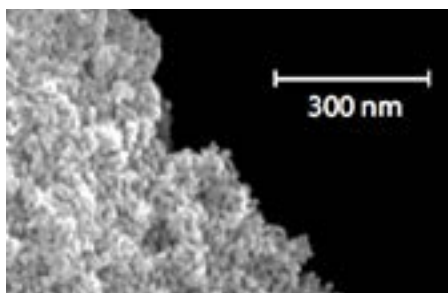


Figure 11. An amorphous silica sample (CPG-75) which contains a network of nanopores ~8 nm in diameter (5). While multiple nanoporous amorphous silica samples are available, samples containing tailored pore size distributions of other mineral phases are not commonly available. *Figure from Stack (2015)*

There are multiple methods for how these materials might be fabricated:

- (1) New synthesis strategies that directly result in a crystalline nanoporous phase;
- (2) Synthesis of nanoparticle phases that are cemented together to form a porous network;
- (3) Extension of etching-based microfluidic technology to smaller scales and to incorporate geologically relevant materials and interfaces;
- (4) Inkjet printing of functionalized films;
- (5) Large decrease in spatial resolution of fabrication methods, including three-dimensional printing, to achieve nanoscale pore dimensions.

Architected Wettability and Chemical Reactivity

The development of a variety of chemical and biological sensors in the past decades opens up a range of opportunities to design geo-architected surfaces for examining the effect of natural and engineered fluids on surface wettability and chemical reactivity. Recent studies have shown that the interfacial tension and contact angles (wettability) of supercritical CO₂ change over time as a mineral surface interacts with fluids. With micro-contact printing, ink-jet printing of film-scontrolled carbon nano-tube growth, and structured and chemically functionalized surfaces, an opportunity exists to advance our understanding of the role of wettability and chemical reactivity heterogeneity on fluid transport, chemical alterations and mechanical response for systems that mimic rock.

Research is needed to use these techniques to create controlled and repeatable surfaces to:

- (1) Examine the effect of spatial heterogeneity of surface properties on transport and trapping of fluids and colloidal particles;
- (2) Delineate the role of surface properties on multi-phase reactive transport;

- (3) Alter/control the surface properties of rock to reduce residual saturation to enhance fluid production.

Architected Fractured Systems

Any subsurface engineering site encompasses a range of mechanical discontinuities that affect the integrity of the rock volume and act as paths for chemical transport and reactivity. Mechanical discontinuities range in scale from micro-cracks (micrometer) to fractures (millimeter to meters) to faults (10s of meters to kilometers). While a core sample may contain 1-2 fractures, it is difficult to obtain samples with natural fracture networks often encountered in the field. Thus, it remains challenging, for example to decipher how natural fracture networks affect initiation and evolution of induced hydraulic fractures.

With the development of 3D laser etching, fracture networks that mimic natural fracture patterns can be etched inside glass and acrylic laboratory samples (**Figure 12**). These scaled patterns can then be subjected to scaled hydraulic fracturing experiments to examine the shape and location of the induced fracture, the effect of the fracture network on leak-off of fluids, and stress shadowing caused by pre-existing fractures. In addition, 3D printing can be used to create scaled transparent fractured porous media that replicates structures obtained from X-ray CT scanning of rock to enable direct visualization of fracture-matrix interactions during transport and hypothesis testing when TMHC conditions are changed. Creating increasingly relevant models will require new developments in 3D printing, such as the use of materials more similar to rock than current plastics, and the use of multiple materials to represent mineral heterogeneity and mixed wettability.

Research involving geo-architected fault systems offers opportunities for measurements that could not be made on natural rocks. For example, geo-architected fault systems etched in soda lime glass samples with 3D laser etching would enable concurrent active and

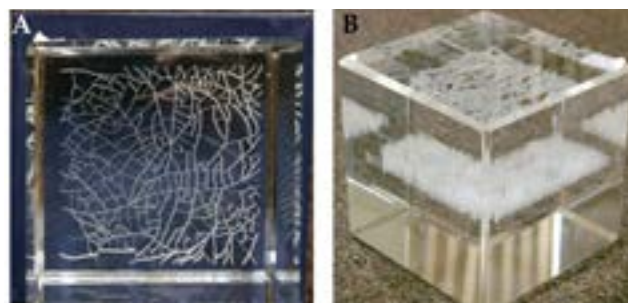


Figure 12. 3D laser etched fractured reservoir in 10 cm on edge acrylic cube (A) top view and (B) side view showing depth in the sample (*courtesy of Seiji Nagakawa*).

passive elastic wave monitoring (e.g. acoustic emission, wave transmission/reflection) and photon emission tomography to link changes in crack/fracture distribution with exact location of the microseismic events as a sample is subjected to loading and fluid pressure conditions similar to that encountered in the subsurface during engineered project. Such research would provide the new insight needed to image and interpret stress from micro-seismic events in the subsurface.

3. Laboratory Studies of Subsurface Processes

Laboratory studies on natural or geo-architected systems will require advanced imaging and chemical analysis methods to reveal the rates and mechanisms of fluid-rock processes and to test models that seek to predict them.

Imaging Transport and Reaction in Fractured or Nanoporous Matrices

Advanced high-resolution three-dimensional imaging techniques, including transmission X-ray microscopy (TXM), can be used to image flow, transport and chemical reactions in nanoporous or fractured materials at resolutions approaching 30 to 100 nanometers (**Figure 13**). Anticipated improvements at X-ray synchrotron facilities are expected to substantially enhance our ability to chemically image nanoporous systems because of the vastly improved transverse coherence of the beam (Miao et al., 2015). A combination of coherent diffractive imaging and ptychography will enable imaging of internal structures, individual nanoscale pores and particles, with a theoretical resolution of below 10 nm. Determination of the full optical properties of the constituent materials will provide improved distinction between organic, fluid and inorganic components. Elemental and chemical mapping can be achieved by the incorporation of X-ray fluorescence or resonant contrast with other traditional techniques. In order to benefit from these advances, new *in situ* sample environments are needed that enable control of applied strain, hydrostatic pressure, temperature and the introduction of relevant fluids.

Capturing Mechanisms of Fast and Ultrafast Subsurface Processes

Key subsurface processes, such as crack initiation or molecular reactions, occur on fast or ultrafast timescales. Monitoring such processes in real time offers significant opportunities for identifying the events that cause them to occur, and for understanding the precise pathway that they follow.

There are presently numerous advances in high-speed 2D and 3D imaging at all spatial scales that can be accessed in the laboratory. Examples that can be applied to critical subsurface processes include: (1) *high-speed transmission electron microscopy imaging in environment cells* has the potential for capturing rare spontaneous events, such as mineral nucleation, with crystal lattice resolution. (2) *high-speed video microscopy* can capture strain fields in 2D through a rock fracturing event. (3) *3D time-lapse X-ray tomographic imaging* (including the new methods described above) can provide extremely rich depictions of fluid flow and rock reactions. In all these areas, new and creative development of *in situ* sample environments, data acquisition schemes, and approaches to handle large data sets will greatly advance our ability to determine mechanisms of rare and fast processes. The application of these methods to geochemical processes in bulk fluids and in nanopores will provide direct tests of the mechanism and rates of transport and reaction.

Recent advances in chemical analysis and imaging techniques can initiate and capture ultrafast steps in molecular reactions. Traditional spectroscopic methods typically require signal acquisition times that are much longer than characteristic reaction time steps. Thus, conventional uses of nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, x-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) provide information that is averaged over all chemical environments and over all steps of a reaction pathway.

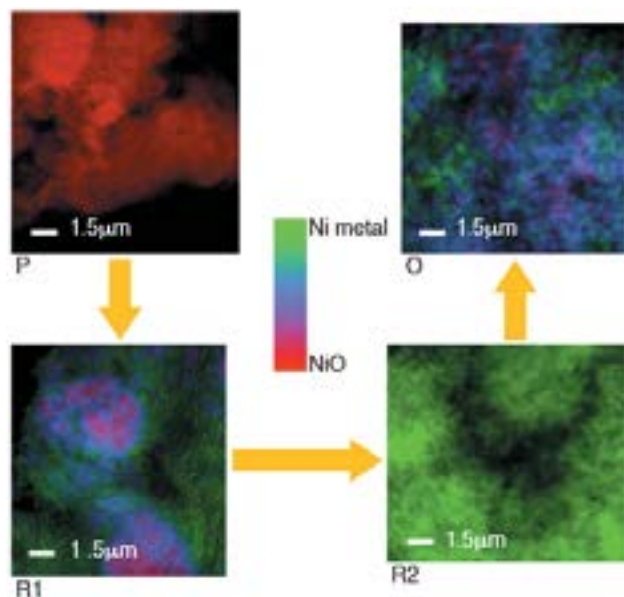


Figure 13. Three-dimensional imaging of chemical phase transformations in NiO electrode during cycling using transmission X-ray microscopy combined with X-ray absorption spectroscopy. (Meirer et al., 2011)

New time resolved modalities involving these methods include:

- (1) *Relaxation methods* can provide information about chemical processes occurring on a characteristic timescale. For example, quasi-elastic neutron scattering can probe rapid diffusional or other processes (e.g., 1 ps relaxation time) (Cole et al., 2006). X-ray photocorrelation spectroscopy (XPCS) can provide information on macromolecular conformation or nanoparticle diffusion dynamics, currently down to the microsecond timescale
- (2) *Pump-probe methods* can provide exceedingly high temporal resolution for chemical reactions such as intermolecular or interfacial electron transfer that can be initiated by a fast laser pulse.

Unambiguous interpretation of ultrafast experimental results requires rigorous interpretation of measured signals or images from atomistic models using either classical or quantum mechanical simulation. While several rigorous strategies are in development or exist already for spectroscopic methods, their application in geoscience is just beginning. The architected nanoporous samples described above will be especially helpful in making direct links between spectroscopic measurements, molecular simulation, and mechanisms and rates of chemical processes.

References

Ajo-Franklin, J.B., J. Peterson, J. Doetsch, T.M. Daley, High-resolution characterization of a CO₂ plume using crosswell seismic tomography: Cranfield, MS, USA. *International Journal of Greenhouse Gas Control* **18**, 497–509 (2013)

Amann-Hildenbrand, A. Ghanizadeh, B. M. Krooss, Transport properties of unconventional gas systems. *Marine and Petroleum Geology* **31**, 90–99 (2012).

Anovitz, L. M., D.R. Cole, G. Rother, L.F. Allard, A. Jackson, and K.C. Littrell, Diagenetic changes in macro- to nano-scale porosity in the St. Peter Sandstone: An (ultra) small angle neutron scattering and backscattered electron imaging analysis. *Geochimica Et Cosmochimica Acta* **102**, 280–305 (2013).

Borgia, A., K. Pruess, T. J. Kneafsey, C. M. Oldenburg, L. Pan, Numerical simulation of salt precipitation in the fractures of a CO₂-enhanced geothermal system. *Geothermics* **44**, 13–22 (2012).

Campillo, M., P. Roux, and N.M. Shapiro (2011), Using seismic noise to image and to monitor the Solid Earth, in *Encyclopedia of Solid Earth Geophysics*, Gupta, Harsh K. (Ed.), 1230–1235, Springer, 2011

Cole, D. R., K. W. Herwig, E. Mamontov, J. Z. Lares. Neutron scattering and diffraction studies of fluids and fluid-solid interactions. *Rev. Mineral. Geochem.* **63**, 313–362 (2006)

Crabtree, G., and J. Sarrao, 2012, *From Quanta to the Continuum. Opportunities for Mesoscale Science*. US Department of Energy, Office of Basic Energy Sciences, Washington, D.C.

Crabtree, G., S. Glotzer, W. McCurdy and J. Roberto, 2010, *Computational Materials Science and Chemistry: Accelerating Discovery and Innovation through Simulation-Based Engineering and Science*. US Department of Energy, Office of Science, Washington, D.C.

DePaolo, D.J., and F.M. Orr, 2007, *Basic Research Needs for Geoscience: Facilitating 21st Century Energy Systems*, US Department of Energy, Office of Basic Energy Sciences, Washington, D.C.

DePaolo, D.J., and F.M. Orr, 2008, “Geoscience Research for Our Energy Future,” *Physics Today*, Vol. 61, no. 8, pp. 46–51.

Doetsch, J., Kowalsky, M.B., Doughty, C., Finsterle, S., Ajo-Franklin, J.B., Carrigan, C.R., Yang, X., Hovorka, S.D., Daley, T.M., Constraining CO₂ simulations by coupled modeling and inversion of electrical resistance and gas composition data. *International Journal of Greenhouse Gas Control* **18**, 510–522 (2013)

Ellsworth, W.L. (2013). “Injection-induced earthquakes.” *Science*, **341** (6142), 142.

Fleming, G.R. and M.A. Ratner, eds., 2008, *Directing Matter and Energy: Five Challenges for Science and the Imagination*, US Department of Energy, Office of Basic Energy Sciences, Washington, D.C.

Kasahara, J., Korneev, V. and M. S. Zhdanov, 2010, Active Geophysical Monitoring, Handbook of Geophysical Exploration Seismic Exploration, editors Helbig, K. and S. Treitel, volume 40, Elsevier, Oxford.

Kelemen, P.B. and G. Hirth, Reaction-driven cracking during retrograde metamorphism: Olivine hydration and carbonation, *Earth Planet. Sci. Lett* 345–348, 81–89, 2012.

Miao, J., T. Ishikawa, I. K. Robinson, M. M. Murnane, Beyond crystallography: Diffractive imaging using coherent x-ray light sources. *Science* **348**, 530–535 (2015).

F. Meirer, J. Cabana, Y. Liu, A. Mehta, J. C. Andrews, P. Pianetta. Three-dimensional imaging of chemical phase transformations at the nanoscale with full-field transmission X-ray microscopy. *Journal of Synchrotron Radiation* **18**, 773–781 (2011).

Pontbriand, C. W., R. A. Sohn, Microearthquake evidence for reaction-driven cracking within the Trans-Atlantic

Geotraverse active hydrothermal deposit. *Journal of Geophysical Research-Solid Earth* **119**, 822–839 (2014).

Scholz, C.H., *The Mechanics of Earthquakes and Faulting* (2nd Edition). Cambridge University Press (2002)

Stack, A.G., Reactions in Pores: A Geochemical Frontier. *Reviews in Mineralogy and Geochemistry* **60**, (2015).

Trebotich, D. and Graves, An adaptive finite volume method for the incompressible Navier–Stokes equations in complex geometries. *Comm. Appl. Math. Comp. Sci.* **10**, 43–82 (2015).

Yang, C. B., K. Romanak, S. Hovorka, R. M. Holt, J. Lindner and R. Trevino (2013). Near-surface monitoring of large-volume CO₂ injection at Cranfield: Early field test of SECARB phase in.” *SPE Journal* **18** (3), 486–494.

Appendix 1: Roundtable Participants

Co-Chairs:

Don DePaolo Lawrence Berkeley National Laboratory and University of California, Berkeley

Laura Pyrak-Nolte Purdue University

Participants:

Nick Davatzes Temple University

Joanne Fredrich BP

Ben Gilbert Lawrence Berkeley National Laboratory

Peter Kelemen Columbia University

Kate Maher Stanford University

John Miller DOE: Office of Basic Energy Sciences

Joe Morris Livermore National Laboratory

Catherine Peters Princeton University

Steve Pride Lawrence Berkeley National Laboratory

Kevin Rosso Pacific Northwest Laboratory

James R. Rustad Corning

Andrew Stack Oak Ridge National Laboratory

Marianne Walck Sandia National Laboratory

Wen-lu Zhu University of Maryland

Appendix 2: Roundtable Summary

Roundtable on Foundational Research Relevant to SubTER

Co-Chairs:

Laura J. Pyrak-Nolte Purdue University

Donald J. DePaolo Lawrence Berkeley National Laboratory and University of California, Berkeley

DOE Contacts:

Tanja Pietrafesa (Office of Basic Energy Sciences)

Purpose:

SubTER (Subsurface Technology and Engineering RD&D) is an intra-DOE working group that comprises representatives from many offices across the department that study or deploy subsurface technologies. The roundtable will convene national lab, university and industry experts in the geosciences to brainstorm basic research areas that underpin the goals of the broader SubTER Technology Team efforts, and are currently underrepresented in the BES research portfolio. The output goal is a document with executive summary (up to 10 pages) comprising prioritized research questions with descriptive narrative that could inform future BES research directions or a potential follow-on workshop.

Logistics:

DOE Germantown, Rm. A410;
Friday, May 22, 2015 (9:00 – 5:00 pm).

Participants:

Participation, by invitation only, will be approximately 12–15 external scientists (DOE laboratories, university and industry). Two co-chairs will help select participants and lead the discussion. Several (3–5) Federal Program Managers from BES, EERE and FE will attend as observers. Total meeting size will be limited to about 20.

Agenda:

The agenda will comprise one day of sessions (9:00 – 5:00 PM with lunch and breaks) including overview talks, discussion sessions, and closing summary. Brief parallel topical breakouts (one hour?) may be considered.

Roundtable Report:

Draft due in 14 days.

Appendix 3: Roundtable Agenda

Roundtable on Foundational Research Relevant to SubTER

Co-Chairs:

Laura Pyrak-Nolte	Purdue University
Don DePaolo	Lawrence Berkeley National Laboratory and University of California, Berkeley

DOE Contacts:

Tanja Pietraß	Office of Basic Energy Sciences
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Agenda

9:00	Opening Comments Harriet Kung, Tanja Pietraß
9:10	The SubTER Crosscut Julio Friedman, Doug Hollett or designee
9:45	Laboratory Working Group Marianne Walck
10:20	Break
10:40	Summary 2007 Basic Research Needs Workshop Don DePaolo or designee.
11:00	Charge to Roundtable Assemble in Breakouts
12:00	Lunch
1:00	Breakouts
3:00	Break
3:30	General Discussion Report Outs
5:00	Closing Remarks

Appendix 4: Acronyms and Glossary

Acronyms

2D:	Two dimensional
3D:	Three dimensional
4D:	3 spatial dimensions and 1 temporal dimension
BES:	Basic Energy Sciences
CO₂:	Carbon Dioxide
CT:	Computed Tomography
EM:	Electromagnetic
FTIR:	Fourier transform infrared spectroscopy
GPS:	Global Positioning System
InSAR:	Interferometric Synthetic Aperture Radar
LiDAR:	Light Detection and Ranging
NMR:	nuclear magnetic resonance spectroscopy
scCO₂:	Supercritical Carbon Dioxide (CO ₂)
THMC:	Thermal, Hydraulic, Mechanical and Chemical processes
TXM:	Transmission X-ray Microscopy
XAS:	X-ray absorption spectroscopy
XPCS:	X-ray photocorrelation spectroscopy
XPS:	X-ray photoelectron spectroscopy

Glossary

Active Monitoring: Time-lapse imaging using a controlled source (e.g. explosion, Vibroseis) to generate seismic or elastic waves to monitor the subsurface. (adapted from Kasahara et al., 2010)

Ambient Noise Monitoring: A type of passive monitoring that uses permanent motion of the Earth's surface from natural (ocean waves, storms, wind), and/or industrial (machinery, traffic, quarrying, drilling) sources of noise that are not related to earthquakes or specific controlled sources. (adapted from Campillo et al., 2011)

Biogeochemical: Refers to processes where microbes or other organisms chemically alter rock and fluids.

Forward Modeling: A modeling approach that uses an assumed geologic model for a site and requires physical/chemical theories or relationships that link measured signals to properties of the system. The computed or simulated properties from the model are compared to the measured data from the laboratory or field. An iterative approach is used; the assumed physical, chemical and geological properties of the

model are modified until the simulated results match the measured data. (adapted from <http://mathworld.wolfram.com/InverseProblem.html>)

Fracture aperture: A measure of the distance between two rough surfaces (or fracture walls) that compose a fracture.

Friction Laws: Friction along interfaces is modeled through constitutive laws that relate shear stress, normal effective stress, and material properties to the slip velocity and slip distance. (adapted from Scholz, 2002)

GPS (Global Positioning System): a global radio satellite navigational system that provides information on position, velocity and time, and can be used to monitor ground motion and deformation over time. (adapted from <http://www.gps.gov>)

Induced Polarization: A geophysical technique that measures the decay of voltage after the removal of an applied current that had caused the separation of charge. The decay rate is linked to the mineralogy, porosity and degree of fluid saturation.

InSAR (Interferometric Synthetic Aperture Radar): A global satellite-based imaging system that performs interferometry using radio – microwave-band radar to measure surface heights. Maps of surface deformation or motion are obtained by monitoring a region over days to years and then differencing the images. (adapted from https://en.wikipedia.org/wiki/Interferometric_synthetic_aperture_radar)

Inverse Modeling: A modeling approach that uses actual geophysical measurements, data and observations to infer the properties of the subsurface. (adapted from <http://mathworld.wolfram.com/InverseProblem.html>)

Joint Inversion: Using two or more geophysical data sets (e.g. seismic and electromagnetic data sets) to constrain the inverse modeling that is used to interpret the subsurface system.

LiDAR (Light Detection and Ranging) & repeat LiDAR: Pulsed laser light is used to determine distances between the source/detector and a surface. The resulting 3D image provides information on the topography/elevation of the surface. LiDAR can be performed on outcrops, in mines and over the surface of the Earth. Land-based vehicles, drones and airplanes can be outfitted with LiDAR instrumentation to map large areas. Repeat LiDAR takes repeated measurements over days-to-years to determine changes in elevation or topography from natural or industrial

processes. (adapted from <http://oceanservice.noaa.gov/facts/lidar.html>)

Mechanical Discontinuities: A term to encompass geomechanical structures that range in scale from nanometers to kilometers and include dislocations, cracks, fractures, joints and faults.

Passive Monitoring: Time-lapse imaging that uses regional or global earthquakes as the source of seismic or elastic waves to monitor the subsurface. (adapted from Kasahara et al., 2010)

Redox: Complementary chemical processes that result in concurrent oxidation and reduction of a substance.

Strainmeter: An instrument designed make continuous measurements of strains and can be installed on the surface of the Earth, in mines and boreholes. In boreholes, the strain can be determined in three directions. (adapted from <http://earthquake.usgs.gov/monitoring/deformation/data/instruments.php>)

Tiltmeter: An instrument to measure the very small changes in the inclination or tilt of surface. Tiltmeters can be installed as arrays on the surface of the Earth or in boreholes. (adapted from <http://earthquake.usgs.gov/monitoring/deformation/data/instruments.php>)

Transwell or crosswell: Measurements taken between 2 or more boreholes/wells.

Well Logging Tools: Tools or instrumentation lowered into a borehole to measure the properties of rock formations with depth using different geophysical techniques that measure electrical resistivity, spontaneous potential, electromagnetic wave propagation, gamma ray density, neutron porosity, natural radioactivity, induced gamma ray spectrometry, nuclear magnetic resonance, acoustic wave propagation, dipmeter, and sample of rock, fluids and pore pressures. Analysis of the data from these tools provide information and understanding of the porosity, lithology, mineralogy, pore geometry, permeability, fluid properties, geomechanical properties and geology in the vicinity of the bore hole. (adapted from http://www.slb.com/resources/oilfield_review/~media/Files/resources/oilfield_review/ors11/spr11/defining_logging.ashx)

X-ray CT Scanning: A non-destructive technique that uses X-rays to interrogate a rock sample to enable 3D visualization of the interior (grains, voids, fluids, fractures).

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