The Role of Chemistry in Fracture Pattern Development and Opportunities to Advance Interpretations of Geological Materials

S. E. Laubach1, R. H. Lander2, L. J. Criscenti3, L. M. Anovitz4, J. L. Urai5, R. M. Polleyea3, J. N. Hooker7, W. Narr6, M. A. Evans8, S. N. Kersit9, J. E. Olson11, T. Dewers1, D. Fisher7, R. Bodnar6, B. Evans12, P. Dove6, L. M. Bonnell5, M. P. Marder13, and L. Pyrak-Nolte14

1Bureau of Economic Geology, The University of Texas at Austin, Austin, TX, USA, 2Geocom LLC, Durango, CO, USA, 3Sandia National Laboratories, Albuquerque, NM, USA, 4Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 5Institute of Structural Geology, Tectonics and Geomechanics, RWTH Aachen University, Aachen, Germany, 6Department of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA, 7Department of Geosciences, Pennsylvania State University, University Park, PA, USA, 8Chevron Energy Technology Company, Houston, TX, USA, 9Department of Geological Sciences, Central Connecticut State University, New Britain, CT, USA, 10Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA, 11Hildebrand Department of Petroleum and Geosystems Engineering, The University of Texas at Austin, Austin, TX, USA, 12Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA, 13Department of Physics, The University of Texas at Austin, Austin, TX, USA, 14Department of Physics, Purdue University, West Lafayette, IN, USA

Abstract Fracture pattern development has been a challenging area of research in the Earth sciences for more than 100 years. Much has been learned about the spatial and temporal complexity inherent to these systems, but severe challenges remain. Future advances will require new approaches. Chemical processes play a larger role in opening-mode fracture pattern development than has hitherto been appreciated. This review examines relationships between mechanical and geochemical processes that influence the fracture patterns recorded in natural settings. For fractures formed in diagenetic settings (~50 to 200 °C), we review evidence of chemical reactions in fractures and show how a chemical perspective helps solve problems in fracture analysis. We also outline impediments to subsurface pattern measurement and interpretation, assess implications of discoveries in fracture history reconstruction for process-based models, review models of fracture cementation and chemically assisted fracture growth, and discuss promising paths for future work. To accurately predict the mechanical and fluid flow properties of fracture systems, a processes-based approach is needed. Progress is possible using observational, experimental, and modeling approaches that view fracture patterns and properties as the result of coupled mechanical and chemical processes. A critical area is reconstructing patterns through time. Such data sets are essential for developing and testing predictive models. Other topics that need work include models of crystal growth and dissolution rates under geological conditions, cement mechanical effects, and subcritical crack propagation. Advances in machine learning and 3-D imaging present opportunities for a mechanistic understanding of fracture formation and development, enabling prediction of spatial and temporal complexity over geologic timescales. Geophysical research with a chemical perspective is needed to correctly identify and interpret fractures from geophysical measurements during site characterization and monitoring of subsurface engineering activities.

Plain Language Summary Fracture patterns in rock strongly affect directions, magnitudes, and heterogeneities of both fluid flow and rock strength. Accurate and testable predictions of patterns are essential for understanding many societally important processes in the Earth and for effectively managing subsurface engineering operations. Chemical processes play a larger role in opening-mode fracture pattern development than has hitherto been appreciated. For fractures formed at depths of ~1–10 km and temperatures of 50–200 °C, new evidence shows chemical reactions are common and more diverse than previously recognized. We describe how viewing fracture formation and evolution from a chemical perspective helps to solve problems in fracture pattern analysis. We outline the main impediments to subsurface fracture pattern measurement and interpretation, assess implications of recent discoveries in...
fracture history reconstruction for process-based models of fracture and cement accumulation, review models of fracture cementation and chemically assisted fracture growth, and discuss promising paths for future work. Potential exists for basic scientific investigations to lead to progress on what has been one of the most refractory practical problems in subsurface science. Results suggest that progress in fracture interpretation and prediction can be made using observational, experimental, modeling, and theoretical approaches that view fracture patterns as the result of coupled mechanical and chemical processes.

1. The Challenge of Natural Fractures in the Earth

Accurate and testable predictions of fracture patterns in rock are essential to understand many societally important processes in the Earth and for effective management of subsurface engineering operations. Fractures strongly affect directions, magnitudes, and heterogeneities of both fluid flow and rock strength (Bear et al., 1993; Berkowitz, 2002; Bonnet et al., 2001; de Dreuzy et al., 2012; Olson et al., 2009; Tsang & Neretnieks, 1998; Wang, 1991). Consequently, they have a first-order control on the production of water, hydrocarbons, and geothermal energy; flow of pollutants in the subsurface; safe storage of CO2 and wastewater; and seismicity, whether natural or induced (National Research Council, 1996; Pyrak-Nolte & DePaolo, 2015). Understanding the role of chemically assisted subcritical fracturing in rock deformation is recognized to be important for the exploitation of hydrocarbons, geothermal resources, and the long-term stability of geological reservoirs for CO2 and nuclear waste sequestration (e.g., Bergsaker et al., 2016; Eppes & Keanini, 2017; Olson et al., 2009). Both natural and induced fractures influence resource extraction in the unconventional resources that are the focus of much recent hydrocarbon exploration and development (Gale et al., 2014; Narr et al., 2006; Pedersen & Eaton, 2018; Solano et al., 2011). Understanding preexisting fractures is key to anticipating and controlling engineered fractures (e.g., Wang et al., 2018).

Because fracture data are difficult to acquire and interpret (Figures 1 and 2 and section 1.2.1), fracture patterns remain stubbornly indistinct and unpredictable despite more than a century of progress in a number of important areas including detection, sophisticated mechanics-based and statistical modeling approaches, and expensive drilling and well testing campaigns in the private and public sector. A review of the challenges reveals that severe limitations remain despite a new round of research drilling (e.g., Gale et al., 2018) and a revolution in outcrop fracture pattern description based on remote and drone-based imaging (e.g., Pollyea & Fairley, 2011; Menegoni et al., 2018; Wüstefeld et al., 2018). These limitations persist because subsurface patterns, particularly on scales of a meter or more, cannot be reliably inferred from borehole samples as they are currently analyzed, and models are difficult to validate. Thus, among the most important and challenging problems in geoscience is identifying and understanding key influences on fracture pattern development and how to recognize these influences with the limited samples that are typically available.

Here, we investigate the proposition that in diagenetic settings chemistry is a key missing ingredient for accurate fracture pattern predictions and meaningful interpretations. Mechanics is an indispensable tool for deciphering how fracture patterns form in rock (Pollard & Aydin, 1988). But is mechanics sufficient? Fracturing is inherently a physiochemical process that involves the breaking of bonds (Marder & Fineberg, 1996). We contend that information regarding chemical reactions could help benefit our understanding of complex fracture processes. The role of chemistry is likely to be valuable in some cases and have less of an impact on other mechanical processes.

Chemical alterations of rocks in the Earth—depending on how high the temperature is—are termed diagenesis (to ~200 °C) or metamorphism or metasomatism (for higher temperatures). Although multiple lines of evidence indicate that chemical reactions within rocks have a profound influence on the development of natural fracture systems, their role in fracture pattern development has not been systematically explored. Within the temperature range of diagenesis, chemical reactions affect fracture development in at least two ways: through chemically assisted fracture growth (Atkinson, 1982, 1984) and by dissolution/precipitation reactions that change the mechanical properties of host rocks and fracture zones as fractures form. As an example of chemical-mechanical interaction, we explore evidence that fracture size and spacing correlate with cement accumulation patterns in fractures (Figure 3). This example illustrates rich opportunities for further insights into pattern development and the need for new experimental and theoretical treatments. The chemical
compositions and textures of naturally occurring cements in fractures also contain underutilized evidence for the rate and timing of pattern formation. This evidence can be used to test predictive models.

We examine the challenges of fracture pattern interpretation and new evidence of reactions in fractures and their possible effects on pattern development. Our focus is on the diagenetic environment that typically represents the upper ~10 km of the Earth’s subsurface. We then outline the current status of theoretical and experimental work on subcritical crack propagation and process-based models of fracture and fracture cement growth, and promising paths for future work. We show that progress in fracture pattern interpretation and prediction can be enhanced by new observational, experimental, and modeling approaches that place emphasis on the ubiquitous chemical processes affecting fractures in diagenetic settings. We make the case that it is useful to view fracture patterns as chemical transformations in a mechanical context.

In this review, we reveal a complementary frontier to current work in reactive transport modeling. Recent studies show that natural fracture patterns may evolve over geologic timescales. This evolution is strongly influenced by a range of chemical processes. These interactions are little explored. Although the role of existing fractures in transporting reactive fluids and of fluids modifying fractures has been reviewed (e.g., National Research Council, 1996; Ord et al., 2016; Steefel & Lasaga, 1994; Steefel & Lichtner, 1998; Steefel et al., 2005, 2015; Taron et al., 2009; Xiao et al., 2018), this previous work does not cover recent developments on the role that chemistry plays in natural fracture pattern interpretation and development. These include breakthroughs and opportunities in using chemical evidence to unravel fracture timing and how patterns develop and rock mechanical properties evolve. A challenge is to extend current modeling and experimental approaches to geologic timescales. Many experimental and modeling tools of modern chemistry have yet to

Figure 1. Types of fractures. (a) Block diagram illustrating fracture types in bedded rocks. Displacement is normal to the discontinuity for opening-mode fractures (Lc) and parallel or subparallel for faults (F). St, stratification; C_L, cluster of opening-mode fractures (after Narr et al., 2006). (b) Opening-mode fractures are commonly called veins (V) if mineral filled (red, with medial line), and joints (J) if they lack mineral deposits; these terms are problematic for diagenetic settings in which fractures that formed at the same time can resemble veins or joints in terms of cement fill or fall into a hybrid category where fractures walls are lined with cement (blue) and may be locally bridged by pillar-shaped bridge cement deposits (Br). Large arrows show opening vectors. (c) Example of calcite (cc)-filled fracture in shale. Arrows show opening displacement. Note medial line. (d) Open, calcite-bridged fracture, Austin Chalk, Texas. Br, calcite bridge. (e) Core cut parallel to bedding, Cozzette Sandstone, Colorado. Br marks open, quartz-lined and locally quartz-bridged vertical fracture. (f) Joints, Precambrian sandstone-shale sequence, NW Scotland. Inset shows traces localized in sandstone beds, an example of stratigraphic control. (g) Cluster (CL), quartz-lined fractures, sandstone, NW Scotland (see Ellis et al., 2012). (h) Part of discrete fracture network realization for subsurface rock. A discrete fracture network model represents fractures realistically and discretely within a matrix grid. Model width dimension, 2 km. Although patterns affect flow, tests in wells, including pressure-transient tests, multiwell pulse tests, and tracer tests, commonly cannot distinguish among patterns, such as between long fractures and small but extensively interconnected fractures that may extend for long distances (kilometer scale).
Fracture patterns recorded in natural and synthetic materials can be characterized by size distributions and spatial arrangements. Other factors include those that describe connectivity, mineral content, and strength. In turn, these parameters strongly influence the transport and mechanical properties of the formation (Adler & Thovert, 1999; Cosgrove & Ameen, 1999; Hancock, 1985; Laubach et al., 2018; Peacock et al., 2018; Sanderson & Nixon, 2015; Walsh & Watterson, 1993; Figures 3–9). Opening-mode fractures occur as disseminated arrays that may be assigned to sets based on shared attributes such as orientation (Hancock, 1985) or based on occurrence within localized, dense arrays including those adjacent to faults (Caine et al., 1996; Faulkner et al., 2010). The combination of all fractures makes up the pattern.

The size component of patterns includes distributions of length, height, and aperture: components that may or may not be correlated (Bernabé et al., 2010; Guéguen & Dienes, 1989; Olson, 2003; Scholz, 2010; Schultz, 2000; Schultz & Fossen, 2002). In general, in sedimentary rocks, fractures within a given set display a wide range of sizes with length and height values ranging from nanometers to hundreds of meters or more and apertures ranging from nanometers to tens of meters (e.g., Anders et al., 2014; Gillespie et al., 2001; Hooker et al., 2014; Odling et al., 1999; Ortega et al., 2006). On the other hand, for specific sets, the size range may be extremely narrow. We focus on examples in the literature that are mostly from microns to hundreds of meters in scale.

Microfractures are those requiring a microscope to detect (Anders et al., 2014). Microfractures and other small-scale features can be nucleation points for subsequent fracture growth. Geomechanical models commonly contain assumptions about the nature and concentration of such nucleation sites. Fracture patterns

1.1. What Are Fracture Patterns?

To understand why a chemical perspective on natural fractures may be useful, it is helpful to start by recapitulating what is known about fractures in the Earth and why they have proven so challenging to characterize and predict. Arrays of naturally occurring opening-mode fractures and faults are widespread in all rock types and geologic settings within the Earth’s crust (Figures 1–8). Naturally occurring fractures range in scale from microns to kilometers in length and come in two main varieties: opening-mode fractures, where rock separates by displacement normal to fracture walls, and faults, where rock is displaced parallel (or nearly parallel) to fracture walls (Pollard & Aydin, 1988; Faulkner et al., 2010; Figure 1). As we will see, owing to chemical effects the loss of cohesion from fracturing can be exceedingly transient (no more than fractions of a second) or persist for millions of years. Both opening-mode fractures and faults are subject to chemical processes, during and after formation.

We focus on opening-mode fractures because their interpretation and prediction has proven to be intractable using geometric observations and mechanics alone (section 1.2). They are also among the most common structures in the crust, and they may be important structures at greater depth (Anders et al., 2014; Hancock, 1985; Pollard & Aydin, 1988). They are also the most difficult to detect or measure. Moreover, the impact of chemical processes is less widely appreciated in the development of these fractures compared to faults, where a range of chemical effects have been described (Davies & Cartwright, 2007; Di Toro et al., 2012; Eichhubl et al., 2009; Fisher et al., 2003; Fossen et al., 2018; Noiriel et al., 2010; Spence et al., 2014).

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are affected by stress concentrations that arise from heterogeneities within the host rock. The location and properties of these often-discontinuous heterogeneities is largely unpredictable and hence are commonly treated as a stochastic uncertainty (Narr & Suppe, 1991; Olson et al., 2009).

Within sets of disseminated, subparallel fractures, patterns of inter fracture distances can range from random arrangements to simple regular spacing (Ladeira & Price, 1981; McGinnis et al., 2017; Narr, 1991, 1996) to complex hierarchical clustering (Marrett et al., 2018; Ogata et al., 2014; Questiaux et al., 2009; Roy et al., 2014; Figures 5, 10, and 11). Recent advances in quantifying spatial arrangement provide tools for analyzing these spatial and size patterns (Hanke et al., 2018; Marrett et al., 2018). As we discuss, when used with timing constraints from naturally occurring mineral cements, data generated using these tools can reconstruct how spatial and size patterns vary through time (Hooker et al., 2018).

Another element of spatial arrangement is fracture stratification (Bertotti et al., 2007; Laubach et al., 2009; Figure 2), the localization of fractures in layers. Fracture stratification—a response to the development of a fracture system in a mechanically layered medium such as sedimentary rocks—can have a strong influence on fracture height, spacing, and orientation. Fracture stratification may be more-or-less complex than the associated lithological and mechanical stratification of host rocks (e.g., Lavenu & Lamarche, 2018), depending upon the initial properties and spatial distribution of rock types and the coevolution of loading and rock mechanical properties.

Contrary to older views, because mechanical property changes reflect diagenesis and fractures evolve with loading history, mechanical stratigraphy and fracture stratigraphy need not and commonly do not coincide (Laubach et al., 2009). Both differ from lithologic stratification. Fracture stratigraphy subdivides rock into fracture units according to extent, intensity, or some other observed fracture attribute. Fracture stratigraphy reflects a specific loading history and mechanical stratigraphy during failure. Mechanical stratigraphy subdivides stratified rock into discrete mechanical units defined by properties such as tensile strength, elastic stiffness, brittleness, and fracture mechanics properties. Mechanical stratigraphy is the by-product of depositional composition and structure, and chemical and mechanical changes superimposed on rock composition, texture, and interfaces after deposition. An example of a set of layer bound, regularly spaced fractures that evolved in a rotating stress field, is shown in Figure 4i.

An important aspect of spatial arrangement is fracture network topology (e.g., Jing & Stephansson, 1997), which defines local to system-wide connectivity (Long & Witherspoon, 1985). From a field perspective, patterns can be categorized as networks of numerous individual structures defined by the orientation, size, and connectivity of individual elements (Andresen et al., 2013; Jing & Stephansson, 1997; Sanderson & Nixon, 2015; Peacock & Sanderson, 2018; Figure 4). This influential topological view focuses on the connectivity of elements, which governs fluid percolation through rocks with low intrinsic permeability.

Cement precipitation and dissolution can profoundly modify where porosity exists within fractures and thus connectivity (Olson et al., 2009). These chemical effects are poorly understood and usually not described for natural examples. We discuss these chemical effects in subsequent sections. Cement patterns are a key but often overlooked element of fracture connectivity and topology. Differences in fracture cement patterns have been shown to govern fluid flow in some instances (e.g., Laubach, 2003) and to correlate with deposits in host rocks (e.g., Weisenberger et al., 2019).

Age, both relative and absolute, is another fracture attribute that can influence overall patterns. For example, preexisting fractures can influence growth of subsequent fractures. The influence of fractures on subsequent pattern development can be fracture age dependent. For example, with time, creep processes can
dissipate stress anomalies. Fractures may close mechanically or fill with mineral deposits. Many of these time dependencies are sensitive to chemical-mechanical processes in the host rock that have uncertain rates. Consequently, how these processes relate to fracture development are unknown or ambiguous. But as we show these processes are now susceptible to study.

In principle, fracture patterns arise as a consequence of loading pathways that are highly variable (Engelder, 1985). However, establishing which loading path or paths caused a particular pattern typically is exceedingly difficult to demonstrate (e.g., English & Laubach, 2017; Virgo et al., 2014). Therefore, the relationships between pathways and many of the fracture patterns that are observed remain undetermined. Patterns may vary greatly within a given set of fractures formed in one episode of deformation, or simple or complex patterns can arise from the superposition of multiple events.

A longstanding impediment to understanding how fracture patterns arise is the lack of constraints on the timing and rate of natural fracture development. Although absolute and even relative timing is notoriously hard to pin down (e.g., Peacock et al., 2018), fracture sets are commonly interpreted to have formed more-or-less contemporaneously over a short period of time (e.g., Caputo, 1995; Hancock, 1985). Yet some natural

**Figure 4.** Conceptual fracture pattern topology. (a–d) After Laubach et al. (2018). Plan view fracture trace patterns on a bedding surface. (a) Interconnected, (b) not interconnected, (c) interconnected, clustered, and (d) ephemeral connections by second set. (e–g) After Sanderson and Nixon (2015). Network topology defined by arrangement of traces and nodes: (e) random array of traces as generated in stochastic models, (f) schematic representation of a network, and (g) network generated by random selection of branches on a square grid. Nodes and branches: I nodes (circles); Y nodes (triangles); and X nodes (diamonds). (h) Fracture trace patterns. Cambrian Flathead sandstone, Wyoming. Intersection pattern annotated for part of pattern. (i) Fracture network, Oman Mountains created by two phases of non-parallel horizontal extension with a rotation of ~20°. Rectangular grid markers spaced 2 m apart. A parallel set of long, evenly spaced fractures formed during the first extension, reactivated in sinistral mixed mode. Second-phase fractures nucleate mostly close to tips of older fractures. Image is a modified part of a rectified high-resolution photograph created by Wüstefeld (2010). For the tectonic, geomechanical and pressure-temperature evolution of the area, see Grobe et al. (2019).
examples (Dunne & North, 1990) and model results (Bai et al., 2002; Nick et al., 2011; Olson & Pollard, 1989; Welch et al., 2015) imply that sets can form contemporaneously and/or over a long period of time (millions of years). Model results (e.g., Olson, 2007) show that complex patterns can arise from simple but protracted (millions of years) loading histories. Loading (not the response) may be constant. In fact, it is a largely unexamined assumption of fracture studies that simple orientation patterns reflect punctuated “events” of finite duration (e.g., Hancock, 1985). Recent advances in direct and indirect methods for dating fracture timing and rates of pattern development show that conventional interpretations of fracture pattern development rates need to be reevaluated (Figure 9). Rate and timing reconstruction is a vital area where chemical approaches can contribute to the understanding of fracture patterns.

1.2. Why Is Pattern Characterization and Prediction a Problem?

The characterization of fracture patterns remains a challenge for three main reasons. First, there are inherent limits on data that can be acquired by sampling subsurface fracture patterns using wellbores or geophysical methods (Figures 1 and 2). Second, many loading paths can lead to seemingly identical individual mechanical discontinuities, yet these apparently identical parts can be arranged in drastically different patterns (Figures 4 and 5). The result is a problem of nonuniqueness. Third, the same loading path can lead to widely differing fracture patterns due to the sensitivity of fracture propagation to differences—including subtle differences—in rock properties.

Several additional factors contribute to our poor understanding of deep-seated fracture patterns and processes: A substantial fraction of research on fractures has been conducted on outcrops where fracture formation is driven by processes that occur over timescales that may differ greatly from those under diagenetic and higher-temperature conditions (e.g., Li et al., 2018). Moreover, as we describe below, fractures may be active over millions of years during which stress conditions and rock properties may undergo substantial changes. Although mineral precipitation during fracturing can lead to feedbacks that affect both individual fracture characteristics and fracture patterns, study of these processes is a recent development with many
unknowns. Postfracture formation mineral precipitation can also add confusing signals (e.g., Weisenberger et al., 2019), but current practice rarely makes even rudimentary differentiation of cements, if they are studied at all.

1.2.1. The Sampling Challenge
Typical sample and fracture dimensions are the reason fracture attributes and patterns are exceedingly difficult or impossible to measure in the subsurface (Figure 1). A review of current research on naturally occurring fractures in rock reveals that, in the subsurface (i.e., depths greater than 1 to 10 km), knowledge about fracture patterns is based on extremely limited samples, and this state of affairs has changed little over the past few decades (e.g., National Research Council, 1996). Subsurface fracture patterns are concealed by the narrow dimensions of rock that can be sampled in wellbores (Figure 1). Data on fracture presence, density of occurrence, local porosity structure, and some aspects of size patterns are rarely abundant enough for representative statistics, and extrapolations of such observations to areas not sampled are hard to justify. A common case is no fracture data in the zone of interest.

Mines provide a local clear 3-D view of fractures but sample too small a rock volume to reveal large-scale patterns. For depths greater than those found in mines, the sampling is primarily performed via wellbores. Scientific and industrial coring programs and the advent of wellbore image logs have revolutionized our

Figure 6. Cement bridges on fracture faces and in cross section. (a) Bridges, cross-section view, Mesozoic sandstone, NE Mexico, outcrop. P, porosity; Br, bridge (all images). Hooker et al. (2015). (b) Quartz bridges and quartz rinds, fracture face, Cretaceous sandstone, Colorado. Fall et al. (2012). (c) Quartz bridges (one example circled) and rinds, Paleozoic shale fracture face, core, West Texas. (d) Dolomite bridge with crack seal texture, Knox dolostone, core, after Gale et al. (2010). Crack seal texture developed across the whole bridge; bridge is composed of multiple crystals. (e) Cambrian sandstone, NW Scotland. Cathodoluminescence (CL) image; after Laubach and Diaz-Tushman (2009). (f) Microfracture, Paleozoic sandstone, Oklahoma. Sd, late siderite crystals. G, grain. Modified from Anders et al. (2014). (g) Cretaceous sandstone, core depth 6,200 m, Wyoming, after Laubach et al. (2016). (h–k) Quartz bridge with crack seal texture, East Texas core. Lq, lateral quartz. Gd, gap deposit quartz. FIA, fluid inclusion assemblage. (h) Transmitted light image. (i) Panchromatic CL image. Inset box shows detail in (j). (j) Panchromatic CL image, detail. (k) Map on CL image, showing location of gap and lateral deposits.
understanding of fractures and have revealed that open fractures exist at far greater depths than previously thought possible (National Research Council, 1996). For example, open fractures with circulating fluids were detected at depths of nearly 12,000 m and pressures of 300 MPa in the Kola Superdeep drill hole in Russia (Popov et al., 1999), and similar, unexpected fluid-filled fractures were encountered in the KTB superdeep drill hole in Germany (e.g., Zimmermann et al., 2000). Open fractures are widespread in hydrocarbon reservoirs at 6- to 8-km depth. Nonetheless, the information obtained from wellbore-based probes, like mines, have limited utility for characterizing large-scale patterns. Consequently, other evidence is commonly combined with direct observations to diagnose fracture attributes. The presence of fractures is commonly inferred from anomalous fluid flow patterns evident in well tests (e.g., Da Prat, 1990; Narr et al., 2006; Solano et al., 2011; Wehunt et al., 2017). Thus, there are intervals in the deep boreholes that are transmissive, and there are also large intervals that have low permeability, often in close proximity. A common inference is that this variability is another indication of the dynamic nature of the pore spaces: contrasts between fractures currently open and transmissive and other (large) regions where they are currently closed. But flow tests sample large-scale permeability fields rather than fracture patterns per se. So although well tests can be used to measure local permeability or to determine permeability and transmissibility pathways between wells, these offer only broad constraints on potential fracture patterns.

Indirect sampling through geophysical methods such as seismic, while useful for many applications, provides at best only broad constraints on patterns given that most fractures have sizes that place them below the limits of resolution (e.g., Casini et al., 2012; Chopra & Marfurt, 2005; Müller et al., 2010; Yielding et al., 1996). Geophysical approaches are increasingly useful for detecting small faults and in some circumstances clustered, persistent fracture concentrations (e.g., Hu et al., 2018; Singh et al., 2008). However, well tests and tracer experiments show that hard-to-detect disseminated or small fractures may significantly influence subsurface fluid flow. Although individual large fractures locally correlate better with flow than do numerous small fractures (Narr et al., 2006), the cumulative effect of even small fractures can be considerable, and these structures cannot be neglected (Aguilera, 2010; Egya et al., 2019; Philip et al., 2005; Solano et al., 2011). The time history of gas recovery from a hydrofractured well can also be used to place constraints on the natural and stimulated fractures that constitute the transport path, but again, these constraints are quite broad (Marder et al., 2018) and separating the natural from the engineered part is highly uncertain. At depths where direct observation of fracture patterns is precluded, an impediment to improving geophysical methods of fracture characterization is the limited ability to validate results of indirect probes by systematic comparison with observation of fractures.
Despite sampling challenges, the potential economic impacts of fractures have motivated an effort to collect high-quality core and image log data sets. These studies aim to determine the location and dimensions of fractures. Assuming fractures have a regular shape, these dimensions are aperture, height, and length. If wellbores intersect fractures, opening displacement sizes (aperture) can sometimes be documented (Ortega et al., 2006). In rare cases the heights of some fractures may be detectable, but the full lengths of fractures in the subsurface are practically unmeasurable.

With the advent of horizontal coring and logging, valuable, albeit rare, information is emerging about fracture population statistics and spatial arrangement (e.g., Hooker et al., 2009; Li et al., 2018; Lorenz & Hill, 1994). These data show that fracture orientations, sizes, spatial arrangement patterns, and degree of cement fill vary considerably (Hooker et al., 2009; Laubach et al., 2016). These observations are compatible with fracture patterns that vary markedly, in some cases over short distances (approximately meters to tens of meters). These data are valuable because they show that differences in fracture patterns are likely responsible for much of the confusing variability evident in measures of fluid flow such as well test results. But costly and inevitably sparse wellbore data as currently analyzed have limited use for identifying patterns owing to the nonuniqueness problem discussed below.
Using core data, attributes that can be measured most reliably are fracture and host rock cement compositions and textures; in other words, information about the mineralogical and structural-chemical attributes of the fracture-host system. The chemical signals recorded in fractures and host rock provide information that may help offset the limitations of sparse sampling (explored in section 2). These chemical records may also make more valuable another source of fracture pattern information: outcrop observations.

1.2.2. Problems and Advantages of Outcrop Fractures

Outcrops provide access to naturally formed fracture patterns (Figures 2 and 4) and a means to compare predictive statistical or mechanical models to nature (Pollard & Aydin, 1988). Data sets from outcrops avoid the limitations of borehole-based sampling and encompass features below the resolution of seismic methods that would otherwise be missed (Bellahsen et al., 2006; Corbett et al., 1987; Gutmanis et al., 2018; Seers & Hodgetts, 2014; Ukar et al., 2019; Watkins et al., 2015; Wennberg et al., 2016; Wüstefeld et al., 2018). Consequently, outcrop fracture studies are an essential element in a strategy for learning about fracture patterns existing at depth. Outcrop fracture mapping is undergoing a renaissance owing to recent advances in remote sensing, drone-based imaging, advanced image processing, and feature extraction of outcrop-based data sets (Bisdom et al., 2014, 2017; Hardebol & Bertotti, 2013; Healy et al., 2017; Madjid et al., 2018; Pollyea & Fairley, 2011; Wüstefeld et al., 2018).

Attributes that are readily or commonly measured in the outcrop include the following:

1. Fracture type and orientation;
2. Size distributions of aperture, height, and length, which are often only partial data sets due to weathering (aperture) and to outcrop size limitations (height and length);
3. Fracture spacings or spatial arrangements;
4. Arrangement and connectivity of fracture pattern elements;
5. Fracture and mechanical stratigraphy and the relationship of fracture attributes to rock type, bed interfaces, and structural position;
6. Spatial distribution of fracture porosity (in a few cases, as applicable);
7. Evidence of rock alteration along fluid flow paths (in a few cases, as applicable); and
8. Variations in fracture-filling cement mineralogy as a function of fracture orientation and/or relative age.

The literature on these measurements is extensive (e.g., Aydin, 2000; Dershowitz et al., 2000; Dershowitz & Herda, 1992; Iñigo et al., 2012; La Pointe & Hudson, 1985; Laubach & Ward, 2006; Marrett et al., 2018; Narr et al., 2006; Sanderson & Nixon, 2015; Tavani et al., 2015; Ukar et al., 2016; Wüstefeld et al., 2016).

Over the past two decades, subsurface sampling shows that at depths in excess of one kilometer in sedimentary basins, fracture patterns often differ from those found in outcrops. Some outcrop observations provide close matches to those in the subsurface (e.g., Gomez-Rivas et al., 2014; Hilgers et al., 2006; Holland et al., 2009), but others do not (e.g., Laubach et al., 2009). In many cases, outcrop fractures differ from those in nearby excavations or cores (Corbett et al., 1987; Narr, 1991; Queen & Rizer, 1990). Near-surface processes including weathering and local topography can cause fractures to form that are not related to fractures formed at depth and observed in nearby excavations (e.g., Aubertin et al., 1996; Miller & Dunne, 1996). Studies aimed at characterizing deep-seated fractures should omit fractures that result from...
near-surface processes unrelated to fractures at depth (Stearns & Friedman, 1972). But near-surface effects may be prevalent in most outcrops, resulting in misleading impressions of what constitutes “typical” patterns at depth. For example, comparative studies of fracture spacing in the same rock type and structural setting observed in the outcrop and sampled in long fracture-perpendicular wellbores show that patterns in exposures can differ markedly from those in the nearby subsurface (Li et al., 2018; Figure 11).

The problem of ambiguous origins of some outcrop fractures has long been recognized (e.g., de Keijzer et al., 2007; Lavenu & Lamarche, 2018; Lavenu et al., 2013; Stearns & Friedman, 1972). Differences arise fundamentally from the low tensile strength of rock and the many loading paths to fracture, including tectonic and localized strain, changes in pore pressure, thermoelastic contraction, uplift-related stress, exposure and topography, and anthropogenic effects (Engelder, 1985). Because processes such as thermoelastic contraction may drive fracture growth (e.g., English & Laubach, 2017), the differing temperature-pressure paths of outcrops and rocks at depth mean that the evidence provided by outcrop patterns on fracture patterns in the deeper subsurface should be used with caution.

Less widely appreciated is the extent to which mechanical properties vary with time as a result of chemical processes (e.g., Laubach et al., 2009, 2010). Equivalent strata exposed at the surface and at reservoir or aquifer depths have necessarily experienced different burial and uplift histories, which typically result in contrasts in diagenetically modified rock and fracture properties between subsurface targets and an outcrop. This latter effect produces profound differences between outcrops and areas of interest in the subsurface that are rarely considered when selecting or evaluating outcrops as subsurface guides. Fracture pattern evolution is sensitive to rock mechanical properties and the progressive diagenesis that causes mechanical properties to evolve (Laubach et al., 2009, and references therein). Rock properties vary with time as a result of initial rock composition and texture together with progressive compaction, dissolution, and precipitation. Thus, we are left with the seemingly intractable challenge of extrapolating patterns from the limited end-state fractures and samples that are available from outcrops that may differ markedly from those found in wellbores.

The wide range of potential loading paths to fracture propagation coupled with time-dependent mechanical properties suggests that even the outcrop fracture patterns that are representative of the subsurface have a limited range of applicability to specific subsurface localities. The most valuable outcrop studies are those

Figure 10. Mechanical effects of cement on fracture patterns is suggested by contrasts between extreme cases: barren joints versus veins that were repeatedly fully cement filled during growth. (a) Joints, Lafonia Group, Falkland Islands. Note narrow aperture size range and regular spacing. (b) Veins, Antarctic Peninsula. Note wide aperture size range and irregular spacing. Insets show modelled nonspanning and spanning quartz cement respectively; modified from Lander and Laubach (2015). Inset key matches Figure 8; black, pore space; red, cement accumulation at fast rate; blue, green, cement accumulation at slow rate. Gray, dark gray, quartz and feldspar grains.
that can be linked quantitatively to those in the subsurface. Yet even for outcrops containing fractures that can be shown to have formed at depth, a challenge is to know how patterns visible in an outcrop are related to specific processes and locations in the subsurface.

Part of the problem with outcrop studies as currently conducted is often that surface and subsurface fractures actually do resemble each other in terms of shapes, orientations, and patterns. These similarities are the reason that it is so difficult to discern and understand differences in origin. Although the diagenetic attributes of fractures in the outcrop and core commonly differ considerably, these features are rarely used as a basis for comparing outcrop and subsurface fractures. Comparing fracture cements in the core and outcrop is the most reliable way to link structures in specific subsurface and outcrop settings (Evans & Battles, 1999; Li et al., 2018; Ukar et al., 2019). Fracture patterns are well exposed in some outcrops, and some fractures are likely excellent indicators of patterns at depth, but from geometry alone a quantitative extrapolation to the subsurface is impossible. Identifying and using these special outcrops will be critical for advancing our understanding of patterns at depth.

1.2.3. The Nonuniqueness Problem

“The joint in the rock, thin as a hair, and straight as a measuring-rod, that piece of petrified geometry, promises much, yet discloses little.” (Nevin, 1942, p. 131). This quote from a once widely used textbook in structural geology remains valid 77 years later. From a geometric and mechanics point of view, fractures grow as their walls move apart and their tips extend into the rock. Under overall compressive stress states in the Earth, opening-mode fractures result from some combination of fluid pressure and other loads. Using shape alone, there is little difference between fractures responding to many different causes (loading pathways). For example, fractures can form as a consequence of folding, fluid overpressure development, uplift, or rough handling during core sample retrieval. Although the shape of a single fracture gives few clues about
its origin, different stress histories may create vastly different fracture patterns. For example, patterns caused by fluid overpressures from natural gas generation could extend over wide regions, whereas those caused by strains associated with bending in a fold are likely to be localized. In other words, although the fractures look alike, the patterns formed by groups of fractures may and usually do differ. Yet these differences in pattern are just what we wish to know.

Fracture attributes such as overall shape that are independent of loading path or are not uniquely determined by the mechanical processes that formed them, obstruct clear interpretations of the structural history. Path-independent structures, as might be seen in individual fractures, either in outcrop or in core specimens, may mask a more thorough mechanistic interpretation. A path independent or nonuniqueness problem underlines some of the issues that limit fracture core analysis and is the main impediment to using outcrop fracture patterns reliably. Outcrop studies show that patterns can vary markedly with rock type and fracture formation mechanism, but the path independence that makes outcrop fracture patterns hard to interpret also makes these patterns impossible to infer from a sample of an individual fracture in either a core or in an outcrop. Thus, fractures, individually, are too simple. This is a case of equifinality (Beven, 2006), where a given end state—a fracture, for example—can be reached by many potential means.

In summary, the preceding sections show that a key problem for fracture pattern assessment is that sparse subsurface and ambiguous outcrop observations make it difficult to extrapolate without a mechanistic understanding of the chemical and mechanical pathways and a way to identify the pathways. Sparse samples as currently analyzed are mostly inadequate guides to the nature of the patterns of which they form a part because they provide little or no evidence of how or why fractures formed. Individual fracture observations provide little guidance concerning the patterns that are likely to be present. For example, is the sampled fracture part of a disseminated or a clustered array? This uncertainty impedes predictive model validation and improvement. These impediments are symptoms of a fundamental limitation to using geometry alone to describe fractures, and mechanics alone to interpret how they formed.

As we discuss below, diagenetic information makes individual fractures and fracture patterns more complicated, yet easier to interpret. The extent and texture of cements, combined with fluid inclusions, and other features can tie fractures to the processes that formed them while also constraining fracture timing and rates. This information, in turn, greatly narrows the potential range of loading paths that cause fracture patterns and allows a more nuanced extrapolation from limited core samples and outcrop analogs.

2. Why Chemistry Is Important in Understanding Formation and Evolution of Fracture Systems

Chemistry in the context of fracture systems refers to the impact that chemical reactions can have on the way that fractures develop and age as well as on fracture and host rock geomechanical and fluid flow properties. Fractures that form at low temperatures under near-surface conditions are largely devoid of diagenetic alteration ("joints"; Pollard & Aydin, 1988). Exceptions include biofilms and some cement deposits or dissolution features in some rock types. On the other hand, in hydrothermal regimes and in metamorphic rocks, fractures are sites of dissolution or are pervasively filled by cements to form veins. Textures in mineral-filled veins typically record evidence of many repeated cycles of fracturing and cement precipitation. Chemical reactions may have only subtle effects under cool, near-surface conditions, although recent work is questioning this paradigm (e.g., Jin et al., 2013), whereas under deep-Earth conditions chemical effects in fractures and on host rocks can be extensive.

Our focus is on a broad intermediate regime—that of diagenesis, between ~50 and 200 °C. The effects of chemical processes on fractures in this temperature range have been presumed to be slight, but recent evidence we describe documents more profound interactions. In this setting of hot fluids, reactive fracture surfaces are prone to dissolution or mineral precipitation. Fractures exist in rocks that are evolving by solution-precipitation creep and other chemical processes. In these intermediate temperature conditions, fractures are complex (Figures 1 and 5–9). Field observations show great variability—from being enlarged by dissolution reactions, to having only minute cement accumulations, to showing partial occlusion by cements but retaining porosity, to fully cement filled (Figures 1 and 6). This intermediate diagenetic regime is where fractures are likely to influence many societally important subsurface engineering operations.
Chemistry is important in natural fracture systems in many ways. In diagenetic settings, these include the following: (1) the properties of cements that have precipitated within fractures have the potential to constrain the timing, frequency, magnitude, and duration of fracturing while also revealing temperatures, fluid pressures, and fluid compositions during fracture development; (2) fluid-mediated chemical reactions at fracture tips that enable fractures to form under much lower stress conditions than would otherwise be possible and constrain rates of fracture tip propagation; (3) dissolution or cements that form within fractures may promote or impede or arrest fracture growth or cause strain to be partitioned differently than in the absence of dissolution or cement; and (4) contact dissolution or “pressure solution” (although pressure may not always be the primary driving force, particularly for quartz: Bjørkum, 1996; Greene et al., 2009; Meyer et al., 2006) can affect stress and strain in the vicinity of fractures while also influencing the geometrical and fluid flow properties of host rocks. Precipitation or dissolution in fractures and host rocks during the course of fracture development may dramatically change geomechanical properties and fracture shapes that govern how fractures develop. Together, these and possibly other chemical processes could lead to feedbacks that affect both fracture patterns and permeability distributions (Figures 3 and 7).

2.1. Using Chemistry to Understand Fracture Growth

Selecting the appropriate analog or model to predict the attributes of a concealed fracture network would be considerably easier if it were possible to link occurrences of fracture formation to a moment in time and to compare experimental and model rates with those in nature. As discussed above, however, fracture size and geometries alone do not constrain the timing and duration of fracture development. Cements within fractures, however, provide unique constraints on why, when and how fast fractures form.

2.1.1. Implications of Fracture Cement Textures

A widely held view among fracture analysts is that cements are deposited as the passive infill of static fractures and have little bearing on fracture inception and growth rates, at most providing evidence of terminus ante quem. But this view is incorrect.

The importance of interactions between fracturing and cementation was first recognized in mineral-filled veins in metamorphic rocks (reviewed in Bons et al., 2012) where blocky, fibrous, and banded cement textures recorded opening kinematics. Evidence of incremental opening and subsequent sealing to partly restore rock strength is widely attributed to mineral-filled fractures in such settings, likely reflecting high-temperature conditions and possibly large, but episodic fluid fluxes (Cox, 2007; Gaviglio, 1986; Holland & Urai, 2009; Nur & Walder, 1992; Smith & Evans, 1984; Walder & Nur, 1984). An example of a crack seal vein from a metamorphic environment is illustrated in Etheridge et al. (1984).

In contrast to metamorphic and hydrothermal veins, many partly cemented fractures in diagenetic settings contain considerable porosity (Figure 6). Although in most respects these fractures that form under cooler conditions do not resemble “crack seal veins,” textures resembling those found in vein deposits occur as highly localized fracture cement deposits (e.g., Evans & Bartholomew, 2010; Evans & Battles, 1999; Evans et al., 2014; Laubach, 1988; Laubach, Olson, et al., 2004; Laubach, Reed, et al., 2004; Ukar & Laubach, 2016; Urai et al., 1991). The precipitating crystals in these fractures include a range of phases and have a rich variety of morphologies and can be fibrous, elongate, blocky, or veneers (rinds) that line fracture pore space (Ankit et al., 2015; Lander & Laubach, 2015). Some cements in diagenetic settings contain abundant evidence for fracture growth concurrent with cement accumulation. Some deposits are extremely spindly and easily damaged cement pillars that are unlike any features found in higher-temperature veins.

Despite containing vein-like records of fracture kinematics, and unlike fully cement-filled metamorphic veins, fractures in diagenetically altered rocks may be effective long-term fluid conduits. In diagenetic settings, crack seal texture may occur in isolated deposits in otherwise entirely open fractures (Figure 6), and such deposits may even form natural proppants holding fractures open when loading conditions might otherwise close them (Laubach, Olson, et al., 2004, Laubach, Reed, et al., 2004).

A crack seal cycle involves formation of a small aperture or gap in fracture cement that is subsequently sealed, at least in part, by crystal growth (Figure 7e). Consequently, the crack seal process implies repeated cycling between a state where a mechanical connection exists across at least part of the fracture (seal) to a state where these connections are broken (crack). In crack seal systems cement texture and fracture growth reflect the cumulative expression of many small widening and lengthening increments. The incremental.
opening displacements recorded in crack seal textures are generally on the order of micrometers (Laubach, Reed, et al., 2004; Williams & Urai, 1989).

Although cement crack seal textures record the opening history of fractures under both metamorphic and diagenetic conditions, for deposits from diagenetic settings recent developments in imaging cement deposits are revealing complex chemical, microstructural and textural features that contain a great deal of information about fracture history (Figures 7 and 8), with developments in imaging indicating the potential for further insights. The value of crack seal textures is that they record sequential, episodic fracture opening and resealing. Cements and fractures develop hand in hand, over an extended period when fractures are active. Therefore, cements having crack seal textures record conditions when fractures formed.

Cement and fluid inclusion properties are thus potential sources of sequential records of temperature, fluid composition, and fluid pressure during and after deformation (Figures 7c and 7d). These properties make it possible to measure cement accumulation patterns and infer fracture and cement growth rates (Ankit et al., 2015; Becker et al., 2010, 2011; Fall et al., 2015; Lander & Laubach, 2015; Figure 8). They also may help constrain fluid flow and mass transfer in the system (Cox, 2007; Denny et al., 2019; Etheridge et al., 1984; Fisher & Brantley, 1992) and fracture strength (Fisher & Brantley, 1992, 2014; Fisher et al., 2019). However, care must be taken to place individual crack seal events into the proper temporal sequence because the formation of new fractures can occur at variable locations within the overall crack seal texture. Advances in imaging allow high-resolution mapping of these relations (Figure 7d).

Of course, a range of behaviors would be expected for different minerals and geological settings and temperature ranges. We discuss the specific example of quartz cement in section 2.1.2.

### 2.1.2. Reconstructing Fracture Development by Cement Characterization

Fracture reconstruction means deducing the past state, including shape and size, of individual fractures and fracture populations. The utility of linking fracture cement characterization and texture analysis is illustrated by an investigation of quartz cement in fractures within a Cretaceous sandstone from the East Texas Basin (Becker et al., 2010; Figures 8 and 9). An essential aspect of this study is the rigorous analysis of high-resolution cathodoluminescence (CL) images of quartz cement in a sealed portion of an otherwise porous fracture with a kinematic aperture of ~1.1 mm. Interpreted CL images reveal 376 recognizable fracture events that are placed into a relative time sequence. Fluid inclusion assemblages provide high-resolution evidence of temperature, salinity, pressure, and other factors (e.g., Bodnar et al., 2013; Fall & Bodnar, 2018; Fall et al., 2016; Yasuhara et al., 2006). Fluid inclusion data provide an extraordinary record of the conditions during fracture development because they are genetically linked to fracture opening by crack seal textures. These data indicate that the fracture formed at temperatures ranging from ~130 to 154 °C. Integrating these data with a burial history for the sample suggests that the fracture was opening over the past 48 Ma. with an overall opening rate of ~23 μm/Ma and an average opening aperture of ~3.4 μm per event.

Fluid pressures during inclusion entrapment in the cement determined from microthermometric and Raman analyses of the fluid inclusions ranged from overpressures that are roughly halfway between the hydrostatic and lithostatic gradients to near hydrostatic pressures at the present day. The first ~8 Ma of fracture development took place during a phase of increasing burial, but the remaining 40 Ma is associated with uplift. The similarity in entrapment temperatures and fluid salinities for neighboring crack seal events indicates that fracturing events were not associated with transient fluid flow events capable of advecting significant heat. The coincidence in time of the onset of fracture formation with rapid organic matter maturation raises the possibility that hydrocarbon charging of the analyzed reservoir triggered fracture formation by increasing fluid pressures.

Reconstruction studies such as Becker et al. (2010) can be augmented with additional characterization methods such as high-resolution stable isotopic analysis of cement and aqueous inclusions using a secondary-ion mass spectrometer (e.g., Denny et al., 2019; Harwood et al., 2013; Yurimoto et al., 2014), which may lead to additional insights into precipitation temperatures and origins of fluids (although isotopic reequilibration during cooling may be an issue). The stable isotopic composition of fluid inclusions can be measured by secondary-ion mass spectrometer using a cold stage (Yurimoto et al., 2014). Similarly, for carbonate cements, the emerging clumped isotope method (e.g., Eiler, 2007) holds promise to provide a simultaneous reconstruction of precipitation temperature and fluid isotopic composition. High-resolution trace-element
characterization of fracture cements has the potential to provide additional constraints on fluid compositions and origins (e.g., Götte, 2018).

In higher-temperature environments, the collection of oriented samples combined with microstructural and microthermometric analyses of fluid inclusions has proven to be useful in relating fluid-rock events to specific stress and tectonic conditions. Vallance et al. (2004) collected oriented samples of quartz veins from the Moulin de Chéni gold deposit in France and showed that the quartz contained two distinct types of fluid inclusions. One type contained an aqueous carbonic fluid and the other a low-salinity aqueous fluid. Moreover, the two different types of fluid inclusion assemblages occurred along sealed fractures with different orientations. The aqueous carbonic inclusions were along fractures with orientations similar to that of large-scale field structures interpreted to have formed during an early shortening (compressional) event, whereas sealed microfractures containing low-salinity aqueous inclusions show orientations consistent with macroscale brittle faults observed in the outcrop. Finally, because gold-bearing fractures have orientations that are the same as the late-stage, low-salinity aqueous inclusion planes, and because these are associated with late-stage extension, gold mineralization was associated with this brittle fracturing event. Combined microstructural and fluid inclusion studies thus offer great potential to relate specific fluid events to specific fracturing events associated with large-scale structural and tectonic activity.

By providing timing information (Figure 9), such studies enable a clear delineation of the tectonic environment, structural setting, and evolution of stresses for fracture propagation—evidence that can be used to better understand fracture patterns. Timing information can be used to correlate fractures in different parts of basins (e.g., Figure 11). Some fracture cements such as illite and K-feldspar (e.g., Daniels et al., 1994) and carbonate phases (e.g., Rasbury & Cole, 2009) are amenable to radiometric dating, a promising direction for future work.

Opening-mode fractures in the Earth form under a state of effective tension that can be reached by either increasing pressure from within or reducing pressure from without. Crack seal textures are interpreted as evidence for cyclic changes in fluid pressure and/or far-field stress (e.g., Fall et al., 2015; Fisher & Brantley, 1992; Hooker et al., 2015). With the additional constraint of timing information, Fall et al. (2015) showed that fractures in a Colorado basin were a response to increasing pressure from methane catagenesis, sourced from interbedded coals and marine shales. For similar sandstones in Mexico, Hooker et al. (2015) concluded that external, tectonic stresses drove fracture development, with fluids driven by gravity passively filling opening fractures. Using timing information from a quartz-cemented sandstone in Wyoming, Laubach et al. (2016) found elevated pore fluid pressure, thermoelastic contraction, and local folding in different burial depth and structural settings. Subsequent work showed that these differences correspond to marked contrasts in key pattern elements including size distribution and degree of clustering (Li et al., 2018).

2.1.3. Compositions of Fluids in the Diagenetic (Sedimentary) Environment

During the last century, an extensive database related to compositions of fluids in the diagenetic environment was established (c.f., Kharaka & Hanor, 2003). Much of this information came from analysis of oilfield brines that were coproduced during hydrocarbon production, and data collected through the mid-1970s were summarized by Collins (1975). These data have been supplemented in recent years by compositions of diagenetic fluids obtained from quantitative analyses of fluid inclusions trapped in diagenetic minerals, including those associated with Mississippi Valley Type Pb-Zn-Cu-F deposits (Bodnar et al., 2014).

While fluids in the diagenetic (sedimentary) environment show wide variability in composition, some systematic variations with depth, rock type, and other factors have been recognized. Hanor (1994) describes three broad groupings of saline waters in sedimentary basins, including (1) waters with anions other than Cl being dominant, such as Na-HCO$_3$ and Na-acetate waters; (2) Cl-dominated waters with salinities between approximately 10–30 wt.%; and (3) Cl-dominated waters with salinities >30 wt.%. Moreover, total salinity and the Ca/Na ratio of waters increases with depth, as has also been observed in crystalline cratonic environments (Frape & Fritz, 1987). Observed changes in brine compositions are consistent with water-rock buffering as the main control on fluid composition (Hanor, 2001). This assertion is supported by studies such as that of Leach and Rowan (1986) who show that the Na/K ratio of sedimentary brines decreases over a distance of several hundred kilometers from the source region to the location where Mississippi Valley Type mineralization is deposited. They attribute this change to the loss of K to the rocks in the form of clay minerals formed during rock alteration.
In deep-basin settings associated with hydrocarbon gas (methane) production, the moderate to high salinity brines contain significant amounts of dissolved methane. Thus, in the Cretaceous Travis Peak Formation in the East Texas Basin, methane-saturated brines containing ~15 wt.% salts are associated with gas generation and migration and the formation of quartz bridges across fractures (Becker et al., 2010). Conversely, fluids associated with tight-gas sandstone reservoirs in the Piceance Basin, Colorado, are also methane-saturated but have much lower salinities—in the range of ~2-3.5 wt.% (Fall et al., 2015). Leach et al. (1991) reported saline brines that were saturated in CO$_2$, rather than CH$_4$, associated with dolomite cement formation in the Ozark region.

In assessing the role that fluids play in fracture formation and fracture sealing, it is critical to consider the fluid composition. As noted by Brantley et al. (1990), crack-sealing rates are affected by fluid chemistry because mineral solubilities and other factors vary with fluid composition. It is well known, for example, that the solubility of silica (quartz) is higher in H$_2$O-NaCl solutions compared to the solubility in pure H$_2$O at the same temperature and pressure (Fournier, 1983). This, in turn, would allow a fracture to seal in a shorter amount of time in the presence of a saline fluid compared to pure H$_2$O, owing to the higher solubilities and rates of dissolution and precipitation. Conversely, the solubility of silica in H$_2$O-CO$_2$ fluids is lower than in pure H$_2$O, although all of the experimental data are for pressure-temperature conditions well outside of the range of interest in the diagenetic environment (Newton & Manning, 2000). Finally, in immiscible fluid systems, one of the two (or more) immiscible phases will preferentially "wet" the mineral surface, and its composition will control mineral solubilities at the rock-water interface and may affect rates at which fractures seal. Compositional effects on sealing rates need further work.

To summarize, fluids in sedimentary, diagenetic environments typically show moderate to high salinities, with both the salinity and the Ca/Na ratio increasing with depth. Potassium and magnesium concentrations are typically low, owing to their loss from the fluid to form clay minerals during diagenesis. While nonaqueous volatiles are relatively rare in most sedimentary brines, aqueous solutions containing methane are common in hydrocarbon gas-forming environments, and CO$_2$ has been reported from dolomite-cementing brines. Studies that examine the role that fluids play in fracture formation and sealing should consider the broad range in fluid compositions that occur in sedimentary basins owing to the significant effect that fluid composition plays in mineral solubility. Moreover, as described in section 2.2, when and how fast fractures propagate (crack growth rate) may depend on the type of fluid present. In other words, altering the type of fluid present could govern when propagation starts and stops, and the rate of propagation. Rates and rate differences can have a strong effect on what fracture pattern arises (e.g., Olson et al., 2009). Fluid inclusions recovered from former crack tips can provide a record of the fluids present in the crack tip through time.

### 2.2. Chemically Assisted Fracture Growth and Pattern Development

Fractures grow because bonds rupture at the crack tip. Chemical reactions, particularly stress-assisted dissolution, allow these bonds to rupture at lower stresses compared to what would be required by purely mechanical processes (see Figure 12). Models that simulate fracture pattern development in natural systems and experiments (Brantut et al., 2013; Espinoza & Santamarina, 2012; Olson, 1993; Olson, 2004; Renshaw & Pollard, 1994; Segall, 1984), as discussed below, imply that fractures form under so-called subcritical conditions over long timescales. Understanding the scope of chemically assisted propagation is challenging because of these long timescales. In natural subsurface systems, intermittent propagation is often interspersed with sealing (or local, partial sealing) by mineral precipitates (e.g., Laubach, Olson, et al., 2004). Over long time spans uncertainty about the natural history of fluids, loading rates, stress state, and pore pressures associated with fracturing is the rule (e.g., Figure 9). A further consideration is the fact that rock properties are not static over time and property histories are difficult to predict. The existing body of experimental results and theoretical treatments therefore are unlikely to be representative of the full spectrum of processes at play in the Earth.

#### 2.2.1. In the Laboratory and Theory

Fluid-rock interactions influence the brittle and ductile deformation of the Earth’s subsurface through fluid-controlled deformation mechanisms such as pressure/chemical solution creep and subcritical fracture growth (e.g., Bergsaker et al., 2016; Brantut et al., 2013). A major challenge is to understand how, and to what extent, microscopic (grain-scale and subgrain to nanoscale) fracture growth processes are linked to the observed macroscale mechanical behavior of rock (Brantut et al., 2013). Fractures can propagate in a
stable, quasi-static manner at values well below the critical stress intensity factor $K_{IC}$ (i.e., subcritical crack growth) for a wide range of rock types (Atkinson & Meredith, 1987; Brantut et al., 2013; Lawn, 1993) as well as in engineered materials such as glass and ceramics. Although a range of micromechanisms can be responsible for subcritical fracture growth, stress corrosion of preexisting cracks and defects is thought to be the main mechanism for fracture growth in the Earth’s upper crust (Atkinson, 1984; Brantut et al., 2013; Ingraffea, 1987). Subcritical fracture could exert a primary control on erosion rates at the Earth’s surface (Eppes et al., 2019). Stress corrosion is a chemically activated process associated with fluid adsorption on crack surfaces and fluid-assisted crack propagation. Figure 12a illustrates the different types of fracture process on a stress intensity factor/crack velocity diagram. Region 1 (low stress intensity factor/low crack velocity) fracture is controlled by the rate of stress corrosion reactions at crack tips. This is the region in which chemically assisted fracture growth operates.

Region 1 is bounded at higher velocities by a transition to a regime in which crack extension is limited by fluid migration rates; at very low velocities, crack extension must compete with healing processes that occur at the tip. Data to constrain these transitions are limited, especially for subsurface conditions.

Creep and subcritical crack propagation experiments on rocks are difficult to interpret. Heterogeneities associated with pores, grains, detrital clay, and authigenic minerals in sedimentary rocks result in a complex
microstructure that induces large local stress fluctuations at the grain scale. These stress fluctuations become even more complex in natural settings in response to depositional heterogeneities and with the superposition of deformation features such as fractures. Recent advances in imaging may allow the evolution of these patterns in nature to be unraveled, opening up possibilities for new experimental work. Two examples are Morgan et al. (2013) and Tal et al. (2016).

Most experimental data on stress corrosion cracking in rocks have been derived from tensile crack propagation in double-torsion load relaxation experiments under ambient conditions (Atkinson & Meredith, 1987) and from triaxial creep experiments (Brantut et al., 2013). Using the latter approach, it was shown that pore water reduces the brittle strength of sandstones due to decreases in the surface energy (Baud et al., 2000). To remove some of the material complexity, some researchers have opted to perform experiments on glass and compare the results to the behavior of crystalline rocks (Mallet et al., 2015).

To date, most fundamental research on subcritical crack growth has been conducted on silicate and multicomponent glasses. Several reviews and key papers cover the history and development of our understanding of subcritical crack growth in glass (Ciccotti, 2009; Freiman et al., 2009; Pallares et al., 2015; Wiederhorn, Fett, et al., 2011; Wiederhorn, Guin, et al., 2011; Wiederhorn, Fett, Guin, et al., 2013, Wiederhorn, Fett, Rizzi, et al., 2013; Wiederhorn et al., 2015). Milligan (1929) and Preston (1942) recognized that both liquid water and water vapor play a role in controlling the strength of glass. The strength of glass was observed to be greater under dry conditions than in humid environments or in water. Several expressions have been developed to predict crack velocity within the stress corrosion region (Region 1, Figure 12a) including the following expression developed by Wiederhorn (1967):

$$v' = v_0 \exp(aK) = A \left( \frac{p_{H2O}}{p_0} \right)^m \exp \left( -\frac{\Delta E_a - bK}{RT} \right) \tag{1}$$

where $p_{H2O}$ is the partial pressure of the vapor phase in the atmosphere; $p_0$ is the total atmospheric pressure; $R$ is the gas constant; $K$ is stress intensity factor; and $A$, $m$, $\Delta E_a$, and $b$ are four adjustable parameters that describe the dependence on glass composition. $\Delta E_a$ can be interpreted as an activation enthalpy in the absence of stress, and $b$ can be expressed in terms of an activation volume by relating the stress intensity factor to the crack tip stress.

The Wiederhorn equation (equation (1)) is the most commonly used description of Region 1 fractures for glasses because it provides a more direct interpretation of the chemical reactions between a glass of a given composition and the environment at the crack tip. For crack propagation in a liquid environment, the term $p_{H2O}/p_0$ is substituted by the activity of water, which is strongly dependent on the liquid composition and affected by pH and ionic concentration. In sedimentary basin environments, aqueous fluid salinities can approach several hundred thousand parts per million total dissolved solids, significantly lowering the activity of $H_2O$ in the fluid (Yardley & Bodnar, 2014). In situations of multiphase flow, capillary condensation of water films at crack tips can alter the local chemistry of the crack tip environment in glass, promoting accelerated growth rates (Ciccotti, 2009; Ciccotti et al., 2008). In the Earth’s subsurface, such a mechanism may be important for considerations of carbon storage (Heath et al., 2014), as condensed water films from supercritical carbon dioxide may partition highly reactive acid gases and have a lower pH than bulk pore solutions.

A geochemical model for subcritical tensile fracture kinetics suggests that the direct correlation between the quartz fracture rate and solution pH is related to solvent-surface interactions to increase the frequency of bond rupture at the crack tip (Dove, 1995). This mechanism-based approach is consistent with fracture models based upon surface free energy and invites further study by suggesting that rates may also be dependent upon solution composition. Some preliminary work has been conducted on the effects of rock composition, fluid type, and salinity on fracture rates (Bergsaker et al., 2016; Nara et al., 2014; Rijken et al., 2002; Rostom et al., 2013).

Nanoscale subcritical cracks in glass have been studied analytically (Wiederhorn, Guin, et al., 2011) using transmission electron microscopy, atomic force microscopy, nuclear reaction analysis, and nuclear reflection. These approaches provide insights into the molecular fundamentals of the fracture process and lead to a deeper understanding of the mechanisms of fatigue and subcritical growth. For instance, the shape of the crack tip, and whether it is atomically sharp or has been blunted by plastic deformation or chemical...
corrosion, can be determined at the nanoscale through direct imaging. Nanoscale cracks may occur in homogeneous materials such as glass as well as at grain boundaries and defects in ceramics, microcrystalline materials, and rocks.

Despite observed differences from distinct material properties, some of the same mechanisms may be responsible for creep and subcritical crack growth in both glass and rock. However, many of the parameters that likely influence fracture growth in nature, with durations of millions of years (e.g., Figure 9), have not been identified or quantified in experiments or theory. The mineralogical and textural complexity of rocks is much greater than glass and may vary from one portion of a fracture to another. Moreover, during the geologic timescales over which fracture systems develop, conditions evolve in response to changes in the fluids and stress conditions as well as in the porosity, mineralogy, and texture of rocks. Field observations show that in natural systems dissolution and precipitation, crack tip blunting (e.g., Ito & Tomozawa, 1982) and other chemical processes could have large effects in the confined environment of the crack tip.

These considerations suggest the potential importance of surface chemistry as a determinant of fracture processes in nature and a need for experiments and theory that explore subcritical crack propagation in complex and evolving materials at long timescales, under confinement, and with realistic fluids. Experiments may require novel proxy materials and time-temperature trade-offs and scaling rules. On the other hand, and in contrast to surface chemistry controlling crack growth processes, there are also certain regimes especially in glass and some single crystals, where transport of dissolved aqueous species away from the crack tip controls the crack growth rate (e.g., Petrishcheva et al., 2019). Rather than surface transport, species transport (e.g., chemical diffusion) in fluid becomes the controlling mechanism.

2.2.2. Propagation and Pattern Modeling

Although evidence for fracture patterns is commonly derived from wellbore or outcrop observations, another approach to predicting interwell fracture geometry is using mechanics-based models of varying complexity and constrained by stress state, preexisting large-scale structures, and rock properties (Camac & Hunt, 2009; Smart et al., 2009). Currently, chemical effects are only incorporated in limited ways, although even these limited chemical effects have a strong influence on the resulting patterns (e.g., Figures 5, 13, and 14). In principle, however, geomechanical approaches can account for many different aspects of the influence of chemistry on fracture propagation. Chemical effects on fracture propagation can be included in the calculations, but the models could be improved by obtaining more exact and nuanced insights from theory and experiments on subcritical crack growth.

Segall (1984) established a framework for predicting the development of fracture populations growing subcritically, and Olson (1993) and Renshaw and Pollard (1994) incorporated those ideas into mechanics-based numerical fracture modeling to further explore the implications of subcritical crack growth on fracture pattern development. An alternate, empirical form of equation (1) can describe fracture propagation velocity, $v$, as a function of the ratio of the stress intensity factor, $K_i$, to toughness, $K_{IC}$ (Atkinson, 1984; Swanson, 1984),

$$v = A \left( \frac{K_i}{K_{IC}} \right)^n$$  \hspace{1cm} (2)

where $A$ is an empirical constant and $n$ is the subcritical index. Although equation (1) is probably more soundly based in theory, it is hard to reject one or the other based on experimental data, largely because the velocities are large. So both are commonly used.

Olson and Pollard (1991) demonstrated that parallel cracks in a uniformly loaded body will have varying stress intensity factors because of crack interaction (stress shielding) effects. Crack-to-crack variation in $K_i$ generates a unique velocity distribution for simultaneously propagating cracks that controls fracture pattern geometry dependent on the subcritical index (Olson, 1993). Attributes such as fracture length distribution and the degree of clustering of the spacing between parallel cracks all showed a strong dependence on the subcritical index. Renshaw and Pollard (1994) extended this work to show the influence of initial flaw density and loading duration on final fracture set geometry, while Olson (2004) established the importance of sedimentary layer thickness for bed-bounded fractures in determining equilibrium fracture spacing, a consequence of the three-dimensional nature of mechanical fracture interaction. In addition, Olson (2007) explored the impact of strain magnitude and strain rate on fracture pattern development, suggesting
subcritical growth of fractures could span tens of millions of years. That patterns could form over such long periods of time contradicts commonly held impressions among many workers studying natural patterns that fracture patterns form rapidly. Although individual fractures or growth increments may happen rapidly, as discussed above, analysis of cements and fluid inclusion data provides independent evidence that indicates exceedingly long durations of fracture pattern development for some patterns.
Figure 14. Results of numerical experiment of simultaneous extension fracturing and cementation (modified from Hooker & Katz, 2015). Orange stripes mark locations of automatically detected fractures. \( f \) is a factor representing cement accumulation rate. \( K_c \) is spring constant (stiffness) of cemented springs, relative to host rock spring constant \( (K_r = 1) \). With increased cementation rate, fractures become narrower and more closely spaced. Red arrows mark apparent clustering. Decreasing \( K_c \) results in more refracturing of extant fractures. “Joint-like” little or no mechanical effect of cement; “vein-like” extensive mechanical effect of cement.
Complex geometries can result from long-term loading conditions. But it is useful to make a distinction between many discrete events occurring over a long time and that of steady-state crack tip velocity. Mechanistically, the distinction is important because the former view allows for poroelastic effects to be included. Thus, transient variations in the pore fluid pressure could easily occur during jerky motion of the crack tip.

2.3. Evidence for Mechanical-Chemical Feedback

There are several important ways in which fracturing affects dissolution and precipitation within fracture systems. Evidence also suggests that cementation within both fractures and host rocks impacts how fracture systems evolve.

2.3.1. Diagenesis and Mechanical Property Evolution

Within the moderate temperature regime of diagenesis, the fracturing process may influence crystal growth in at least three ways: (1) by creating new pore space that growing crystals can invade; (2) by increasing permeability and fracture connectivity, which can affect crystal growth (and dissolution) rates by increasing fluid flux, fluid mixing, and heat advection; and (3) by breaking crystals in such a way that the newly exposed surfaces do not correspond to euhedral (faceted) faces.

Regarding the third effect, for minerals that preferentially deposit (nucleate and template) on the same phase in the fracture wall (syntaxial overgrowths) such as quartz and some carbonate minerals, a range of factors governs whether or not cements span the gap between opening fracture walls (Lander & Laubach, 2015). Among these are the slower precipitation rates on euhedral crystal faces compared with fresh fracture surfaces, which are crystallographically rough, a phenomenon that can be inferred from cement distribution in fractures (Laubach, 1988; Urai et al., 1991) and replicated in the laboratory (Lander et al., 2008; Williams et al., 2017). In the case of quartz, for example, experimental data indicate that growth rates increase by around a factor of 20 along the same crystallographic orientation on fractured surfaces compared to euhedral faces (Lander et al., 2008; Lander & Laubach, 2015; Williams et al., 2017). Similar observations have been reported from studies in which fractures in quartz are healed in the laboratory to produce synthetic fluid inclusions (Bodnar & Sterner, 1987; Sterner & Bodnar, 1984). In addition to crystallographic orientation, local surface curvatures are also critical in determining the healing rates (Beeler & Hickman, 2004, 2015; Hickman & Evans, 1987; Renard et al., 2000; Smith & Evans, 1984).

Diagenetic alteration of host rocks also affects fracture development given that host rock physical properties are a fundamental control on the mode and extent of deformation for a given set of environmental conditions. Geomechanical models that predict fracture systems require properties such as Young's modulus, subcritical crack index, and permeability as input (Olson, 2004; Olson et al., 2009). Constraining such properties, however, is difficult given that the relevant rock properties are those from the time when the deformation occurred. Given that many natural fractures in the subsurface formed in the geologic past, the extent of diagenetic alteration at the time of deformation most likely differs from that observed in the present day. In such cases there is no way to directly measure the rock properties at the time of deformation. Values must be inferred. Additionally, the fluid flow and geomechanical properties of the host rocks during the time that fractures are active may differ from those properties during the times when the fractures are not active.

To illustrate the problem, consider the potential evolution of host rock properties for an example involving fractured Cretaceous sandstones at the MWX site in the Piceance Basin where Fall et al. (2012) determined that fractures formed over a period ranging from ~40 to 7 Ma. This analysis used the Touchstone sandstone diagenesis model (e.g., Lander et al., 2008), which incorporates the permeability model of Panda and Lake (1994, 1995) and the rock physics modeling approach of Drège et al. (2006).

The simulated evolution in Young's modulus, permeability, and quartz cement abundance are shown in Figure 15 together with the “Model 1” temperature history of Fall et al. (2012). The results show that the onset of fracture opening at ~40 Ma corresponds to the initiation of rapid quartz cementation. Quartz and later-stage carbonate cement growth cause substantial changes in the predicted fluid flow and elastic properties for the unfractured portion of the host rock. In particular, for the host rock Young's modulus increases by nearly 50% during active fracturing whereas permeability drops by more than an order of magnitude. Even if the absolute values for these rock property predictions are offset from the actual values, these results suggest
the geomechanical properties of the host rock likely underwent significant changes during the period when fractures were actively forming.

Host rock and fracture diagenesis are inextricably intertwined in the development and evolution of fracture systems. To accurately predict fracture and host rock properties through time or space, process-oriented approaches must incorporate cementation models. Such models need to do more than merely predict cement volumes given that fracture geomechanical and fluid flow properties depend on the spatial distribution of fracture cements.

2.3.2. Fracture Size and Spatial Arrangement Patterns

The common occurrence of crack seal texture in fracture cements indicates that cements grow at average rates that are equal to, or faster than, fracture opening rates. Conversely, fracture size distribution also appears to be related to cement characteristics (e.g., Clark et al., 1995; Hooker et al., 2012, 2013; Laubach et al., 2010).

Cements that span fractures are likely to influence fracture evolution by reducing the size of stress disturbances associated with fracture voids and necessitating refracturing for continued fracture opening. Cements that line but do not span fractures may also affect fracture evolution by changing fracture compliances or by altering paths for fluid flow (Laubach, Reed, et al., 2004; Laubach et al., 2010).

Natural fracture systems show correlations between the extent to which cements span across fractures during fracture development and fracture attributes such as length and height dimensions, aperture size distributions, degree of bed boundness, and spatial arrangements. To date, however, no systematic experimental studies have explored the mechanical effects of cements on fracture growth, although some experimental work (Lee et al., 2015) has been conducted on the bonding strength of cement in fractures.

The concept of spanning potential (Lander & Laubach, 2015) is a useful way to quantify the extent of cementation during fracture growth. The ratio of the net fracture opening rate to crystal growth rate is a fundamental control on whether cement spans between fracture walls during intermittent fracture growth. In addition to temperature, the amount that a crystal can grow is a function of the orientation of preferred crystal growth directions, the diameter of the growth substrate, and fluid chemistry. The spanning potential for the euhedral crystal faces is greatly outstripped by that of the noneuhedral surfaces. The spanning potential can be used as a guide for distinguishing natural examples having more or less interaction between cement accumulation and fracture growth. Crack seal texture marks competition between cement precipitation and opening rates during opening-mode fracture growth.

Field studies (Hooker et al., 2012, 2013; Hooker et al., 2018; Laubach et al., 2014; Li et al., 2018) and some model results (Hooker & Katz, 2015; Virgo et al., 2014) show correlations between the amount or strength of cement accumulated during fracturing and fracture size distribution, spatial arrangement, and connectivity. Correlation between the degree of spanning and fracture aperture size distribution also has been found in carbonate rocks (Hooker et al., 2011).

Hooker et al. (2013) described two fracture sets in the same rock, where mechanical properties were identical but spanning potential differed. In that example, aperture size and height, and spatial arrangement varied with spanning potential. One fracture set with crack seal cement texture, which indicates repeated, episodic fracture growth, had a wide range of kinematic aperture sizes. However, the other fracture set with minor quartz spanning and extensive open pore space had a narrow range in kinematic aperture size (Hooker et al., 2013). The driving forces associated with the fracture sets and the temperature conditions during fracturing differ.

Studies have also investigated contrasts in spanning potential in cases where temperatures during fracture were identical. Sandstones may differ in spanning potential owing to their composition because quartz, feldspar, and clay mineral substrates accumulate cement deposits at different rates (e.g., Lander & Laubach, (2012). Simulated evolution in Young's modulus, characteristics derived from the Williams Fork sandstone data set of Ozkan et al. (2011). Model simulation, R. H. Lander using compositional and textural characteristics derived from the Williams Fork sandstone data set of Ozkan et al. (2011).
2015). By examining damage-zone aperture, length, and spacing variation in adjacent sandstones crossed by the same faults, Laubach et al. (2014) correlated spanning potential with marked differences in the number of fractures, aperture and length distribution, spatial arrangement, and preserved fracture porosity.

Can the mechanical strength of cement influence fracture size and spacing patterns? Some conceptual models suggest how fracture growth and cement accumulation could interact. Caputo and Hancock (1998) inferred a crack-jump mechanism—a variant of crack-seal—whereby some sealed fracture increments are partitioned into the host rock. The tendency to partition depends on the degree of sealing. Compatible with this mechanism is the observation that in many rocks, discontinuities within crack seal texture and microfracture opening displacements in host rocks are comparable in size. New microfractures subsequently form after partitioning takes place. Hooker et al. (2014) further argued for such a mechanism based on scanning electron microscope-CL images. They indicated that quartz-cemented fractures grew as single, discrete structures throughout most of their traces that occur within diffuse zones of closely spaced cracks where the fractures cut quartz grains. It was interpreted that locally faster cementation— itself a result of quartz templating upon broken quartz surfaces—created spanning cement deposits over quartz grains. Further widening of the fracture required local refracturing of those deposits. Fractures that were not sealed could widen without further rupturing. Of the initial set of fractures, those that were fully sealed were not reactivated. But for partly sealed fractures, some reactivated and others did not. The degree and pattern of reactivation depended on the pattern and amount of sealing.

Where cements span across growing fractures, additional fracture opening may require that they reocrack. Energy used to generate this added fracture surface area would presumably come at a cost to fracture propagation and could thereby influence fracture patterns. Numerical modeling of such a process was presented in Hooker and Katz (2015) where they assumed a purely brittle-elastic response of the host rock and cement to lateral extension. The stress distributions around growing fractures showed markedly increased tension lateral to sealed fractures (Figure 13), reflecting the stress buildup that repeatedly cracks spanning cements during crack seal. The results indicate that, for constant layer-extension rates, increasing cement precipitation rates produced narrower and more closely spaced fractures at equivalent strains than would be the case in the absence of cement (Figure 14).

Modeling that explores the impact of natural propping of fractures illustrates the potential importance of diagenetic feedback for the determination of final fracture attributes such as the aperture distribution (Figure 14), a key component for determining fracture fluid flow properties. Merely changing the degree of propping (a chemical effect) has an impact on subsequent stress states and thus how the fracture pattern evolves. These models do not account for rates and amounts of long-term creep, which would further vary the manner in which patterns evolve.

In addition to altering the mechanical process of fracture porosity creation, simultaneous diagenesis during and after fracturing modifies the storage and flow capability of the fracture network (Laubach, 2003; Philip et al., 2005) as well as how these properties vary with thermal exposure (Laubach & Diaz-Tushman, 2009). Some of these latter effects can be incorporated into geomechanical models through simple means such as invoking rules that seal parts of fractures according to the principles of diagenesis. Olson et al. (2009) show how fracture cements that only slightly alter fracture porosity can reduce fracture permeability by orders of magnitude because of the loss of fracture connectivity that results from plugging the smallest aperture connections between otherwise open fractures.

These numerically generated fracture patterns also illustrate that extensive opening-mode fracture patterns can be generated with small incremental strains, on the order of $10^{-4}$, which would probably be undetectable if not for the fracture patterns they left behind. The model prediction of substantial fracture growth at small strain is consistent with field-measured fracture strains on the order of $10^{-4}$ for closely spaced, mineralized joints in granite (Segall & Pollard, 1983) and with small fracture strain values measured from tight-gas sandstones (Hooker et al., 2009).

3. Questions for Future Research

Looking ahead, new observational, experimental, and modeling approaches present many opportunities to take our current understanding of fracture formation and fracture patterns to the next level. One focus will
surely be to explore fracture patterns as chemical transformations that occur in a mechanical context. Accurate and testable predictions of opening-mode fracture patterns in rock will be essential to effectively manage subsurface engineering operations and to understand many societal important processes in the Earth (National Research Council, 1996). Such predictions cannot reliably be extrapolated from surface/subsurface observations or obtained from kinematics and mechanics-based approaches alone.

Accounting for the complexity and duration of the fracture pattern formation process requires new experimental approaches and theoretical treatments. Important topics for future research include aspects of sub-critical crack propagation, crystal growth rates, cement strengthening effects, and coupled models of fluid flow, fracture, rock modification processes, temperatures, and stress conditions over geologic timescales and how these geochemical alterations affect the geophysical location of fractures and monitoring of fracture evolution during engineering operations. More work is also needed to characterize fracture systems in order to provide a deeper understanding of driving forces and rates as well as benchmarks for evaluating the performance of fracture models.

Below we discuss research topics that we believe hold promise for improving our understanding of natural fracture systems.

### 3.1. Characterization and Reconstruction of Natural Fracture Systems

Currently, the measurable fracture system attributes in the subsurface include apertures, cement volumes and cement spatial distributions within individual fractures, spatial arrangement (for suitably oriented wells), and statistical measures of intensity. Fracture length and height distributions, connectivity, and spatial arrangement can be added to this list for outcrops. Additionally, analysis of fracture cements and associated fluid inclusions provides essential constraints on the timing, conditions, and rates of fracture formation as discussed previously. These studies of natural fracture systems should include large-scale (regional) characterization of the tectonic and stress environment, combined with collection of oriented samples that allow fluid inclusion and cementation properties to be related to the large-scale tectonic and structural setting. Advanced imaging of the host rock (e.g., Anovitz et al., 2015; Anovitz & Cole, 2015) suggest useful future directions for analysis of the host-fracture system.

As discussed in section 2, several reconstructions have been made of individual fractures through time (Becker et al., 2010; Denny et al., 2019; Fall et al., 2015; Lander & Laubach, 2015). Using these methods, entire fracture patterns can in principle be reconstructed. Some progress has been made in reconstructing natural 1-D aperture size patterns (Hooker et al., 2018). Considerable additional work is needed to characterize ensembles of fractures and the behavior across a broader range of driving forces, rock types and properties, and timescales.

An essential question is whether the timescales of tens of millions of years for the development of fracture systems in the few studies that have been performed to date (e.g., Becker et al., 2010; Fall et al., 2015; Laubach et al., 2016) are typical for fractures that form in the subsurface, and if not, what differences in the rates of pattern formation exist and what controls the differences? Long timescales for fracture formation in the upper 10 km of the crust increase the potential significance of cementation or dissolution on changes in host rock and fracture mechanical and fluid flow properties and the potential importance of local diffusive mass transport as opposed to regional mass advection for controlling the properties of fracture systems. Experimental and simulation techniques that have been used on other problems can be brought to bear on this question (e.g., Hu & Hueckel, 2013; Kerisit & Liu, 2009, 2012).

Throughout our review, we emphasize evidence for what, on timescales of millions of years, appears to be steady-state extension of some fractures. But much remains to be learned about the actual rates and patterns of fracture movement and quiescence. Some reconstructions include long pauses (e.g., Laubach et al., 2016), and neither theory nor experiment precludes complex histories. The difference is that chemical evidence may reveal the natural variability of real rates. In any case, a steady-state rate characterization is not precise. Crack seal structures indicate episodic extension events. These events may occur over long time durations with more-or-less regular intervals, but there is a substantial difference between the strictly constant velocity of an extending crack front, and the average velocity, which might be constant over a long period of time. Jerky, episodic motion is common in fracture experiments and, of course, is the rule during slip events along faults.
Mechanics-based modeling together with outcrop and subsurface observations yield fine-scale information about patterns that needs to be extrapolated to realizations of thousands of fractures for many engineering needs such as flow simulation and control of hydraulic fracture growth. Improved mechanistic models allow the input for such large-scale discrete fracture models to be improved. Moreover, with firm evidence of how patterns developed in simulated or sampled locations, models can be adjusted for other areas of the subsurface.

For example, systematic adjustment is possible for key parameters such as rock properties, strain rates, type of fluid present in crack tips, degree of cement or dissolution accompanying the pattern formation, and extent of postfracture chemical overprint. Indeed, outcrop fracture patterns deemed good analogs for particular subsurface localities could be used as input for modeling and patterns adjusted to reflect other parts of the subsurface. Because such chemistry-cognizant models make specific predictions about materials in fractures and host rocks, information that can be used to validate model predictions will be more readily sampled, helping overcome one of the principle impediments to model improvement.

A breakthrough for fracture characterization would be a subsurface imaging method that could map three-dimensional fracture patterns at a resolution that is high enough to resolve fractures across the region of interest. Such a method would be enormously useful for constraining fluid transport and geomechanical characteristics over engineering timescales. Even if such a method could be developed, however, it likely would have at least two significant shortcomings with respect to understanding fracturing processes: (1) it probably would rely on the spatial distribution of fracture porosity and could not be used to detect the volumes and distributions of cements in the fractures, making it impossible to measure overall fracture patterns and kinematic strains; and (2) it would not directly constrain the timing, duration, or rates of fracture development.

Because of the sampling challenge, a key impediment to improving imaging methods is validation. Even sparse samples analyzed from a chemical/diagenetic perspective could provide a way to validate new imaging methods. Thus, fracture cement characterization and fluid inclusion studies would remain as essential areas of research in helping to attain high-resolution and large-scale three-dimensional fracture mapping methods.

While the focus of this review is on fracture pattern formation, fundamental questions exist on the role of fracture array patterns, mineral bridges, and mineral rinds on elastic wave propagation and scattering in systems. Fracture-specific stiffness is commonly used in theoretical and numerical studies of wave propagation in fractured media to determine the effect of fractures and fracture sets on seismic wave attenuation and velocity (Bakulin et al., 2000; Choi et al., 2014; De Basabe et al., 2011; Nakagawa & Schoenberg, 2007; Pyrak-Nolte et al., 1990a, 1990b; Schoenberg & Douma, 1988; Shao et al., 2015; Shao & Pyrak-Nolte, 2016). Fracture stiffness as currently conceptualized captures the complex topology of a surface in contact with voids of variable shape and aperture and is fundamentally related to fluid flow and seismic wave attenuation and velocity for fractured media (Petrovitch et al., 2013; Pyrak-Nolte, 2019; Pyrak-Nolte & Nolte, 2016). Future work needs to include time-dependent stiffening (or softening) of host rocks on fracture compliance (e.g., Olson et al., 2007).

Key fundamental research questions that need to be addressed include the following: Do mineral bridges enhance cross-coupling fracture stiffnesses (Nakagawa et al., 2000) in fractures yielding converted modes not observed for fractures without bridges? Do chemically altered fractures have different signatures than mechanically altered fractures (impedance contrast from void-filling or reaction halos or mineralized contacts)? Are there gradients in mineralization along a fracture or among fracture sets that result in a spatially varying fracture properties and seismic wave focusing (Oliger et al., 2003)? How are flow and fracture stiffness related when geochemical-geomechanical coupling affects the connectivity of pores and contact area between two surfaces? How do evolving host rock properties affect fracture properties? Given the field observations discussed in this review, these questions need to be addressed to accurately account for energy partitioning in fracture systems.

### 3.2. Controls on Subcritical Crack Growth

The controls on subcritical crack growth in complex geologic media under moderate to deep subsurface conditions over geologic timespans remain poorly understood. To this point, the focus has been on chemically
assisted crack propagation rather than on pattern-forming aspects of the problem. Some experimental work on subcritical crack growth in natural minerals and rocks has been done (e.g., Baud et al., 2000; Chen et al., 2017, 2019; Holder et al., 2001; Nara et al., 2012, 2017; Parks, 1984; Rijken et al., 2002), but rigorous theoretical frameworks suitable for application to geologic conditions and timescales remain elusive apart from the chemical-mechanical equations used to describe stress corrosion in quartz developed by Dove (1995).

Our understanding of fracture mechanisms can be significantly advanced by applying new experimental tools to geological materials. For example, atomic force microscopy (Ciccotti et al., 2008; Grimaldi et al., 2008; Wondraczek et al., 2006), nuclear reaction analysis, and neutron reflection (Wiederhorn, Fett, Guin, et al., 2013) have led to breakthroughs in the understanding of fracture mechanisms in engineered materials.

In addition to a program of laboratory experiments, theoretical studies are needed to explore the processes that recent fracture studies reveal at relevant time and length scales. At atomistic scales, molecular dynamic modeling of reactive force fields can handle covalent bond making/breaking in a way that allows for simulations of large atomic-scale systems needed to capture fracture growth, something that is beyond the current reach of electronic structure methods. Modeling using molecular dynamics reactive force fields like ReaxFF (van Duin et al., 2001; Fogarty et al., 2010; Pitman & Van Duin, 2012; Yeon & Van Duin, 2015) provide an opportunity to study subcritical fracturing at the atomistic scale and represent an important potential approach for understanding fracturing in geologic materials. Zhang et al. (2014) examined the stress corrosion process of strained α-quartz in liquid water and showed that crack growth is primarily induced by the hydrolysis of strained Si-O bonds.

Recently, Rimsza et al. (2018a) investigated crack propagation in an atomistic amorphous silica model using ReaxFF by introducing a slit crack and tensile stress applied through far-field loading (Figure 12b). Atomic displacements and forces and an upscaling method were used to calculate the J-integral of fracture mechanics around the crack tip. The calculated fracture toughness (K/Ic) agrees with experimental values. In addition, stress fields and dissipation energies around the slit crack indicate the development of an inelastic region ~30 Å in diameter (Figure 12c). Simulation results indicate that the addition of water to a fracture in silica reduces silica fracture toughness by ~25%, consistent with experimentally reported results (Rimsza et al., 2018b).

This method can readily be extended to investigate the impact of solution composition on crack tip propagation and to investigate fracture in mineral phases. Such techniques applied to minerals involved in fracturing in sedimentary rocks undoubtedly would lead to important insights into the controls on subcritical cracking in nature, particularly if the experimental results were compared with high-resolution analyses of fracture tips in rocks. New opportunities exist to make in situ observations of local microfracturing processes using a variety of electron and optical imaging. Two recent examples of the latter are studies by Tal et al. (2016) and Morgan et al. (2013).

### 3.3. Cementation and Dissolution in Fractures and Host Rocks

As discussed above, several lines of evidence indicate that cementation and dissolution within both fractures and host rocks impact fracture patterns and properties. Therefore, any comprehensive approach toward prediction of fracture properties necessarily must incorporate geochemical water-rock models. Important work has been done on certain aspects of this problem, such as the development of reactive transport models (RTMs) that consider chemical reactions and mass transfer (e.g., Xiao et al., 2018) and geometrical models of crystal growth in rocks and fractures (e.g., Ankit et al., 2013, 2015; Lander & Laubach, 2015; Zepeda-Ruiz & Gilmer, 2015; Zhang & Adams, 2002). These methods have yet to be combined, however, and have important uncertainties in input parameters and boundary conditions. In addition to making such models fully 3-D, the mechanical properties of the cement and cement interactions with growing fractures need to be taken into account (e.g., Hooker & Katz, 2015) and models need to simulate distribution for mechanically important deposits within evolving fracture patterns through temperature- and opening-rate-sensitive parameters like spanning potential (Lander & Laubach, 2015).

With few exceptions (e.g., Geloni et al., 2018; Jones & Xiao, 2005; Whitaker & Xiao, 2010), RTMs (e.g., Bethke, 2008; Lichtner et al., 1996; Xiao et al., 2018; Zhang et al., 2012) in their current form are not designed to consider the substantial changes that occur over millions of years as diagenesis transforms loose sediments into rock. As such, they generally do not consider the changes over this timespan in (1) stratal...
geometry due to deposition, erosion, faulting, folding, or diapirism; (2) hydrologic driving forces that reflect changes in topography/hydrologic head or a large-scale permeability structure associated with faulting; (3) compaction state and its impact on rock volumes, geometries, permeability, reactive surface area, and geomechanical properties; or (4) far-field stress conditions. The thermodynamics in RTM can account for temperature variation over significant geologic time, but exploration of natural reactions at long timescales is sparse. And basin models in particular incorporate such timescales and chemical reactions. Some of these shortcomings could be addressed by coupling RTMs with basin and petroleum systems models (e.g., Hantschel & Kaurerauf, 2009) and process-oriented diagenesis models (e.g., Geloni et al., 2018; Lander & Walderhaug, 1999).

An additional significant current limitation of RTMs is that they do not explicitly predict the impact that dissolution/precipitation reactions have on the morphology and microstructure of host rocks and fractures. Esch (2019) recently developed a methodology for relating the volumes of dissolved and precipitated phases predicted by RTMs to petrographic modal categories in sandstone host rocks. These results, in turn, may be linked to existing models for predicting sandstone permeability (Panda & Lake, 1994, 1995) and bulk elastic properties (Drege et al., 2006). Similar approaches are needed for other common rock types.

The geometrical arrangement of cements within fracture systems is an essential control on stress distributions near fractures, geomechanical properties of the fractured region, and transmissivity of fracture networks. Consequently, we must go beyond purely geochemical models to explicitly predict the form and spatial distribution of cements within fractures, with the ultimate goal of understanding the mechanical effects that cements have on fracture growth. A number of modeling approaches have been developed to predict cement morphology within fractures (e.g., Ankit et al., 2013, 2015; Becker et al., 2011; Bons, 2001; Bons et al., 2012; Gale et al., 2010; Hilgers et al., 2001; Hubert et al., 2009; Lander et al., 2008; Lander & Laubach, 2015; Nollet et al., 2005; Wendler et al., 2016). These models generally consider anisotropy in crystal growth rates as a function of crystallographic orientation and, in some cases, in response to crystal breakage from fracturing. A promising method is the phase field technique (e.g., Ankit et al., 2013), which has the capability to model crystal growth and fracture sealing in 3-D, compute the mechanical and transport properties of the partly sealed fracture and simulate the propagation of new fractures in the system.

An unresolved issue in cementation and dissolution models is the derivation of kinetic parameters capable of providing an accurate basis for prediction of reactions that occur in geologic conditions where deviations from equilibrium tend to be small—timescales on the order of millions of years—and the reactions occur in “dirty” rocks with diverse mixes of phases and complex micron-scale textures that evolve with time. The traditional method for constraining reaction kinetics involves carefully crafted laboratory experiments. By necessity these experiments tend to be conducted under conditions where rates are fast enough to provide readily measurable extents of reaction over timescales of hours to weeks. Thus, experiments tend to be made at high temperatures and at saturation states that deviate greatly from equilibrium.

Although these experiments provide crucial insights into the reactions of interest, kinetic parameters derived from them, particularly for silicate reactions, are orders of magnitude faster than kinetic constraints derived from field data (e.g., Adukiewicz & Lander, 2010; Blum & Stillings, 1995; Brosse et al., 2000; Lander & Bonnell, 2010; White & Brantley, 2003). Consequently, important topics of research are (1) derivation of a theoretical framework capable of rectifying kinetic parameters for the same reactions based on experimental data and geologic constraints and (2) determination of kinetic parameters that are appropriate for geological conditions and materials for the large number of reactive minerals found in sedimentary rocks.

3.4. Coupled Modeling Systems

It is highly unlikely that a direct subsurface imaging technique will soon be developed that is capable of accurately discerning three-dimensional fracture patterns over large regions at high resolution. Our assessment is that the most viable approach for predicting the characteristics and patterns of natural fractures in the subsurface is to develop systems that couple models of mechanical, chemical, and mass transport processes over the timescales and conditions where fractures form. Existing modeling approaches address certain aspects of fracture formation but omit or oversimplify important aspects of the fracture formation process and fail to consider the important changes in rock geomechanical and fluid transport properties that can occur over the timescales where fracture systems form.
Work is needed to improve existing models, develop new models that address unresolved problems, and integrate models into simulation systems that account for important feedbacks and interactions. Additionally, methodologies need to be developed for quantifying the performance of fracture modeling systems on benchmark natural data sets. Such methodologies will make it possible to use machine learning techniques to more precisely constrain input parameters and boundary conditions for modeling systems.

In the sections that follow we consider the state of various fracture model components and work that could be done to extend them.

### 3.4.1. Mechanical Effects of Cement

Modeling fracture growth in rocks with preexisting fractures is challenging. Fractures impose mechanical heterogeneities in the rock. While the micromechanics of failure in such complex systems can be modeled using linear elastic failure mechanics in high-strength materials (e.g., He & Hutchinson, 1989; Martínez & Gupta, 1994; Banks-Sills, 2001), or discrete element methods (Virgo et al., 2014), continuum-based methods do not yield satisfactory results for rocks in which nucleation of new fractures, fracture tip damage mechanics, and dynamic effects have a large effect on the crack geometry (Patricio & Mattheij, 2010). Approaches to account for these effects in continuum numerical methods could include a combination of energy-based and strength-based fracture criteria (Leguillon & Martin, 2013; Paluszny & Zimmerman, 2011; Parmigiani & Thouless, 2006) and statistical introduction of micromechanical heterogeneities (e.g., Tang et al., 1998).

Although some research on the strength of the fracture wall/cement interface has been done (e.g., Lee et al., 2015), further effort is needed to understand mechanical strengths of cement and how they evolve. An unexplored component of fracture pattern modeling is the inclusion of the effects of simultaneous mechanical evolution of host rocks and fractures on fracture opening and propagation. In addition to cement in the host rock, Olson et al. (2007) compared modeled fracture opening rates to estimated simultaneous mechanical evolution of host rocks and fractures on fracture opening and propagation. In cementation and bridging within the fractures themselves. A campaign of experimental rock mechanics testing under reactive conditions is needed. Some work in this direction is already being undertaken (e.g., Brantut et al., 2012, 2013; Bernabé & Evans et al., 2014; Evans, 2005; Kubicki & White, 2008; Rinehart et al., 2016; Wang et al., 2016). Possibly, the use of artificial or engineered rock/fracture systems with artificial cement could circumvent challenges of replicating high-temperature/pressure conditions.

In the past two decades, digital rock physics has allowed computation of mechanical and transport properties of rocks using grain and pore geometry (review by Andrä et al., 2013). Recently developed “digital sedimentary petrology models” extend this modeling approach to rigorously simulating diagenetic processes in host rocks at the micron scale in 3-D, including mechanical compaction, contact dissolution (“pressure solution”), and cementation (Lander & Bonnell, 2018; Prajapati et al., 2018). These modeling approaches could be adapted to simulate concurrent fracturing and cementation while also providing constraints for fluid flow and mechanical properties for larger-scale geomechanical models.

### 3.4.2. Fault Healing Rates and Other Reactions

At temperatures higher than those commonly encountered in the diagenetic environment (≥~200 °C), the role of chemistry in fracture evolution is likely to be more significant, compared to lower-temperature environments. At higher temperatures, solubilities of most common minerals are increased, and dissolution and precipitation reactions to seal or heal fractures proceed more rapidly. For example, Brantley et al. (1990) showed through experiments and modeling that 1- to 10-μm cracks in quartz heal in a few months at 300 °C, and in a few days at T > 400 °C. Thus, cements may fill open fractures essentially instantaneously in higher-temperature environments, with the concomitant effects described above for cements in the diagenetic environment.

Even under diagenetic temperature conditions, cement accumulation can be fast and complete, depending on open gap sizes and opening recurrence intervals (i.e., depending on spanning potential; Lander &
Laubach, 2015). Under these conditions, the kinetics associated with cementation of fractures is fast enough to play a fundamental role in the earthquake cycle through the effect of fracture healing on the critical stiffness of fault zones (Rice & Ruina, 1983) over the interseismic period (Fisher et al., 2019; Gratier, 2011; Renard et al., 2000). Downdip and rock-type variations in the cementation (i.e., healing rate) of fault zones could be one of the controls on the updip limit of the seismogenic zone (Moore & Saffer, 2001) as well as of the lateral strength and strengthening rates along faults (Laubach et al., 2014).

As a possible source of fracture opening in the context of CO₂ sequestration (e.g., Taron & Elsworth, 2009), for natural fracture growth, however, conceptual models of crystal growth typically assume crystals do not exert a force on the rock. Taber (1916), Wiltschko and Morse (2001), and Hilgers and Urai (2005), however, proposed that the widening of a fully cement-filled fracture in weak rocks such as shale could be due to the force of crystallization. On geometric grounds the likelihood of this process in only partly cement-filled fractures has been doubted (Laubach, Olson, et al., 2004). The load exerted by growing crystals is poorly understood but, if sufficiently large, could significantly contribute to fracture development where strong fracture-occluding cements form in weak rocks where fracturing takes place along the cement-fracture wall interface.

Although volume changes associated with reactions are likely to be unimportant in many natural fracture systems in which the most volumetrically significant fracture cements are quartz and carbonate minerals, host rock volume changes may be important in some fine-grained, porous carbonate rocks and shales. Numerical modeling (Okamoto & Shimizu, 2015) and mineralogical observations (Hooker et al., 2017) suggest that fractures resulting from volume-decreasing reactions can increase permeability and facilitate continuation of reactions causing fracture, via increasing reactive surface area in contact with fluids. In other words, fracture strain makes physical space for fluid access and reactant minerals. Other fluid-rock reactions that increase solid volume may fill porosity, reduce permeability, and produce reaction rims to stop reactions (Schwarzenbach, 2016). Alternatively, reaction products may be microporous to nanoporous, providing fluid pathways (Tutolo et al., 2016).

On a larger scale, volume change may also cause differential stress and fracture (MacDonald & Fyfe, 1985; van Noort et al., 2017). The genesis of widespread fault arrays by volume changes driven by diagenetic reactions is well attested (Cartwright et al., 2003; Cartwright & Dewhurst, 1998). Although possibly only prevalent in some materials, volume change processes deserve further scrutiny given that the materials where this process is potentially active are fine-grained, reactive rocks such as shale, which are the focus of significant subsurface engineering operations.

### 3.4.3. Coupled (THMC) Models at Geologic Timescales

Simulation tools that couple thermal, hydraulic, chemical, and mechanical (THMC) processes in geologic media have been developed to study engineering problems in geologic settings (Kim et al., 2012; MacQuarrie & Mayer, 2005; Podgornoy et al., 2011; Rohmer et al., 2016; Rohmer & Seyedi, 2010; Rutqvist, 2011; Rutqvist et al., 2008; Rutqvist & Tsang, 2003, 2012). To date, THMC simulators for site-scale problems invoke the multiple interacting continua fractured rock approximation (Pruess, 1985), which was developed for simulating fluid flow and heat transfer within and between rock matrix and interconnected fracture networks. This multiple interacting continua representation accurately reproduces heat transfer from wall rock into flowing fractures under high thermal and pressure gradients (Pruess, 1983) and offers an opportunity to couple THMC processes in an integrated framework.

Although an intriguing avenue, changes and improvements are needed to use this approach on geologic timescales. Like RTMs, THMC simulators are not currently designed to consider changes in stratal geometry due to geologic processes or changes in hydrologic driving forces that reflect changes in topography/hydrologic head or large-scale permeability structure associated with faulting or fracture pattern evolution. Furthermore, as currently designed, they do not consider how concurrent cementation or dissolution affects fracture propagation and flow properties.

Work by Taron and Elsworth (2009) illustrates the potential of THMC simulation involving fractures for engineering timescale problems. These authors used the dual continua approximation to develop a modular THMC simulator that combines a reactive transport simulator with a system for modeling continuum-scale problems of solid deformation. In this approach, an interpolation module sequentially iterates between the two component simulators by first solving the stress equilibrium equations and...
integrating RTM and THMC simulation with data analytic frameworks that are based on machine learning
resolving stress-dependent matrix and fracture permeability. The new pressure and permeability fields are
then passed into the reactive transport simulator, which solves the transient equations for mass and heat
flow and fluid-rock geochemical reactions, the latter of which is parsed on the basis of time-independent
local equilibrium or time-dependent geochemical kinetics. In this formulation, permeability change due
to dissolution and/or precipitation is approximated by constitutive relationships between permeability
and porosity, for which the latter is updated using the changes in the molar volume of reacting solid
phases. This modular THMC simulator accurately reproduces analytical solutions for the individual pro-
cesses (Taron & Elsworth, 2009) and was implemented in a theoretical study of an enhanced geothermal
system to show that thermal-hydro-mechanical fracture dilation dominates reservoir performance in early
time, whereas chemical precipitation near the wellbore may dramatically affect long-term performance.

Continuum-scale THMC simulation has been approached through sequential coupling between an RTM
(Sonnenthal et al., 2014) and a finite-element poromechanics solver (Kim et al., 2015). By sequentially iter-
ating between flow, geochemistry, and geomechanics, this implementation is conceptually similar to Taron
and Elsworth (2009); however, the sequential coupling initially solves the flow equations in a locally fixed
stress field. This fixed stress algorithm for thermo-hydro-mechanical coupling has been proven uncondition-
ally stable over a wide variety of geological scenarios (Kim et al., 2011a, 2011b), and recent advances in par-
allel solver architecture are presently being implemented to improve run times (Sonnenthal & Smith, 2015).
The numerical accuracy of this approach has been tested against field data. The model reproduces measured
well-head pressure and reservoir properties based on previous model calibrations. Using the Kim et al.
(2015) thermo-hydro-mechanical formulation, the enhanced geothermal system model reproduces the four-
fold increase in injection flow rate with remarkable temporal accuracy, and observed microseismic events
from a field experiment are reproduced as Mohr-Coulomb failure events for relatively modest overpressures
of 0.1 MPa (Sonnenthal et al., 2014).

To date, this numerical simulator has been utilized solely for EGS; however, the test case illustrates that
THMC simulation can capture fundamental links between thermal, hydraulic, chemical, and mechanical
processes in geological fluid systems at engineering timescales. For longer timescales, models will need to
simulate both extensive, long-term material gains and also massive material loss in evolving fracture systems
where dissolution predominates. Examples of the scales involved are the up-to-29-m-tall dissolution cavities
at 6- to 7-km depth existing along some fault zones (e.g., Garland et al., 2012; Zhu et al., 2019). Doing so will
involve solving some basic issues in natural rates of precipitation and dissolution (e.g., Maher et al., 2006;
Nogues et al., 2013).

3.4.4. Chemical-Mechanical Approaches and Machine Learning

Integrating RTM and THMC simulation with data analytic frameworks that are based on machine learning
is one exciting new area of research with the potential to unlock new knowledge about the feedbacks
between chemical and mechanical processes in geological materials. For example, RTM and THMC simula-
tors are computationally expensive and reliable predictions are dependent on complex and spatially distrib-
uted parameter sets for constitutive relations, elastic moduli, rock strength, fault/fracture orientation, and
mineral dissolution/precipitation rates, among other parameters. Moreover, initial and boundary conditions
are often poorly constrained. In the context of engineering problems, these issues are generally manageable
through further site investigation and/or model tests, including uncertainty analysis (Pawar et al., 2013),
response surface analysis (Pollyea, 2016; Wu et al., 2018), or stochastic methods (Lee et al., 2013).

In contrast, model uncertainty in natural systems compounds significantly due to the substantial differ-
ence between engineering timescales ($10^3$ to $10^5$ years) and geologic timescales ($10^3$ to $10^9$ years). Over
geologic time, small errors in parameter selection, initial/boundary conditions, or constitutive relations
may propagate nonlinearly, resulting in highly variable predictions and misleading results. This uncertai-

nergy is exacerbated because the material properties and constitutive relations that govern fracture net-
work attributes may change over geologic time, resulting in substantial epistemic uncertainty for
modeling natural geologic processes. In this context, further study of the coupled chemical-mechanical
system is clearly warranted to unlock new mechanistic understandings of material properties that govern
fracture network initiation and development. Such advances can be achieved by integrating RTM and
THMC simulators with exciting new developments in the application of machine learning and artificial
intelligence to simulation analytics.
Among the advantages of machine learning algorithms is their ability to efficiently analyze numerous data sets simultaneously and potentially identify previously unrecognized relationships and/or correlations within the data, particularly in high-dimensional space (Bergen et al., 2019). This capability offers the geosciences a new paradigm for modeling and simulation because there now exists sufficient computational power to generate ensembles of multiphysics simulations. Thus, rather than selecting the best parameter set or constitutive relationship or initial/boundary condition for a modeling study, we can simulate a range of plausible (or equally probable) inputs or conditions, and machine learning algorithms can help us interpret the results. One recent example of this approach is the development of visual analytic methods for ensemble simulation (Dahshan et al., 2019).

For visual analytic methods, graphical outputs for each simulation within a high-dimensional ensemble are linked with their underlying parameter set. After this linkage, weighted multi-dimensional ensemble reduces the high dimensional ensemble parameter space into two dimensions utilizing Euclidean distance weighting criteria between parameter values. The analyst then interacts with all graphical representations of the ensemble in a 2-D workspace to organize them on the basis of subjective (expert) criteria, for example, similarity, dissimilarity, and reasonableness. The result of this interaction "teaches" the machine that features are most important to the analyst, and inverse weighted multidimensional scaling translates the resulting 2-D arrangement back into high-dimensional space, thus providing the analyst with quantitative rankings of the dominant parameters (and by extension, dominant processes). This “user-in-the-middle” approach offers a compelling strategy for combining expert (human) sense making with the rapid data-processing power of machine learning algorithms. Because fracture network patterns are the result of complex feedbacks between coupled thermal, hydraulic, chemical, and mechanical processes that occur over a wide range of spatial and temporal scales, ensemble simulation methods can be used for testing genetic hypotheses, while machine learning analytics can provide the underlying foundation for interrogating high-dimensional parametric relationships or feedback-controlled processes that may exist beyond the cognitive capability of the geoscientist.

4. Conclusions

A chemical perspective provides insight into the three main impediments to fracture pattern characterization: inadequate samples, ambiguous outcrop patterns, geometric observations, or mechanics-only models that cannot readily be tested. An array of powerful chemical concepts and analytical tools will undoubtedly help improve understanding of fracture patterns in the Earth. An increased emphasis on the role of chemistry in how fracture patterns evolve will lead to insights not otherwise obtainable. Exploration of this realm of natural chemical experiments over geologic timescales could yield great societal benefits including more accurate predictions of subsurface fluid pathways and more reliable subsurface engineering. With new integrative mechanical and chemical models on the horizon, the community is on the cusp of finding solutions to what has been one of the most challenging practical problems in subsurface science. Among the challenges and opportunities identified are the following:

1. Fractures in rocks within sedimentary basins that have reached temperatures in the range of 50 to 200 °C generally have experienced some degree of chemical alteration, with partial or extensive cementation or dissolution being common. Cements may greatly reduce both the local permeability and the large-scale flow connectivity of fracture systems and dissolution may greatly increase them. The chemical effects on network connectivity need to be systematically investigated and included in fluid flow prediction.

2. Uncertainty about natural patterns is a major impediment to understanding how subsurface rocks respond to engineering operations. Currently, it is impossible to create 3-D maps of fracture patterns in the deep subsurface (1–10 km). The geometries and dimensions of samples from fracture systems alone cannot be used to accurately diagnose associated fracture patterns. The results of chemical interactions, such as dissolution features or cement deposits, have the potential to be more diagnostic of distributed patterns. Chemical markers of fracture growth need to be documented and correlated with fracture patterns.

3. Outcrop studies of fracture systems are important but must be calibrated by chemical markers to identify their suitability as analogs for deep subsurface conditions. The fingerprints of chemical processes in
fractures may allow diagnosis of differences between the outcrop and the subsurface locality due to contrasts in factors such as burial history.
4. Some fracture cements typically form concurrently with fracturing; others form later. The properties of cements and their fluid inclusions therefore may be used to constrain the timing, duration, and conditions of fracture development. Data and theoretical arguments suggest that mechanical effects of cements also materially affect how fracture systems evolve, resulting in important modifications to fracture patterns and properties, including size distribution, clustering, and fracture stiffness.
5. The few fracture reconstruction studies conducted to date indicate that some fracture systems are active for tens of millions of years. Over such timescales, stratal geometries, host rock geomechanical and fluid flow properties, temperatures, fluid pressures, and far-field stress conditions are likely to undergo important changes that affect how fractures develop.
6. Fracture growth in sedimentary basins may take place under subcritical conditions in response to chemical weakening at the fracture tip. Important consequences of this chemical influence on fracture propagation are (1) the formation of fractures at much lower stress intensities than would otherwise be required and (2) rates of propagation that are slower by orders of magnitude compared to critical crack growth.
7. Many important aspects of fracture system development remain poorly understood. More work is needed to obtain additional fracture history reconstructions, improve understanding of subcritical crack growth in geologic settings, develop comprehensive models of cementation and precipitation in host rocks and fractures, and create accurate models relating the simulated petrology of diagenetically altered rocks to fluid flow and geomechanical properties.
8. For propagation and pattern modeling, the limited range of chemical effects used partly reflects the scope of experimental and theoretical work on subcritical crack propagation. Advances in understating subcritical crack propagation and increasing the number of different chemical effects in geomechanical models is a path to new, potentially more informative pattern realizations.
9. New experimental and modeling methods are poised to advance our understanding of fracture formation and development. Accurate predictions of fracture system properties are likely to come from simulations that incorporate principles of the important chemical and mechanical controls on fracture development while also accounting for changing conditions over geologic timescales. Considerable effort is needed to build, apply, and validate such systems, including tests of the conceptual foundations.

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