Syn- and postkinematic cement textures in fractured carbonate rocks: Insights from advanced cathodoluminescence imaging

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Abstract

In calcite and dolomite deposits in fractures, transmitted light and optical cathodoluminescence methods detect crack-seal texture in some fractures, but scanning electron microscope-based cathodoluminescence (SEM-CL) combined with secondary-electron images and element maps, reveals crack-seal and cement growth textures where previous SEM-CL imaging methods found massive or featureless deposits. In a range of fractured carbonate rocks, patterns and textures of calcite and dolomite cements precipitated during and after fracture growth resembles complex accumulation patterns found in quartz in sandstone fractures, suggesting that some apparent differences between carbonate mineral and quartz deposits in fractures reflect the limits of previous imaging methods. Advances in delineating textures in widespread carbonate mineral deposits in fractures provides evidence for growth and occlusion fracture porosity.

Keywords

Calcite; Carbonate rocks; Crack-seal texture; Dolomite; Fracture; Porosity; Vein

1. Introduction

Fracture-filling cements in fractured and faulted upper crustal rocks provide information on the elemental and isotopic chemistry of formation fluids, and fluid pressure and temperature (e.g., Jensenius and Burrus, 1990; Evans and Battles, 1999; Lee and Morse, 1999; Budai et al., 2002; Blyth et al., 2004, 2009; Drake et al., 2009; Holland and Urai, 2010; Cobbald et al., 2013; Fall et al., 2015). Cement textures can record evidence of cycles of fracture opening (Hulin, 1929; Ferguson and Ganett, 1932; Durney and Ramsay, 1973; Ramsay, 1980; Cox and Ethridge,

1983; Laubach, 1988; Laubach et al. 2004a,b; Nüchter and Stöckhert, 2007; Bons et al., 2012), so fracture cement deposits potentially record time sequences of fluid properties (Becker et al., 2010; Evans, 2010; Fall et al., 2015). In sedimentary rocks, deciphering sequences of geochemical and mechanical processes during and after fracture opening is essential to understand evolution of fracture patterns, preservation and destruction of fracture porosity during and after deformation, and fracture permeability (e.g., Hood et al., 2003; Laubach, 2003; Olson et al., 2009).

A challenge for unraveling fluid histories from cement deposits in fractures are textures that are poorly resolved by some imaging methods. Cathodoluminescence (CL) reveals subtle differences in trace element composition and crystal structure that can be used to delineate textures that are not readily visible using other imaging methods (e.g., Pagel et al., 2000; Boggs and Krinsley 2006). As an imaging method CL is well suited to reveal brittle structure in both un-metamorphosed and metamorphosed rocks (e.g., Sprunt and Nur 1979; McLimans, 1991; Dawson et al., 1994; Trave et al., 1998; Milliken and Laubach, 2000; Hood et al., 2003; Blyth et al., 2004; Rimsa et al., 2007; Holland and Urai, 2010; Vanderginste et al., 2013; Lavenu et al., 2013; Kotta, 2014).

In quartz-rich deposits, scanning electron microscope-based cathodoluminescence (SEM-CL), which generates high resolution, high magnification images, has been effective for imaging structurally significant quartz cement textures (e.g., Sprunt and Nur, 1979; Knipe and Lloyd, 1994; Laubach, 1997; Parris et al., 2003; Laubach et al., 2004a, b, c; Hanks et al., 2006; Laubach and Ward, 2006; Hooker et al., 2009; Becker et al., 2010; Fall et al., 2012, 2015) including crack-seal textures, crystal growth textures, crosscutting relationships, and microfractures.

51 In contrast, in calcite, dolomite and other carbonate mineral deposits, SEM-CL has
52 generally not revealed the same level of textural detail evident in quartz SEM-CL images. Many
53 calcite and dolomite deposits appear—and may be—massive and featureless. But even where
54 optical evidence shows that crack-seal and other structural significant textures *are* present in
55 calcite deposits, SEM-CL images are rarely sufficiently resolved to unravel fracture histories to
56 the same extent as can now be done for quartz deposits. This apparent imaging limitation
57 impedes structural interpretation of fractures containing calcite and dolomite/ankerite, which are
58 the most common phases in fractured limestones and dolostones as well as being widespread in
59 fractures in sandstones and shales.

60 CL has long been used in carbonate rock diagenesis studies (Marshall, 1988; Richter et
61 al., 2003) including delineation of fractures (e.g., Montanez 1994; Marquez and Mountjoy, 1996;
62 Gale et al., 2004; 2010). The intrinsic blue CL of calcite is transient, but luminescence in longer-
63 wavelength emissions in calcite and dolomite takes a relatively long time to decay (up to 1000+
64 msec) following cessation of excitation by the electron beam. This phenomenon, termed
65 phosphorescence, produces an orange-to-red smearing on the image as the electron beam is
66 rastered over the area of interest (Reed and Milliken, 2003; Lee et al., 2005) because these longer
67 wavelengths are persistent. For this reason, and owing to greater convenience and accessibility,
68 most imaging of carbonate cements in fractures has been done using optical-CL (e.g.,
69 McLimans, 1991; Trave et al., 1998; Hood et al., 2003; Rimsa et al., 2007; Holland and Urai,
70 2010; Vanderginste et al., 2013; Lavenu et al., 2013; Kotta, 2014). The spatial resolution,
71 magnification, and sensitivity--for direct observation--of optical-CL is, however, much lower
72 than that of SEM-CL.

In this paper we document fracture cement textures in mostly fibrous/tabular cement deposits in a suite of fractured carbonate rocks using a state-of-the-art SEM and MonoCL 4 detector system and a combination of SEM-CL, secondary-electron images, and element maps. Samples were selected based on coverage of a range of rock types and sample depths for sedimentary rocks. Fractures also have similar macroscopic patterns of cement deposits to those found in other sedimentary rock fractures (Laubach, 2003; Gale et al., 2014). Sampling is therefore representative rather than comprehensive. We show that with minimal phosphorescence, some apparently massive and featureless fracture calcite deposits contain crack-seal and cement growth textures. A key result is the discovery of calcite cement deposits that have bridge-like shapes and crack-seal texture that resembles textures in quartz in more thoroughly studied sandstone fractures, suggesting that some of the apparent differences between carbonate mineral and quartz deposits in fractures is an artifact of limitations in imaging.

2. Sample suite

Petrographic, SEM-CL and elemental analysis (EDS) are used to document cement textures from ten carbonate rock units (Figure 1, Table 1). Rock types include wackestone, packstone, silty limestone, dolomitic mudstone, dolomitic packstone, dolostone, and calcareous shale. Samples are from core and outcrop. The opening-mode fractures are oriented at a high angle to bedding, in beds having dips that range from nearly horizontal to as much as 30 degrees. Possible loading paths that created these fractures include lowered effective stress caused by some combination of burial loading, regional stretching, thermoelastic contraction, and elevated fluid pressure including gas and/or liquid generation and migration.

3. Advanced CL imaging methods

3.1 Sample preparation

CL image quality varies with sample coating and polish. Several sample preparation techniques have been tested for optimizing CL imaging of carbonate minerals. We tried three types of conductive coating: a 20-25 nm-thick carbon coat, a 5 nm-thick iridium coat, and a 10 nm-thick iridium coat. Due to relatively large sample currents generated or contamination from samples containing hydrocarbons, carbon-coated samples may bubble during acquisition and artifacts are introduced into CL images. In contrast, iridium-coated samples are more stable. If no bubbling occurs, quality of CL images is similar with both types of conductive coatings. Thinner iridium coats correspond with sharper images.

A tradeoff of working at low kV as described below is that because the generation volume of photons is reduced, surface features such as scratches on standard polished thin sections may become visible. Such surface artifacts can be avoided by ion-milling. Iridium coatings tend to bring out surface scratches, so unless the sample is well polished or ion-milled we found that carbon-coated samples give better images. Samples having problematic surface artifacts were ion milled with a Leica TIC 020 triple cross-sectional ion beam for 10 hours. The images presented here are mostly from carbon-coated standard polished thin sections, unless otherwise stated in the figure caption.

3.2 Optical and CL methods

Excitation of samples by high-energy electrons produces photon emission in the visible range, or cathodoluminescence (CL). Intrinsic or primary luminescence has been ascribed to natural defects in mineral crystal lattices (vacancies, dislocations) whereas brighter luminescence at higher wavelengths results from the presence and concentration of trace element and rare-earth

element activators (Götze et al., 2001, 2004; Boggs and Krinsley, 2006; Götze 2012; Edwards and Lee, 2014).

Optical-CL microscopes are microscopes with a CL detector that allows a specimen to be bombarded with high-energy electrons from a cathode gun (also called cold-cathode CL) to produce a color CL emission at visible wavelengths (Lee et al., 2005; Boggs and Krinsley, 2006; Götze and Kempe, 2008). The integration of light over time of exposure or digital acquisition required by optical-CL works well for phosphorescent minerals. However, SEM-CL has a number of advantages over optical-CL, including higher spatial resolution and magnification, higher sensitivity (lower-intensity emissions are detectable), and ability to image wavelengths outside of the visible range, such as ultraviolet and infrared emissions. In principle, with sensitive infrared and ultraviolet cameras, some of these emissions could be detected with microscope-based systems. In addition, secondary electron (SE), backscattered electron (BSE) images, and X-ray maps (EDS) can be simultaneously or sequentially obtained for the same area as SEM-CL images, and properties revealed by the different emissions can be correlated.

Lee (2000) showed that increasing the dwell-time of the electron beam at each point in the raster—so that the luminescence contribution from each point to net signal is minimal—reduces phosphorescence and improves panchromatic images formed using all light emitted. However, required dwell times of 1,200 ms increases acquisition time for a high-resolution image to several tens of minutes. Another method is to extend the inter-pixel delay, allowing decay of CL from one pixel before the next pixel is collected, but this also increases acquisition time. Reed and Milliken (2003) reduced phosphorescence by using a filter to excise the long wavelength orange-to-red CL emissions characteristic of carbonate minerals. They produced sharp SEM-CL images solely using ultraviolet (UV) to blue wavelengths, termed limited-

wavelength images. Because short-wavelength luminescence decays more rapidly than longer wavelengths, limited-wavelength images can be acquired using shorter dwell times than those suggested by Lee (2000). However, using hyperspectral mapping, Lee et al. (2005) demonstrated that there is a nonlinear relationship between luminescence intensity variations at UV-blue wavelengths and intensity variations at orange wavelengths, indicating that short-wavelength emission is an imperfect proxy for longer wavelengths. Thus, images of features such as CL zoning formed from UV-blue emissions only may not capture the signal found in panchromatic images (Lee et al., 2005; Boggs and Krinsley, 2006).

Besides phosphorescence, another problem in SEM-CL imaging of carbonate minerals is lack of luminescence. Almost all CL in carbonates is caused by trace elements, including rare earth elements (REE), which can act as activators, sensitizers, and quenchers (Fairchild, 1983; Richter et al., 2003). The UV-blue luminescence of calcite is believed to be activated by Ca^{2+} and/or CO_3^{2-} sites, whereas orange wavelengths are predominantly activated by Mn^{2+} (Calderón et al., 1984). On the other hand, Fe^{2+} appears to be the most important luminescence quencher in carbonate minerals, although the relationship between Fe^{2+} concentrations and luminescence is nonlinear, because the luminescence of orange wavelengths is also strongly influenced by the abundance of Mn^{2+} (Machel et al., 1991; Habermann et al., 1998; Reed and Milliken, 2003). The precise relationships between luminescence intensities and absolute concentrations of Mn^{2+} and Fe^{2+} and Mn/Fe ratios remain unclear (Budd et al., 2000). Nevertheless, one impact of iron quenching is that minerals that have high concentrations of Fe^{2+} such as ankerite are low-luminescent in SEM-CL and internal structures are obscured.

Our SEM and CL detector are configured to collect high-resolution structural and diagenetic information of over wide areas (mm) of rock for structural analysis. Aztec (Oxford

Instruments) and Digiscan (Gatan) software allow automated imaging and stitching of multi-square millimeter areas of samples.

The Zeiss Sigma High Vacuum Field Emission SEM (HV FE-SEM) is equipped with an Oxford X-Max 50 mm² Silicon drift detector (SDD) for low energy detectability, a pole piece-mounted electron backscattered (BSE) detector, and a Gatan MonoCL4 system. The instrument is equipped with a GEMINI column designed to work at low kV to minimize sample damage and reduce phosphorescence. A large chamber with a 5-axis Cartesian stage can accommodate 12×12 cm samples. The system has two modes for imaging the effects of defect structure and trace element variation: a MonoCL4 system that provides monochromatic, panchromatic, and colored-CL images with high spatial and spectral resolution, and a Zeiss variable pressure secondary electron (VPSE) detector that generates charge contrast images (CCI) that detect defects in a way similar to SEM-CL but having higher resolution because the CCI signal is composed of secondary electrons generated from a much smaller interaction volume than photons utilized in CL (Watt et al., 2000). These types of CL or CL-like signals are complementary.

Optimal working conditions for carbonate panchromatic imaging with the MonoCL4 detector are 5 kV (in contrast to 12-15 kV in our Philips XL30), 120 mm aperture, 150-200 ms dwell time and high current, generating sample currents on order of 3.5 nA and routine SEM-CL images with spatial resolution as low as a few nanometers per pixel. At these operating conditions, smearing caused by phosphorescence is rarely a problem. Where present, phosphorescence can be minimized by increasing dwell time to 400-800 ms.

The VPSE detector is operated at an accelerating voltage of 20 kV with an electron beam spot of a nanometer size that excites a CL-like response from a sample region of about a few hundred nanometers, thus electron beam-induced CL-like images can provide higher spatial

resolution than optical-CL. Because no mirror is involved in this configuration, the VPSE detector can generate relatively high resolution images (up to 0.5 nm per pixel) at magnifications as low as 30 $\times$.

3.3 Color-CL for carbonate minerals

The panchromatic CL image obtained by standard SEMs is an image in scales of gray. With the MonoCL4 detector, color CL images can be generated by combining three images obtained with red, blue, and green filters. Grayscale images captured through these filters can be combined in standard image processing or Digiscan software. Although image combination is involved, colors have a quantitative relationship to true colors rather than being arbitrarily assigned and unrelated to emitted wavelengths. Depending on how images are processed they can have colors comparable to those collected using optical devices (Boggs et al., 2002). Because only a portion of the total emission is captured, quality of images collected using filters is typically lower than panchromatic images collected without a filter. Methods that use filters to image carbonate minerals therefore have degraded image quality.

Generation of defects by electron bombardment changes CL emission. Thus, CL signals emitted by carbonate minerals can change over time (Townsend and Rowlands, 2000). If the same area is rastered over a long period of time (>500 msec), or sequential blue, green, and red filtered images are acquired, carbonate minerals, especially calcite, become progressively more orange-red luminescent, degrading image reproducibility and rendering CL color time-dependent. These effects can be minimized by acquiring valuable blue filter images first, rastering once per filter, and by using panchromatic images for texture mapping.

4. Fracture cement textures

Fracture-filling cement textures may record geochemical and kinematic evidence (Passchier and Trouw, 1996; Bons et al., 2012; Anders et al., 2014). In the following, we separate textures based on whether they record evidence of fracture movement or not. Crack-seal texture, crack-seal bridges, and stretched or fibrous crystals are *synkinematic* in the sense that the texture records episodic fracture widening and thus is broadly contemporaneous with movement of the fracture walls. Most of our examples are cement-filled opening-mode fractures (or veins) and fracture walls moved away from each other as the fracture grew. To form crack-seal textures, deposits need to connect between fracture walls as widening proceeds, so the textures really only prove that for a particular fracture opening rate, the growth rate of the mineral phase exceeded the spanning potential (Lander and Laubach, 2015), which depends on crystallography, growth habit, temperature, and other factors.

Many fracture cement textures are not diagnostic of accumulation contemporaneous with movement of the fracture walls, including many textures related to passive infill of pre-existing fractures and to competitive crystal growth. Such textures can arise in static fractures (walls not moving) or in situations where crystal growth rates are below the spanning potential. Other textures include unfractured deposits that overlap synkinematic deposits. Although rare in metamorphic veins, such postkinematic deposits (Laubach, 2003) are common in fractured sedimentary rocks where persistent fracture porosity during fracture growth results from growth rates near the spanning potential. Evidence for post-fracture opening porosity or cement includes isolated cement bridges containing crack-seal textures, surrounded by fracture pore space that can be filled by other deposits after fractures cease widening. Finally, in carbonate rocks, dissolution features can be widespread.

4.1 Synkinematic calcite-dolomite bridges

SEM-CL imaging reveals calcite bridges with crack-seal textures within fractures of sedimentary carbonate rocks (Figures 1a and 2). Tabular calcite crystals in Figure 2 form isolated deposits oriented nearly perpendicular to the fracture wall (bridges) (Figure 1a). The cores of some calcite bridges show tabular crack-seal gap-filling deposits that are surrounded by crack-seal-free lateral cements (Figure 2a). In this bridge, shorter, several micron-wide gap-filling deposits are surrounded by wider lateral cements, and cross-cutting relationships among gap-filling deposits and lateral cements are apparent. Crack-seal gap-fill shapes are fairly regular, exhibiting straight boundaries and triangular ends that reflect crystal growth.

Although calcite bridges with tabular crack-seal gap deposits are common, others show deposits that are irregular in shape with curvilinear outlines and texturally complex, anastomosing bright- and dark-luminescent areas (Figures 2b and 2c). Moreover, some bridges show a herringbone-like structure of crack-seal deposits that are tabular along the margins and triangular in the center (Figure 2b). Such textures might arise from a combination of crack-seal and calcite growth textures, such as fir-tree sector zoning (Raven and Dickson, 1989). It is noteworthy that crack-seal bands in Figures 2a-c are bright-luminescent; whereas, lateral cements are dark even though these deposits are the same phase deposited at about the same time as demonstrated by the quartz precipitation model of Lander and Laubach (2015). Crystal growth modeling suggests that the gap deposits accumulate rapidly compared to lateral deposits (Lander and Laubach, 2015). Differences in accumulation rate might correspond to different defect structure (Götze et al., 2001) or trace element substitution (Nielsen et al., 2012) and thus luminescence. The bridge in Figure 2b contains hydrocarbon fluid inclusion trails along the center of some crack-seal deposits.

A handful of tabular calcite crystals with idiomorphic terminations that are at a high angle to the fracture wall display anomalous textures (Figure 2d). These cement deposits show a ragged lining of sharp, bright-luminescent cement along the boundaries of the crystals. This lining is made up of triangle-like zones that are about 1 to 5 microns in amplitude and similar wavelengths. Possibly these could be small crystal outlines, sector zones, or twins. In contrast, the center of the crystal is composed of a mixture of irregular bright- and dark-luminescent zones of calcite cement (Figure 2d). These textures are unlike those present in crack-seal-bearing bridges within the same sample. The association of these textures with bridges suggests they might be related to crystal growth in widening fractures.

Dolomite bridges are usually rhomb shaped, and may be composed of one or more crystals (Figures 1b, 1c, and 3). Most dolomite bridges are composed of idiomorphic, crack-seal free dolomite where growth textures may (Figure 3a) or may not (Figure 3b) be apparent. For example, a fracture from a depth of about 4444 m contains dolomite bridges surrounded by postkinematic calcite (Figures 3b and 3c). Bridges are substrated on zoned dolomite crystals in the fracture walls that are cut by and can be correlated across the fracture, whereas dolomite overgrowths within the fracture are crack-seal free. In some cases, such dolomite crystals do not span the entire fracture but have idiomorphic terminations (Figure 3c). These textures indicate dolomite overgrowth prior to postkinematic calcite, most likely during a single fracture opening increment, or during multiple increments where fracture opening rate exceeded dolomite growth.

Some dolomite bridges, on the other hand, display crack-seal textures. In some cases, crack-seal gap-filling deposits cut across the entire bridge (Figure 3d); whereas, in others crack-seal texture is restricted to the center of dolomite crystals and these core zones have been overgrown by concentric, crack-seal free dolomite that grew into void space following crack-seal

growth (Figure 3e). The example in figure 3f contains at least 4 cross-cutting generations of crack-seal microfractures overgrown by zoned, crack-seal free dolomite cement. It is noteworthy that in the examples we found unlike calcite bridges, crack-seal bearing dolomite bridges are mostly comprised of crack-seal free dolomite and crack-seal deposits are only locally present.

Gap deposit widths measured normal to the fracture wall are a measure of the incremental opening displacement sizes below the spanning potential that contribute to fracture widening. The gap deposit sizes we found are in the range of 0.001 to 0.01 mm, similar to the small sizes reported by Hooker et al. (2012) for fractures from two bridges in dolomite rocks, where the gap size distribution in each fracture was best fit by a log-normal distribution. Our bridges also appear to have a narrow range of gap sizes.

4.2 Stretched/ataxial calcite fibers

Wall-perpendicular, fibrous cement infills are common in carbonate veins (Figures 1d-i and 4). Unlike isolated bridges, stretched calcite fibers usually infill the entire fracture. Some show a similar crack-seal-bearing core surrounded by lateral cement as the calcite bridges described above (Figures 4a and 4b). Incremental bands in most calcite stretched fibers imaged in this study are tabular with straight edges, but a few stretched fibers show bands that are straight on one side and curvilinear on the other (Figure 4b). Unlike crack-seal gap deposits in calcite bridges, crack-seal deposits in stretched fibers are strictly parallel to one another (do not cut across each other), and become systematically taller in one direction (from the right to the left in Figures 4a and 4b). These textures indicate that at least some stretched fibers systematically grew at the vein wall interface (syntaxial growth) and not by random fracturing within the vein.

Stretched fibers in Figure 4e contain wall-parallel solid inclusion-bands of rock mass– shale (Figure 1g). Fracture-fill calcite is patchy dark- and bright-luminescent, irregular, and anastomosing along the wall-rock inclusion bands, whereas calcite cement away from the solid inclusion band is free of inclusions, homogeneous, and idiomorphic. These textures indicate that calcite cement nucleated at the solid inclusions and continued to grow away from them. Calcite cement in between inclusion bands contains growth textures marked by dark- and bright-luminescent zones.

Fibrous calcite crystals that resemble stretched fibers in shape may show idiomorphic or no internal textures, such as calcite and dolomite fibers in Figure 4d and dolomite crystals in Figure 4e. Because these fibers do not show evidence for repeated fracturing and sealing during growth, crack-seal mechanism cannot be directly inferred as the formation mechanism. However, it is possible that the fibers formed by a crack-seal process but without leaving textural evidence like bands of inclusions. Lander and Laubach (2015) show that a crack-seal process can form fibrous textures if opening increments are small relative to crystal growth rates. It is also possible that subsequent recrystallization of dolomite obliterated crack-seal textures.

4.3 Antitaxial calcite fibers

The fractures in Figures 4f-h contain a single fracture wall-parallel band of rock-mass inclusions along the center of the fracture (median line or zone) (Figures 1h and 1i). In the center zone, calcite fibers extend away from this band in the direction perpendicular to the inclusion band, whereas away from it, fibers bend in opposite directions towards the fracture wall indicating shear during antitaxial growth. Similar to calcite fibers in Figure 4c, calcite is patchy dark- and bright-luminescent, irregular, and anastomosing along the wall-rock inclusion bands. Away from the inclusion band, fibers show two main textures: a) some fibers are composed of

irregular dark- and bright-luminescent zones similar to those found along the inclusion band, whereas b) most fibers comprise alternating dark and bright bands, a few microns wide that are perpendicular (not parallel) to the fracture wall (Figure 4g). Where calcite fibers bend, alternating dark- and bright- bands become irregular and stubby. Such textures differ from those observed in most stretched fibers and bridges in this study.

4.4 Complex dolomite crystal growth texture

The dolostone sample in Figure 5a contains wall-perpendicular, elongated dolomite crystals that span from one wall of the fracture to the other (Figure 1j). Unlike calcite fibers described above, dolomite fibers have ragged edges, in many cases displaying triangular terminations. This morphology indicates they are probably made up of an array of multiple adjacent dolomite crystals. Dolomite fibers lack internal structures in SEM-CL and are surrounded by calcite that also lacks internal microstructures. Similar composite dolomite crystals are present in Figure 4e, but in this case dolomite fibers are surrounded by stretched calcite fibers that display crack-seal microstructures. Serrated edges and embayment of calcite in dolomite, however, indicate crack-seal, synkinematic growth for both minerals yet dolomite kept no record of it. The parallel arrangement and cross-cutting relationships between dolomite and calcite fibers in this sample indicate they most likely grew contemporaneously during fracture opening. In Figure 5a, such embayments are lacking or they are ambiguous, resembling triangular idiomorphic terminations of dolomite rather than embayments proper. Therefore, calcite is most likely postkinematic in this sample.

Less commonly, dolomite crystals may form crystal arrays that are parallel to the fracture wall. The Cupido Formation fracture in Figure 5b is lined by tightly packed dolomite fibers (lacking internal textures) with idiomorphic terminations that are overgrown by quartz crystals

with dolomite inclusions (Figure 1k). Due to the lack of internal structures or a gradation in size from the fracture wall towards the center of the fracture, whether these are stretched fibers (formed by synkinematic crack-seal) or elongate blocky crystals (syntaxial growth into void space) is undetermined (see Figure 9). Idiomorphic terminations, however, indicate the latter is more likely. Dolomite fibers are overgrown by quartz crystals that are idiomorphic and in CL contain a core of irregularly shaped, regularly spaced bands that are parallel to the fracture wall. This core is surrounded by a zone of planar bands that parallel the idiomorphic of the quartz crystal forming an angular unconformity with the bands in the crystal core. This texture resembles lateral cement in quartz bridges. Bands in quartz cores, however, show textures that are unlike crack-seal. While crack-seal deposits are tabular and straight-sided, bands in this sample have one straight and one ragged boundary of bright-luminescent cement (Figures 5c and 5d). All bands are identical in shape resembling the teeth of a key. The straight side of each band is closest to the fracture wall, and the gap between the ragged edge and the straight edge of the next band is infilled by dark-luminescent quartz cement (Figures 5c, 5d and 5e). Where no marked boundary between the bright-luminescent and dark-luminescent cement is present the straight boundary of individual bands appears gradational rather than abrupt. In a few crystals, both boundaries of a band are ragged, and dark-luminescent cement separates individual light-luminescent bands (Figure 5b).

Idiomorphic dolomite crystals are hosted in embayments within the ragged edge of individual bands (Figures 5c, 5d, and 5e). In some cases, several dolomite crystals are concentrated along the ragged edge of the same band, forming fracture wall-parallel arrays. Moreover, dolomite crystals tend to concentrate at the same position within each band, forming arrays of crystals that are not only parallel to but also perpendicular to the fracture wall (Figure

5e). Bands grew at the vein wall interface and not by random fracturing of the vein, as indicated by the lack of cross-cutting relationships between different bands. Bright-luminescent quartz cement precipitated syntaxially on the fracture wall after each fracturing increment. Closely spaced dolomite inclusions could form wall-perpendicular dolomite fibers like the ones described above (Figures 4d and 5a).

4.5 Microfractures

Microfractures are fractures that cannot be seen without magnification (Anders et al., 2014). In many limestones, microfractures are obscured because the main constituent of both microfractures and host rock is calcite, and because the luminescence of calcite cements within microfractures is usually similar to that of calcite in the host rock (Figure 6a). Although microfractures in Figure 6a are transgranular (cut across several grains) they are only visible where some contrast exists between the rock mass and fracture cement. Examples with good SEM-CL contrast between host rock and fracture cement, however, indicate that crack-seal textures are widespread in carbonate microfractures (Figure 6b and 6c). In microfractures with multiple crack-seal gap deposits, calcite forms tabular crystals with crack-seal textures (bridges), (Figures 1L and 6c) but unlike macrofractures, microfractures tend to be completely infilled by cement bridges with no or little fracture porosity preserved.

4.6 Competitive growth textures

Blocky and faceted cement deposits arise from growth into fracture cavities under the influence of growth competition (Bons, 2001; Hilgers and Urai, 2002; Zhang and Adams, 2002; Bons and Bons, 2003; Hilgers et al., 2004; Nollet et al., 2005; Nüchter and Stöckhert, 2007; Okamoto and Sekine, 2011). Inward-projecting faceted crystals and blocky cements are common

textures that could contain evidence for rates of porosity destruction, fluid flow, and other processes.

The most common anhedral (blocky) cements in our sample suite are calcite, dolomite, ankerite (or Fe-dolomite), and anhydrite. Crystal sizes may be unimodal, bimodal, or show a range in grain sizes within the same fracture (Figures 1m, 7a, and 7b). Blocky cements usually show growth textures, such as alternating bright- and dark- luminescent, concentric bands that are parallel to crystal faces. In other cases, compositional interfaces do not coincide with and are not parallel to the growth interface, representing sectorial zoning (Reeder, 1991) (Figure 2a). Fir-tree arrays (Raven and Dickson, 1989) of sharply defined zigzag boundaries are a typical sector zoning texture in blocky calcite cement in our sample suite (Figures 2c and 7c). In some cases, however, blocky calcite cements are textureless in SEM-CL (Figures 5a and 5b).

In our sample suite, idiomorphic crystals of ankerite, calcite, and dolomite line many fractures, especially those that contain other forms of synkinematic cements. Moreover, in some cases, faceted crystals that line fracture walls contain a crack-seal core, indicating these deposits are synkinematic (Figures 7d and 7e). A common relationship is where blocky cements surround faceted crystals (Figures 7a, 7b, and 7d). In Figures 7a and 7b, the fractures are lined by faceted dolomite crystals that contain a veneer of bitumen along the outermost part. Faceted dolomite is in turn surrounded by anhedral to subhedral calcite that range in size from a few to about 100 microns. Faceted dolomites are cut by dark-luminescent calcite-filled microfractures that are confined within individual dolomite crystals, indicating they probably represent crack-seal recracking of dolomite crystals before precipitation of blocky calcite. Crack-seal textures indicate the fracture continued to open after precipitation of dolomite. However, without further evidence it is not possible to tell whether subsequent anhedral calcite precipitated in actively

opening or dormant fractures. In Figure 7b, some of the faceted dolomites have been pulled away from the fracture wall and the gap has been filled by anhedral calcite. Most likely this relationship indicates fractures were actively opening while at least some of the anhedral calcite was being precipitated. Thus, such evidence can aid in determining the time of precipitation of faceted and anhedral cements relative to the opening of the fracture.

4.7 Postkinematic cement textures

Although some synkinematic cement-bearing macrofractures may preserve fracture porosity, most crystals with synkinematic textures in our sample suite are surrounded by porosity-filling cements that postdate fracture widening (Figures 2, 3b, 3c, 5, and 7). The most common postkinematic cement in our sample suite is calcite, followed by dolomite, ankerite, and anhydrite. Cements that surround and postdate intact bridges that span across fractures must have precipitated after fractures ceased opening and are postkinematic cement—more fracturing would have broken the bridge. Similarly, cements that surround crystals with synkinematic textures that do not span across the entire fracture may be syn- or postkinematic (Figure 7).

Similar to blocky cements described above, postkinematic calcite cements in our sample suite show a range of growth and/or sectorial zoning, fir-tree array patterns, or are textureless in SEM-CL. Growth textures were identified in ankerite (Figure 7d). It is noteworthy that ankerite in Figure 7d is cross-cut by areas that are darker luminescent than the surrounding ankerite, and which contain inclusions of zoned calcite (Figure 7f). These textures probably indicate secondary refracturing of postkinematic ankerite.

Postkinematic cements in carbonates may also surround crystals with idiomorphic terminations (Figures 7a and 7b). SEM-CL reveals the presence of the same postkinematic cement in the carbonate rock mass (Figure 7a). Postkinematic overgrowths can be difficult to

distinguish in the rock mass, especially those that grow syntaxially on rock mass particles of the same mineralogy

4.8 Dissolution and reprecipitation textures

A characteristic to carbonate rocks is the ease of dissolution and reprecipitation of carbonate minerals under a wide range of temperature conditions (Tucker and Bathurst, 1990), although the importance of dissolution in porosity generation in the deep subsurface has been disputed (Ehrenberg et al., 2012). These processes can lead to the formation of fracture cement textures that are unlike those in siliciclastic or crystalline rocks where dissolution is less common. For example, the fracture in Figures 1n and 8 contains isolated cement pillars that superficially resemble cement bridges formed by crack seal, but the internal textures are not compatible with repeated fracture and cement deposition. SEM-CL imaging reveals that these pillars are made up of stacked up tabular calcite crystals and isolated idiomorphic dolomite crystals and crystal aggregates. Tabular calcites are arranged obliquely to the fracture wall, forming zig-zag or chevron-like arrays. Fragments of the rock mass are entrapped within these cement accumulations, forming layers (Figure 1n and 9g). These cement accumulations are surrounded by fracture porosity. The pillars of crystals by themselves could have formed by localized cement accumulation, but the irregular edges of blocky calcite crystals that line the fracture indicate dissolution of preexisting fracture cement. The layering between rock-mass fragments and idiomorphic calcite and dolomite crystals suggests reprecipitation of cements following dissolution. Porosity may therefore have been superposed on pre-existing massive vein textures. Although dissolution and reprecipitation features can be expected in carbonate rock fractures, in the sample suite we examined, where textures mostly formed at great depth, few unambiguous textures that might reflect dissolution and reprecipitation were found.

5. Discussion

In fractures within many rock types over a wide range of temperatures from diagenesis to metamorphism, calcite and dolomite deposits are widespread and have been the focus of many studies. Although optical-CL studies of opening-mode fractures in sedimentary carbonate rocks yield important insights (e.g., Trave et al., 1998; Hood et al., 2003; Holland and Urai, 2010; Vandergiste et al., 2013; Lavenu et al., 2013; Kotta, 2014), compared to SEM-CL, the low spatial resolution, magnification, and sensitivity of optical-CL means that only broad textural distinctions are possible rather than the fine resolution needed to document crack-seal gap deposits that track increments of fracture widening that may be only a few to tens of microns wide. Optical-CL studies of carbonate minerals reveal coarse zoning patterns between red-, blue-, and bright- and dull-luminescent areas from walls to inner parts of fractures in many deformed sedimentary (Trave et al., 1998; Hood et al., 2003; Berryman, 2013; Lavenu et al., 2013) and crystalline rocks (Blyth et al., 2004; Maskenskaya et al., 2014). High resolution SEM-CL imaging of carbonate rock fractures demonstrate that at least some fracture calcite, dolomite, and ankerite have kinematically significant textures that are made visible or are more sharply defined than those revealed by optical-CL. Such textures could be used to unravel fracture histories. Sharp imaging is in part due to the high sample currents and associated high luminosity generated at relatively low beam currents—minimizing interaction volume and sample damage—and the improved spatial resolution of modern FE-SEMs.

Our study reveals the presence of synkinematic calcite and dolomite bridges in limestones and dolostones, respectively. High resolution SEM-CL imaging of carbonate fractures show similar textures in carbonates to those found in quartz-filled fractures in sandstones, specifically isolated bridges in otherwise open fractures. Although currently filled with cement,

the textures we found are most readily explained by sequential formation of bridges and subsequent infill of pore space between bridges. The bridges illustrated in Figure 2 are the first example of this type of structure in calcite fracture cement. Simplified diagrams of the basic textural types identified in this study are shown in Figure 9. In quartz, crack-seal gap deposit shapes are tabular and fairly regular, exhibiting straight boundaries and triangular endings that reflect crystal growth (Laubach et al., 2004a; Lander and Laubach, 2015).

The cores of some calcite bridges show similar tabular crack-seal textures that are surrounded by crack-seal-free lateral cements, but complex textures not identified in quartz also abound in calcite bridges. Unlike tabular quartz and calcite bridges, dolomite bridges are usually rhomb shaped, and may be composed of one or more crystals. While in quartz and calcite crack-seal gap deposits and associated lateral cements comprise most of the bridge, dolomite bridges are usually textureless or are composed of zoned dolomite with localized crack-seal gap deposits that may or may not extend beyond the core of the bridge (Figure 9a). These differences partly reflect differences in crystallography, habit, and growth kinetics and rates between the different minerals. In addition to differences related to crystallography, differences between quartz and dolomite textures on the one hand, and calcite on the other, arises from the tendency for quartz and dolomite to preferentially grow on quartz or dolomite substrates, respectively, whereas calcite deposits commonly are not limited by calcite substrates (Gale et al., 2010).

The widespread occurrence of quartz bridges in sandstone can be explained by largely temperature-controlled accumulation rates on fracture and non-fracture surfaces (Lander and Laubach, 2015). An adaptation of this model explains dolomite cement geometries in dolostone fractures (Gale et al., 2010). Our observation of bridges in calcite fracture deposits is evidence that in some circumstances this model is applicable to calcite accumulation in fractures. In

carbonate systems testing this hypothesis will need to account for the role of saturation state, the appropriate precipitation kinetics, nucleation kinetics in cases where the carbonate minerals do not form as overgrowths, and solute transport (Lander and Laubach, 2015). Stretched calcite fibers are a type of synkinematic cement deposit in the sense that they are tabular cement deposits that span fractures, but unlike bridges described above, stretched fibers imaged in this study show systematically arranged increment bands and onlapping lateral cements that indicate crystals grew at the vein wall interface after each opening increment rather than by random fracturing within the vein (syntaxial growth) (Figures 4 and 9b). Similarly, veins with wall-parallel inclusions of host rock display textures that indicate that calcite cement nucleated at the solid inclusion band trapped along the fracture-wall interface after each opening increment and continued to grow away from the inclusions (Figures 9c and 9d). These textures alone, however, cannot discriminate between cement that grew syntaxially (Figure 9c) in one direction (away from the wall), or antitaxially in opposite directions (Figure 9d). Similar observations that stretched veins grow at the vein interface rather than randomly was postulated by Ramsay (1980) and Hilgers and Urai (2002) and are now confirmed by SEM-CL textures. In carbonate rocks, it is common for more than one carbonate mineral phase to grow contemporaneously giving place to the formation of crystal arrays of a different cement phase within mineral fibers (Figures 5, 9a, 9b, and 9e).

In quartz cement, sharp delineation of crack-seal textures using SEM-CL allows the sequence of cement accumulation in a few-micron wide crack-seal deposits to be documented (Laubach et al., 2004a, b). In many quartz bridges, individual crack-seal gap deposits are marked by a band of fluid inclusions trapped by crystal growth during fracture opening. Relative timing information from texture maps allows fluid-inclusion assemblages to be put into time sequence

to estimate fracture opening duration, absolute ages, and rates (Becker et al., 2010; Fall et al., 2012, 2015; Lander and Laubach, 2015). In carbonate cements, crack-seal increments are also associated with fluid-inclusion assemblages (Figures 1a and 2b). In a few examples where quartz and ankerite grew concurrently, the size of opening increments can be shown to be the same narrow size in both phases. An improved ability to accurately map crack-seal textures in carbonate cements would allow delineation of temperature sequences during fracture opening in carbonates, following a similar method to that used for quartz-filled fractures in sandstones (Becker et al., 2010; Fall et al., 2012, 2015). Although fluid-inclusion sequences usually cannot now be sequenced in detail *within* carbonate deposits in fractures, fluid inclusion temperature patterns within units and fracture sets in some areas (i.e., Evans et al., 2012) suggest that valuable additional temperature and salinity *sequence* information may exist there.

Crack-seal texture is present in some microfractures within sandstones (Laubach et al., 2004a, b). Microfractures that are a few to tens of microns in opening displacement can display crack-seal textures similar to those described in mineral bridges within macrofractures. The narrowest fractures, however, tend to lack crack-seal textures probably because they formed in a single crack-seal opening increment. While microfractures in sandstones tend to be completely sealed with quartz cement (Laubach et al., 2004a, b, c), in dolostones microfractures are usually infilled by dolomite and in limestones by calcite (Laubach, 2003; Gale et al., 2010). Examples with good SEM-CL contrast between host rock and fracture cement in our sample site indicate that, similar to sandstones, crack-seal textures are widespread in carbonate microfractures (Figures 6b and 6c).

Similar to quartz in sandstones, carbonate bridges and faceted crystals that line fracture walls in carbonates are typically surrounded by porosity or postkinematic cement with growth

textures (Figures 2, 5, 7, and 9b). High resolution SEM-CL images allow for identification of low-contrast, postkinematic cements within the carbonate rock mass that are too indistinct or fine to be differentiated or resolved using optical-CL or lower-resolution SEM-CL. An accurate measure of the proportion of postkinematic cements within fractures and the rock mass is essential to understand the porosity evolution of the rock-fracture system. For example, the abundance of postkinematic cement in small pieces of the rock-mass can be used to predict whether or not large fractures are likely to be occluded by postkinematic cement in cases where fracture populations are incompletely sampled (Laubach, 2003). Such estimates can yield valuable predictions of well performance in areas where natural fractures are the dominant pathways for hydrocarbon delivery to wellbores.

In addition to documenting some notable similarities, our study reveals carbonate cement textures that are unlike those found in quartz. For example, bridges with curvilinear and herringbone-like crack-seal bands appear to be unique to calcite. These textures may arise from a combination of crack-seal with sector zoning growth in calcite. Additionally, carbonate cement deposits that lack internal structures, such as some dolomite bridges and crystal arrays and postkinematic calcite cements, are far more abundant than textureless quartz. Finally, antitaxial calcite fibers (Figures 4f-h) in carbonaceous shales display alternating bright- and dark-luminescent bands that are perpendicular rather than parallel to the fracture wall.

Antitaxial veins have been assumed to form by a crack-seal mechanism (e.g., Cox, 1987; Passchier and Trouw, 2005; Barker et al., 2006; Lander and Laubach, 2015), even though the remarkable symmetry shown by many antitaxial veins is hard to reconcile with crack-seal processes, which seem to require simultaneous fracturing on both surfaces (walls) of an opening fracture, an unlikely scenario because opening of the fracture on one side would relax the tensile

stress and inhibit simultaneous opening of the fracture on the other side (Bons et al., 2012). An alternative mechanism is growth on the interface between cement-filled fracture and wall rock (e.g., Fisher and Brantley, 1992; Means and Li, 2001, Bons and Montenari, 2005; Hilgers and Urai, 2005). Textures of antitaxial fibers found in our study differ from those found in stretched fibers and bridges. However, crack seal may not be ruled out as the formation mechanism of antitaxial veins; for example, similar fracture opening and cementation rates would not give rise to fracture wall-parallel bands within calcite fibers. The exact meaning of wall-perpendicular, alternating bright- and dark-luminescent bands within calcite shown by high-resolution SEM-CL, however, needs further investigation.

Tabular cement deposits in fractures in carbonate rocks can arise from other processes that are not related to synkinematic fracture opening. For example, the tabular deposits in Figure 1n and 8 lack crack-seal texture and have rounded habit, and have interlayered, chevron-like arrays of tabular calcite and layers having high silt content (compared to host rock). Although the origin and significance of these chevron-like arrays of tabular calcite cements for fracture growth is unknown and needs further study, their shapes and textures are compatible with dissolution-reprecipitation possibly aided by biological agents (microbes) (Figure 9g).

6. Conclusions

In calcite and dolomite deposits in fractures, recent developments in scanning electron microscope-based cathodoluminescence (SEM-CL) along with other SEM-based imaging methods, reveal structurally significant crack-seal and cement growth textures where previous SEM-CL imaging methods found massive or featureless deposits. Textures in some calcite deposits resemble the complex cement accumulation patterns found in crack-seal bridges in

quartz in sandstone fractures, a texture not previously found in fracture calcite. Fibrous synkinematic carbonate cement textures that show systematically arranged bands indicate stretched fibers grew at the vein wall interface after each opening increment instead of by random fracturing within the vein. Microfractures and competitive growth textures are also more sharply defined, allowing improved interpretation of crosscutting relations, fracture sizes, and the relative timing of fluid-inclusion assemblages. Examples from several fractured carbonate rocks suggest that some apparent differences between carbonate mineral and quartz deposits in fractures reflect the resolution limits of previous imaging methods applied to carbonate minerals. For the widespread carbonate mineral deposits in fractures in a wide range of rock types, improved delineation of textures provides evidence for growth and decay of fracture porosity.

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Figure captions

Figure 1: Photomicrographs of cement-filled fractures analyzed with SEM-CL. a) Calcite bridges surrounded by postkinematic calcite in sample S-1. Small box indicates inset in figure 2b. Large box indicates inset equivalent to that in figure 7d. Note that this is not the exact location. b) Dolomite bridges surrounded by fracture porosity in sample Ca-1. Box indicates inset equivalent to that in figure 3a. Note that this is not the exact location. c) Dolomite bridges surrounded by postkinematic calcite in sample K-1. Box indicates inset in figure 3c. Note that image is rotated 90°. d) Calcite stretched fibers in sample S-2. Box indicates inset equivalent to that in figure 4a. Note that this is not the exact location. e) Calcite and dolomite stretched fibers in sample T-1. Large box indicates inset equivalent to that in figure 4b and small box equivalent to 4e. Note that these are not exact locations. f) Crack-seal microfractures with calcite and dolomite fibers in sample C-1. Box indicates inset equivalent to that in figure 4d. Note that this is not the exact location. g) Fracture wall-parallel rock mass inclusions within a calcite-filled fracture in sample Ma-1. Box indicates inset in figure 4c. h) Calcite fibers in sample H-1. The fracture contains a median line of host rock inclusions. Fibers bend in opposite directions towards the fracture wall indicating shear. Box indicates inset equivalent to that in figure 4f. Note that this is not the exact location. i) Calcite fibers near the median line in sample V-1. Box indicates inset equivalent to that in figure 4h. Note that this is not the exact location. j) Bimineralic calcite and dolomite stretched fibers in sample C-2. Box indicates inset equivalent to that in figure 5a. Note that this is not the exact location. The image is rotated 90°. k) Complex dolomite, quartz, and calcite fracture fill in sample C-3. Large box indicates inset equivalent to that in figure 5b. Note that this is not the exact location. Medium and small boxes indicate insets in figures 5c and 5e, respectively. l) Microfractures with calcite bridges in sample S-3.

882 Microfractures converge to form a wider (up to ~0.4 mm) fracture. Box indicates inset equivalent
883 to that in figure 6c. Note that this is not the exact location. The image is rotated 90°. m)
884 Idiomorphic dolomite lining surrounded by calcite in sample B-1. Box indicates insets equivalent
885 to those in figure 7a and 7b. Note that this is not the exact location. The images are rotated 90°.
886 n) Blocky calcite along the fracture wall. Layered, dissolution-reprecipitation calcite + dolomite
887 + silt-sized quartz forms a cement pillar in sample Cr-1. These pillars are surrounded by fracture
888 porosity (P). Cement pillars overgrow blocky cements along the fracture wall. Large box
889 indicates inset equivalent to that in figure 7c and small box that in figure 8. Note that this is not
890 the exact location. F = Fracture wall.

891 **Figure 2:** Calcite bridges in sample S-1. a) Calcite bridges showing tabular crack-seal
892 increments in the core surrounded by lateral cements. b) Cross-cutting relationships of individual
893 crack-seal gap deposits. c) Irregular anastomosing textures along the fracture wall. d) Calcite
894 bridges with anomalous textures. Cc = calcite; F = fracture wall.

895 **Figure 3:** Dolomite bridges in dolostone samples. a) Crack-seal free bridge (Ca-1). b) Zoned
896 dolomite overgrown by textureless dolomite within the fracture (K-1). The dolomite bridge is
897 surrounded by postkinematic calcite within the fracture. c) Textureless dolomite overgrowth with
898 idiomorphic termination surrounded by postkinematic calcite (K-1). d) Crack-seal gap deposits
899 may cut across multiple crystals, or are restricted to the core of the bridge which is overgrown by
900 crack-seal free, zoned dolomite (Ca-1). e) Inset of d) showing crack-seal gap deposits
901 terminating against the edges of the crystal (bridge). f) At least 4 generations (numbered from
902 older to younger) of cross-cutting crack-seal gap deposits overgrown by zoned, crack-seal free
903 idiomorphic dolomite (Ca-1). Cc = calcite; Dol = dolomite; F = fracture wall.

Figure 4: Stretched fibers in calcite-filled fractures. Fracture orientations are as in figure 1. Fracture walls in all images are oriented N-S and fibrous crystals are roughly E-W. Fracture walls are outside of the field of view except in cases where the fracture walls are labeled (F). a) Stretched fiber with crack-seal gap deposits that become progressively longer towards the left indicating syntaxial growth direction of the cement during fracture opening (S-2). F = fracture wall; S = relatively short crack-seal gap cement deposit; L = relatively long crack-seal gap cement deposit. b) Stretched fibers with bright-luminescent core (T-1). 5-nm Iridium-coated sample. c) Stretched fibers in carbonaceous shale containing solid inclusions of wall rock arranged parallel to the fracture wall (Ma-1). d) Bimineralic fracture fill showing textureless, fibrous calcite and dolomite (C-1). e) Bimineralic fracture fill showing growth increments with curvilinear edges within calcite (T-1). 5-nm Iridium-coated sample. f) Calcite fibers in antitaxial vein. Fracture walls are parallel to the median line defined by solid inclusions of wall rock (H-1). Box shows inset in g). g) Detail showing alternating bright- and dark-luminescent bands in calcite fibers. h) Calcite fibers in antitaxial vein showing similar textures to those in f)-g) (V-1).

Figure 5: Complex cement crystal arrays within fractures. a) Bimineralic crystal arrays. Calcite is textureless and most likely postkinematic (C-2). Fracture walls are perpendicular to the fibers (roughly E-W in the image). b) Textureless dolomite stretched fibers lining the fracture wall overgrown by quartz with dolomite inclusions. Quartz is surrounded by postkinematic calcite (C-3). c) Quartz crystal with fracture wall-parallel growth bands and idiomorphic dolomite inclusions (C-3). D) Inset of c) showing growth bands with one straight and one ragged side. e) Idiomorphic dolomite inclusions form arrays both parallel and perpendicular to the fracture wall (C-3). Fracture walls are perpendicular to mineral fibers; roughly E-W in a), and N-S in b, c, d (see Figure 1).

Figure 6: Microfractures in limestone. a) Microfractures in molluscan packstone showing little contrast with the host rock (S-2). b) Microfracture calcite fill shows good contrast with wackestone rock mass (S-3). Box marks the location of inset shown in c). c) Crack-seal texture within microfractures (S-3).

Figure 7: a) Faceted dolomite along fracture wall surrounded by postkinematic calcite. Dolomite crystals have a rim of bitumen. The same postkinematic calcite that infills fractures is present infilling porosity within the rock mass (B-1). b) Faceted dolomites have been separated from the fracture wall (pulled) and the gap has been infilled by postkinematic calcite. Microfractures cut dolomite crystals (B-1). c) Possible fir-tree texture in blocky calcite cement (Cr-1). See Figure 1n for location on blocky cement within the fracture. d) Idiomorphic ankerite overgrowing synkinematic calcite bridges that line the fracture wall. Ankerite contains inclusions of zoned, fracture cement calcite (S-1). Boxes 1 and 2 mark the location of insets in e) and f), respectively. e) Calcite bridges with crack-seal cores. f) Zoning within ankerite. Ankerite is darker where calcite inclusions are present (S-1). Cc = calcite; Ank = ankerite.

Figure 8: Reprecipitation textures (S-1). SEM-CL image reveals pillars are made up of stacked tabular calcite and dolomite crystals and entrapments of wall rock. Dashed lines outline the chevron-like of tabular calcite. See Figure 1n for location within the vein.

Figure 9: Summary figure of the basic fibrous/tabular fracture cement texture types identified in this study. Each diagram shows the evolution through time from left to right. a) Formation of calcite and dolomite bridges that show crack-seal cores and crack-seal-free lateral cement during fracture opening (synkinematic). Filling of the fracture by cement after the fracture has ceased opening (postkinematic) obliterates fracture porosity. b) Formation of stretched calcite and dolomite fibers. Unlike bridges described above, calcite stretched fibers imaged in this study

show systematically arranged increment bands and onlapping lateral cements that indicate crystals grew at the vein wall interface after each opening increment rather than by random fracturing within the vein. c) Formation of calcite fibers with wall-rock inclusion bands indicating syntaxial cement growth. Fracture opening and cementation was localized at the fracture front after each step. d) Formation of calcite fibers with a median line or zone of wall-rock inclusions indicating cement growth away from the median line in opposite directions (antitaxial). e) Formation of complex mineral fibers containing fracture wall-parallel zones with differences in luminescence and idiomorphic mineral inclusions of a different mineral phase. f) Formation of elongate blocky fibers by passive growth into the fracture of preferentially oriented crystals. Gradation in size indicates growth direction, in this case syntaxial, away from the fracture wall. After Bons et al. (2012). g) Formation of tabular cement accumulations by partial dissolution of preexisting fracture cement/rock mass and reprecipitation into void space, probably aided by microbes.

Table 1: Rock units analyzed.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

a) Synkinematic calcite-dolomite bridges

b) Stretched fibers

c) Syntaxial fibers with wall-rock inclusions

d) Antitaxial fibers with median line

e) Complex crystal growth textures

f) Elongate blocky (growth competition)

g) Dissolution-precipitation textures

Time →

Figure 9

Table 1

Sample	Age/Formation	Rock type*	Depth/location (m)	Phases/textures	Reference	Figure
C-1	Cretaceous/Cupido	Dolomitic packstone	outcrop	Cc and dolomite stretch fibers	Gale et al. (2004)	1f, 4c
C-2	Cretaceous/Cupido	Dolostone	outcrop	Dol stretch fibers + quartz with dol inclusions + postkinematic Cc	Gomez, 2007; Monroy-Santiago, 2012	1j, 5a
C-3	Cretaceous/Cupido	Dolostone	outcrop	Cc+calcite bimineralic crystal array	Gomez, 2007; Monroy-Santiago, 2012	1k, 5b, 5c, 5d
V-1	Jurassic-Cretaceous/Vaca Muerta	Calcareous shale	outcrop	Cc stretch fibers with median line of wall-rock inclusions	This study	1i, 4g
S-1	Jurassic/Smackover	Wackestone	3010	Cc bridges; Postkinematic Cc + ankerite	This study	1a, 2, 7d, 7e
S-2	Jurassic/Smackover	Molluscan packstone	3087	Cc stretch fibers; microfractures	This study	1d, 4a, 6a
S-3	Jurassic/Smackover	Wackestone	3006	Microfractures	This study	1l, 6b, 6c
H-1	Jurassic/Haynesville	Calcareous shale	3361	Cc stretch fibers with median line of wall-rock inclusions	This study	1h, 4f
Cr-1	Jurassic/Carmel	Silty limestone	outcrop	Blocky Cc; Dissolution-reprecipitation tabular Cc + dol	This study	1n, 7c, 8
T-1	Triassic carbonates	Dolomitic mudstone	2852	Cc + dol stretch fibers	This study	1e, 4b, 4d
Ca-1	Pennsylvanian/Canyon	Dolostone	2370	Dol bridges; zoned dolo overgrowth	Gale et al. (2010)	1b, 3a, 3d, 3e, 3f
Ma-1	Devonian/Marcellus	Calcareous shale	outcrop	Cc stretch fibers with wall-rock inclusion trails	Pommer (2013)	1g, 4e
K-1	Ordovician/Knox	Dolostone	4444	Dol bridges; postkinematic dol	Gale et al. (2010)	1c, 3b, 3c
B-1	Ordovician/Bighorn	Dolostone	outcrop	Faceted dol + postkinematic Cc	This study	1m, 7a, 7b