Nanograin formation and reaction-induced fracturing due to decarbonation:

Implications for the microstructures of fault mirrors

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Abstract

Principal slip zones often contain highly reflective surfaces referred to as fault mirrors, shown to consist of a nanogranular coating. There is currently no consensus on how the nanograins form, or why they survive weathering on a geological time-scale. To simplify the complex system of a natural fault zone, where slip and heat generation are inherently coupled, we investigated the effect of elevated temperatures on carbonate rock surfaces, as well as their resistance to water exposure. This allows us to isolate the role of the decarbonation process in the formation of nanograins. We used cleaved crystals of Iceland spar calcite, manually polished dolomite protolith, as well as natural dolomite fault mirror surfaces. The samples were heated to 200 - 800°C in a ~5 hour heating cycle, followed by slow cooling (~12 h) to room temperature. Subsequently, we imaged the samples using scanning electron microscopy and atomic force microscopy. Nanograin formation on all sample surfaces was pervasive at and above 600°C. The Foiana fault mirror samples were initially coated with aligned naturally-formed nanograins, but display a non-directional nanogranular coating after heating. The nanograins that were formed by heating rapidly recrystallized to bladed hydroxides upon exposure to deionized water, whereas the nanograins on unheated fault mirror samples remained unchanged in water. This shows that the nanograins formed by heating alone are different from those formed in fault zones, and calls for a better characterization of nanograins and their formation mechanisms. Furthermore, we find a characteristic star-shaped crack pattern associated with reacted regions of the carbonate surfaces. The existence of this pattern implies that the mechanical stresses set up by the decarbonation reaction can be sufficiently large to drive fracturing in these systems. We propose that this mechanism may contribute to grain size reduction in fault zones.

30 **Keywords**

31 Fault mirrors; decarbonation; microstructures; dolomite; calcite; seismicity

1. Introduction

Natural fault zones typically consist of a damage zone and a fault core that occasionally contains a thin, localized principal slip zone that accommodates the main deformation (Faulkner et al., 2010, Smith et al., 2011). Such a principal slip zone often contains a highly reflective surface referred to as a fault mirror (Fondriest et al., 2013, Siman-Tov et al., 2013). The nanoscale resolution provided by state-of-the-art imaging techniques has shown that the mirror-like optical properties of these surfaces stem from sub-micrometric roughness, typically less than 100 nm, created by a compact or sintered layer of particles of nanometric size (Fondriest et al., 2013; Goldberg et al., 2016; Han et al., 2010; Siman-Tov et al., 2015; Smith et al., 2012; Verberne et al., 2014). This is similar to the surface structures found on shiny wear surfaces in metals (Adachi and Kato, 2000).

Fault mirrors have been found in natural fault zones of different lithologies, and have been produced experimentally for carbonate (e.g. Fondriest et al., 2013; Siman-Tov et al., 2015) and silicate rocks (Kuo et al., 2016; Toy et al., 2017). In this study we focus on carbonate rocks, since a larger body of literature is available concerning the formation of mirror-like slip surfaces in these lithologies. Carbonate rocks are known to host earthquakes of M5 and higher, for example in the Italian Apennines (Mirabella et al., 2008) or in the Longmenshan Fault Zone in China (i.e. the 2008 Mw 7.9 Wenchuan earthquake, Chen et al., 2013). Several carbonate outcrops with fault mirror samples have been shown to have a nanogranular coating (Collettini et al., 2013; Fondriest et al., 2015, combined with this study; Goldberg et al., 2016; Siman-Tov et al., 2013), with occasional signs of decarbonation (such as vesicles and poorly crystalline and/or amorphous phases). Decarbonation is inferred to occur during seismic slip of carbonate-rich faults, caused by the heat produced during the fast sliding (Collettini et al., 2013). High velocity (> 1 m/s) friction experiments on calcite and dolomite also suggest decarbonation as a potential mechanism responsible for frictional weakening and nanograin formation (De Paola et al., 2011; Fondriest et al., 2013; Han et al., 2010).

A number of experimental studies have looked specifically into the formation and microstructure of carbonate fault mirror surfaces. These experiments were performed either on relatively pure calcite rocks and gouges or on dolomite rocks and gouges. Experiments have been performed over a range of sliding velocities. Complete fault mirrors are only found in fast (≥ 1 m/s) friction

experiments (Fondriest et al., 2013; Green et al., 2015; Han et al., 2010; Siman-Tov et al., 2015; Smith et al., 2012; Spagnuolo et al., 2015). Both fault mirror coverage and roughness have been shown to correlate with sliding rate, and it has been proposed that fault mirror surfaces can be used as markers for seismic slip in carbonate rocks (Fondriest et al., 2013; Siman-Tov et al., 2013). However, shiny patches covered with nanoparticles are also found in low velocity experiments on calcite. For example, Tisato et al. (2012) found a smooth sliding surface covered with sub-micrometric and platy particles at slow sliding velocities, whereas fast sliding led to nanometric and nearly spherical particles. Slow sliding, aseismic experiments on calcite gouge have also produced surfaces with nanofibers composed of aligned, ~100 nm diameter nanospheres (Verberne et al., 2014). Despite these being low velocity experiments, it is hypothesized that high temperatures can be generated locally by high strain rates due to localization. A short summary of the publication history of mirror fault surfaces can be found in Rowe and Griffith (2015).

Another intriguing feature of natural fault mirror surfaces is that they have survived weathering whilst being exposed in outcrops over decades. Manually polished carbonate surfaces, on the other hand, do not stay shiny, as commonly observed in weathering studies of tombstones. Surface retreat over 100 years is measurable for a wide variety of locations, except at a few extremely dry localities (Meierding, 1993). On the nanoscale in atomic force microscopy (AFM) dissolution studies, manually polished calcite (Levenson and Emmanuel, 2013) and dolomite (Saldi et al., 2017) have been found to dissolve faster than cleaved or fluid-equilibrated grain surfaces. This is attributed to high curvature, highly reactive features on polished surfaces. Goldberg et al. (2016), also using AFM, found that a carbonate fault mirror coating dissolved at a much slower rate than a manually polished rock from the same location.

The chemical composition of the fault mirror coating might provide indications of both the formation mechanism and the origin of the weathering resistance of these surfaces. However, precise chemical analysis of these nanoscale features is a challenge. In experiments with calcite gouge or limestone, detailed studies have found that the nanoparticles in the reflective principle slip zone are composed of calcite (Siman-Tov et al., 2015; Spagnuolo et al., 2015; Tisato et al., 2012; Verberne et al., 2014). Experiments on dolostone have shown the presence of Mg-oxide and Mg-calcite (Fondriest et al., 2013), and traces of Si, Al and Fe have been found in natural

92 fault mirrors of dolostone (Goldberg et al., 2016). It was suggested that these non-native
93 elements were mobilized in fluids flowing along the fault, and incorporated into the slip surface
94 during its formation. An alternative possibility would be contamination from one of the faulted
95 layers, as often happens during clay smearing.

96 There is currently no clear consensus on how the nanogranular coating on natural fault mirrors
97 forms. Proposed mechanisms can be grouped into two main categories: heat-controlled or slip-
98 controlled. In the heat-controlled scenario, frictional heating gives rise to decarbonation of
99 calcite and dolomite and the subsequent formation of oxide nanoparticles (De Paola et al., 2011;
100 Green et al., 2015; Han et al., 2010; Smith et al., 2012). Slip is required to generate heat, but slip
101 in itself is not required to generate nanoparticles. On the other hand, in the slip-controlled
102 scenario, nanograins are formed mechanically through the generation and subsequent pile-up of
103 dislocations (Fondriest et al., 2013; Siman-Tov et al., 2015; Spagnuolo et al., 2015; Verberne et
104 al., 2014).

105 In this study, we set out to simplify the complexity of a natural fault zone, and isolate the effect
106 of heat (and thus the role of decarbonation) alone. To this end, we compare the morphology and
107 reactivity in water of naturally formed fault mirrors and manually polished dolomite surfaces
108 heated to different temperatures. For comparison purposes we treat cleaved calcite crystals in the
109 same manner.

110 **2. Methods**

111 **2.1 Sample description**

112 The dolomite samples were obtained from the Foiana Fault Zone in the Italian Apennines
113 (described by Fondriest et al., 2015) that cuts through Triassic dolostones of the Mendola
114 Formation. We used both fault mirror samples and dolostone protolith. X-ray powder diffraction
115 analysis shows that the bulk rock is 100% dolomite (Fondriest et al., 2015), but there is no
116 analysis available that determines the chemical composition of the mirror surface itself. The fault
117 mirror samples display a natural smooth polish, interpreted to be associated with deformation
118 and former seismicity in the area. We manually polished cm-sized samples of the undeformed
119 host rock using regular carbide paper (stepwise, up to #4000 grit) and water, and finished to be
120 visually mirror-smooth using a diamond suspension with 1 μm particles. These were cut into

smaller blocks of roughly 1 x 1 x 0.5 cm. Before heating, samples were imaged with a scanning electron microscope (SEM) and an atomic force microscope (AFM). The SEM images show that before heating, the manually polished protolith samples (Fig. 2a,b) are smooth, with local polishing artefacts and occasional faint outlines of larger grains. The surface has pits up to 2 μm diameter, interpreted to be remnants of porosity or plucked out grains. The AFM indicates a smooth surface, without any nanoparticles coating the micron-sized grains. The fault mirror (Fig. 3a) is smooth under the SEM, with outlines of grains up to 40 μm and pits up to 5 μm diameter. The AFM images (Fig. 3b) show nanoparticles between 5 and 50 nm, often aligned to resemble nanofibers (terminology c.f. Verberne et al., 2014). Calcite samples were cleaved from a single crystal of Iceland spar calcite of optical quality.

2.2 Experimental procedure

Samples were heated in a Naber N100/G chamber kiln to the target temperature using the following thermal cycle: 230 min ramp up to 100°C below the target temperature, T_t , and then with a fixed ramp to T_t where it stays for 90 min, followed by slow cooling overnight. Samples were taken out of the oven when the temperature was between room temperature and 200°C. The oven calibration was checked with an external K-type thermocouple and found to be within 10°C of the set temperature. All samples and heating temperatures are listed in Table 1. After the thermal cycle, samples were imaged with an atomic force microscope (AFM) and/or secondary electron microscope (SEM). The maximum temperature for samples imaged with AFM is 600°C, and 700°C for SEM. For higher temperatures the samples lost cohesion, and could not be imaged any more. We used a Hitachi SU5000 Schottky field-emission scanning electron microscope (FESEM) at an accelerating voltage of 15 kV (in some cases also 10 kV, indicated in the images), capable of high resolution, on gold-coated samples. AFM topography measurements were made with a JPK Nanowizard 4, using cantilevers of type ContAl-G in Quantitative Imaging mode, where in each pixel the cantilever is moved at a constant velocity in the sample normal direction until reaching a given deflection setpoint. Note that as control, we imaged one of the dolomite samples heated to 600°C after exposure for one month to ambient conditions. This showed no change in morphology, indicating that ambient moisture does not affect the results. For selected samples, after recording the starting structure, deionized water was added to the sample holder using a syringe. For the samples where a reaction took place, the reaction proceeded too quickly for the reaction dynamics to be captured by AFM. Therefore, only the final, stable topography

was imaged by AFM, still under water (see Table 1). After drying, we coated and subsequently imaged these wetted samples with high resolution SEM.

TABLE 1. Samples, conditions and summary of the main results. T_t is target temperature, RT stands for room temperature.

Sample type	T_t	Imaged with		Nanograins	Grain boundary cracks	Star-shaped cracks	Lustre
		AFM	SEM				
Cleaved calcite	400°C			NO	n/a	NO	unchanged
	500°C			NO	n/a	NO	unchanged
	600°C			YES	n/a	YES	<div>↓</div> Progressive loss of lustre
	700°C	***		n/a	n/a	Probably	
	800°C	***		n/a	n/a	Probably	
Manually polished dolomite	RT*			NO	NO	NO	unchanged
	200°C			NO	YES	NO	unchanged
	300°C			NO	YES	NO	<div>↓</div> Progressive loss of lustre
	400°C			Possibly	YES	NO	
	500°C			YES	YES	NO	
	600°C	*	**	YES	YES	YES	
	700°C			YES	YES	YES	
	800°C	***		YES	***	***	
Fault mirror	RT	*		YES	NO	NO	unchanged
	600°C		**	YES	YES	YES	lustre loss

* these samples were wetted under the AFM after dry imaging

** imaged both the initial heated sample as the dried sample after the wet AFM experiment

*** Not imaged.

3. Results

3.1 Effect of heat on the morphology of a cleaved crystal of calcite

To the eye, the calcite samples exposed to low temperatures samples looked similar to unheated samples. Samples heated to 600°C and higher turned opaque. The 700° samples fell apart upon touch, with only a few unaltered central grains remaining. The 800°C sample turned to dust completely. At low temperatures, below 600°C, no changes are detected under SEM (Figure 1a). At high temperature, i.e. 600°C, a clear change occurs in the morphology, where the SEM images show abundant star-shaped cracks of variable sizes (Figs. 1b-d). These cracks are surrounded by rhombohedral ‘halos’ that appear lighter than the matrix, both in backscatter and

secondary electron mode. At nanoresolution these are shown to be porous zones with cracks of 100's of nm length (Figure 1d). Under the AFM these halos are shown to be 100's of nm deep pits that follow the rhombohedral cleavage planes of the calcite crystal in 3 dimensions (Figure 1e). Inside these pits there are equant 10-100 nm grains and an overall roughness of < 100 nm. Figure 1f shows the topography of the flat areas in between the star-shaped cracks, where more nanoparticles (bright spots) have formed along the cleavage steps, and only few can be found on the terraces.

FIGURE 1. Cleaved calcite crystal at different temperatures. a) secondary electron image of calcite heated to 500°C, showing the pristine smooth surface b-f) calcite heated to 600°C (b, c, d, secondary electron image; e, f, AFM image). Approximate locations of high resolution images as indicated. This surface is covered with star-shaped cracks surrounded by nano-porous halos and nano-spherules. Even when imaging an apparent smooth patch under the AFM there are signs that the reaction started (Fig. 1f).

3.2 Effect of heat on the morphology of dolomite

3.2.1 Manually polished dolomite

For manually polished dolomite samples, by eye, the samples changed color from slightly pink/pearly white to light grey/off-white, and with increased temperature they lost their lustre. Up until 600°C, the polished surfaces were recognizable in the heated samples by being slightly shinier than the non-polished surfaces. Samples heated above 600°C became crumbly. The 800°C sample was pervasively fractured and significantly whiter.

FIGURE 2. Manually polished dolomite at different temperatures. a) and b) secondary electron image images of room temperature dolomite, showing a smooth surface with polishing artefacts. c) secondary electron image, 600°C. Grain boundary and star-shaped cracks with light halos (similar to calcite). d) secondary electron image, 700°C. The arrow points at a patch of sintered particles. e) AFM images from 300 to 600°C (top to bottom). With increasing temperature there is an increased coverage of nanograins.

For the manually polished dolomite samples, grain boundary cracks (compare Figure 2a, b to 2c) become wider and more pronounced with exposure to increased temperatures. The SEM images showed that at 600°C the first star-shaped cracks appeared, just as in the calcite samples. Under the AFM, the topography of the 200°C and 300°C samples was typical of polished samples, displaying polishing grooves and little other recognizable structure (see Figure 2e). At 400°C, some nm-sized irregular bumps could be found. At 500°C, nanospherules were clearly present, although they did not cover the entire surface. At 600°C, the nanospherules were pervasive over the entire surface (Figure 2e). They were fairly uniform in size, and about 20 nm. At higher temperature (800°C), the nanoparticles had become visibly larger and the surface roughness greater. Under the SEM at 700°C, micron-sized patches of sintered nanoparticles could be seen on the surface (arrow in Figure 2d).

FIGURE 3. Dolomite fault mirror heated to different temperatures. a), b) fault mirror at room temperature (a, secondary electron image, b) AFM), showing a smooth surface with aligned nanoparticles. c), d), e) fault mirror heated to 600°C (c, e, secondary electron

images and d, AFM image). This heated sample exhibits the same characteristics as the manually polished sample that was heated: grain boundary and star-shaped cracks with nanoporous halos, and a uniform non-directional nanogranular coating.

3.2.2 Fault mirror

The fault mirror shared all of the main characteristics with the manually polished samples. Heating to 600°C changed the color to light grey/off-white, and the sample lost lustre. The heated sample also contained visible grain boundary cracks (Figure 3c). Within the larger grains, and along some grain boundaries, star-shaped cracks were present (Figure 3c, e), surrounded by lighter elliptical halos. Under the AFM, the 600°C fault mirror sample was found to exhibit pervasive non-directional nanospherules, with grain sizes up to 50 nm (Figure 3d).

FIGURE 4. The effect of wetting dolomite samples with a nanogranular coating: heated, dry samples are smooth and covered in nanograins. After immersion in deionized water the surface is covered by bladed hydroxides, decreasing its shiny appearance. a-e: a manually polished sample heated to 600°C; a-b) before wetting (left AFM, right SEM). c-e) after wetting (left AFM, right SEM). f-j) a fault mirror sample heated to 600°C; f-g) before wetting of (left AFM, right SEM). h-j) after wetting (left AFM, right SEM). Note the different scales in e) and j), used to illustrate different features of what are essentially identical structures.

3.3 Effect of water on the morphology of a dolomite surface

Manually polished samples and fault mirror samples that were not heated did not exhibit any change after exposure to deionized water under the AFM. For the samples that had been heated to 600°C, the manually polished and the fault mirror showed exactly the same morphological changes (compare Figure 4a-e and Figure 4f-j). Exposure to deionized water lead to rapid recrystallization within minutes to tens of minutes. Due to the rapid topography change compared to the duration of a high resolution AFM scan it was not possible to capture the full dynamics of the process. Imaging after drying showed a highly porous top layer of bladed crystals (Figure 4 c-e; h-j), that grew over the pre-existing surface morphology created by heat (i.e. over the grain boundary and star-shaped cracks).

4. Discussion

4.1 A simple recipe for nanograins

We have shown that heating of calcite and dolomite using a ~17h heating/cooling cycle covers the sample surface in nanocrystals, observed with AFM for the first time. This is in agreement with earlier decarbonation studies of calcite (Rodriguez-Navarro et al., 2009) and dolomite (Rodriguez-Navarro et al., 2012), using SEM and TEM, that also indicate the presence of nanocrystallites. Rodriguez-Navarro et al. (2009) found that decarbonation of pure calcite crystals starts at 600°C and is fully complete at 850°C. Decarbonation is one of the reaction types, along with many other metamorphic reactions (Brodie and Rutter, 1985; Jamtveit et al., 2016), that can modify grain size and/or mineralogy in fault zones, with the potential to speed up with decreased grain size (for decarbonation this is shown by Siman-Tov et al., 2016). The decarbonation reaction in calcite has been shown to proceed by the formation of “reaction pockets” of CaO crystals that follow specific crystallographic directions (Rodriguez-Navarro et al., 2009), preserving the rhombohedral shape of the parent crystal. Crystallites formed from the decomposition of CaCO₃ to CaO range in size from 17 to 76 nm, where the smallest sizes are for decomposition in vacuum (as opposed to air), as well as at lower temperatures (Rodriguez-Navarro et al., 2009). Due to the volume reduction from CaCO₃ to CaO, the final porosity is 54% when the process is complete. Following these observations, we interpret the lighter areas surrounding the star-shaped cracks in the SEM images (Figure 1b) to correspond to a high

porosity network of CaO crystallites, left behind after decarbonation of calcite. High resolution AFM observations indicate that the nanocrystallites range in size from 10-100 nm (Figure 1e) on calcite crystals heated to 600°C, which is the lowest temperature at which the decarbonation reaction in calcite takes place. In the areas that appear unaffected when imaged with high resolution SEM, signs of progressing reaction are still visible on the nanometer scale (Figure 1f). As expected, the increase in oven temperature from 600 to 800°C allows the reaction to proceed further into the sample. The high porosity after complete decarbonation is what makes the calcite samples heated to 800°C extremely fragile.

Figure 5 Possible mechanisms for creating star-shaped cracks, drawn for a cubic lattice to simplify. 1) Fracturing due to decrepitation: a) Heat-induced overpressurization of fluid inclusion below mineral surface; b) Fracture propagation extending up to the free surface, releasing pressure in fluid inclusion; c) Reacted region forms around damage zone, following the crystal lattice. 2) Reaction-induced fracturing: d) Unreacted surface with dissolution pit or other defect; e) Reaction initiates and progresses outward and downward from dissolution pit, following crystal lattice. Tensile stresses concentrate around the initiation point due to shrinkage during reaction; f) Fracturing of the reacted layer, nucleated on the central defect.

For dolomite, Rodriguez-Navarro et al. (2012) describe how thermal breakdown takes place through a topotactic transformation from $(\text{Ca,Mg})\text{CO}_3$ to pure CaO and MgO nanocrystals at temperatures of 500°C and above, although they note that decomposition at 400°C cannot be ruled out due to the limits of their detection method. Using our nanoresolution AFM images we can confirm that the reaction progresses from very local nanograin formation at 400°C to

pervasive nanograin formation at 600°C and above. Following (Rodriguez-Navarro et al., 2012), the reaction is complete at temperatures exceeding 800°C. As for calcite, the reaction progresses from the surface towards the center of the sample. The single dolomite crystals investigated by Rodriguez-Navarro et al. (2012) were shown to be a porous aggregate of oxide nanocrystals at temperatures of 600°C and above. As expected based on composition, our natural samples of manually polished wall rock dolomite, as well as the heated fault mirror, exhibit similar characteristics after heating to those reported in decarbonation experiments on calcite crystals. The lighter areas in the SEM images of dolomite (Figs. 2c, 2d, 3c, 3e) are porous zones in which the reaction progresses (as for calcite, Figure 1d), and the surface of both the manually polished and fault mirror sample is pervasively coated in randomly oriented nanoparticles.

A characteristic feature of the nanograins of natural fault mirrors found in the field is that they form a compact layer, where experimental evidence points to sintering during shear (Fondriest et al., 2013; Siman-Tov et al., 2015). Sintering of nanograins can take place through thermally activated plastic deformation at elevated temperatures. The application of normal stress, i.e. “hot pressing”, can reduce the sintering temperature and even allow carbonates to sinter below the thermal decomposition temperature (Fondriest et al., 2013; Siman-Tov et al., 2015). In decarbonation reactions, a progressive level of sintering of the oxide products is found as the temperature increases (Rodriguez-Navarro et al., 2012; Rodriguez-Navarro et al., 2009), and we observed what appeared to be patches of sintered material on the samples that were heated to the highest temperatures.

4.1.1 What keeps natural fault mirrors shiny?

In our experiments, the heat-created nanocrystals rapidly recrystallized to a porous network of bladed crystals upon exposure to water, which decreased the shiny appearance of the surface. Given that dolomite decarbonation creates Mg,Ca-oxides, we assume these bladed crystals to be Mg,Ca-hydroxides. This happened for both the mechanically polished and fault mirror sample after heat treatment. However, for non-heated samples, the aligned nanoparticles found in the original fault mirror did not react to exposure to water, even though the particles are similar in size and shape as those created by heat.

The nanocrystalline coating found in natural fault mirrors has been inferred to be the cause of their weathering resistance (Goldberg et al., 2016). In our samples however, despite the presence

of nanoparticles, those created by heat only are highly reactive and not a protection against water. High temperature sintering would also not be enough to make the surface weathering resistant, since using temperatures above 1000°C is standard industry practice to create reactive CaO (lime). This implies a difference between heat-induced nanoparticles (i.e. oxides) and the nanoparticles found on natural fault mirror surfaces. Based on chemical analysis of the nanoparticle fault zone layer investigated in Goldberg et al. (2016), it has been suggested that the resistant nature of the fault mirror surface is due to impurities. The presence of chemical species (dissolved locally or at distance) in fluids that percolate through the fault zone might result in the precipitation of chemically resistant nanoparticle phases (Fondriest et al., 2015; Goldberg et al., 2016). We found the natural fault mirror surface to be resistant to water, but not to heat. The heated natural fault mirror was covered in reactive particles that recrystallized upon water exposure in exactly the same manner as the manually polished surfaces. Since their chemical response is similar, it implies that the manually polished surface is chemically similar to the fault mirror. However, we cannot fully dismiss small chemical differences that may have a large effect on the stability of the surface.

4.2 Creating the stars

In addition to the nanogranular coating, the heated samples exhibit two types of heating-induced cracks: grain boundary cracks (only in the dolomite samples; Figure 2c, 3c) and star-shaped cracks (in calcite and dolomite samples; Figure 1b, 2c, 3c). We expected grain boundary cracks to form in the natural polycrystalline dolomite rock, due to anisotropic thermal expansion of neighbouring grains in an unconfined system. The grain boundary cracks are hence easily explained, and will not be discussed further here. The star-shaped cracks are more intriguing. They form in grain interiors, and are surrounded by reaction halos that are rhombohedral in calcite (Figure 1 d, c) and elliptical in the dolomite samples (Figure 2b, 2c; 3b, 3c). The occurrence of oriented, star-shaped cracks has previously been reported for samples of single crystal dolomite subject to decarbonation at 700°C (Rodriguez-Navarro et al., 2012), but their formation mechanism was not discussed. We observe that the legs of the stars usually follow the cleavage orientation of the crystals in which they form, but the central junction in each individual star is predominantly symmetric. Generally, this is interpreted to be indicative of cracks that nucleate from a single defect (Liu et al., 2016; Toga and Alaca, 2006). We propose two alternative formation mechanisms for the star-shaped cracks we observe, both of which involve

crack nucleation from a single point during heating: decrepitation and reaction-induced fracturing initiating at defects (Figure 5).

Decrepitation in carbonate minerals refers to the fracturing of mineral grains due to overpressurization (Figure 5a) and subsequent bursting of fluid inclusions at elevated temperatures. It takes place over a range of temperatures, starting from 100°C (Gaffey et al., 1991) up to perhaps 500°C (Ujiie et al., 2008), and is commonly most pronounced around 400°C (Dollimore et al., 1994). Due to the energy required to break larger samples, one might expect that decrepitation in cm-sized crystal- or rock samples, such as these, would not lead to complete fragmentation, but rather to a micron-sized erupted crack on the surface of the grain (Figure 5b). With further heating to the decarbonation temperature, the decarbonation reaction would initiate preferentially at edges and corners, using then the newly opened decrepitation cracks. The reaction would progress outward from the decrepitation site, possibly following the lattice directions. This would lead to symmetric fracture patterns surrounded by reacted zones (Figure 5c), consistent with some of our observations. However, three observations do not line up with this hypothesis: 1) we find no star-shaped cracks or any other features that might be interpreted as star-precursors before samples reach the temperature at which decarbonation sets in. This is particularly obvious in the single calcite crystal samples (Figure 1). 2) The arms of the star-shaped cracks do not extend outside the reacted zone, but 3) there are smaller reacted zones without a center star.

The second possible explanation is that the decarbonation reaction initiates at local defects, such as dissolution pits (Figure 5d). The reaction will progress outwards from the nucleation site following the lattice orientation, as well as down into the sample. Since the reaction products (in this case CO₂) need to diffuse away from the reaction site, the downward reaction will be slower than the lateral, leading to the formation of a thin film of decarbonated material that forms topotactically on the parent mineral. Due to the substantial decrease in volume, tensile stresses are set up in the reacted film, analogous to the shrinkage of mud, clay or coffee-water suspension layers during drying (Toga and Alaca, 2006). Star-shaped cracks, initiating from point defects, are characteristic features of these experiments and interpreted to be due to the tensile stresses that form during drying. Star-shaped cracks also form during cooling-induced shrinkage and fracturing of the surface oxidation layer in glassy carbon (Liu et al., 2016). In these elastically

isotropic systems, cracks that initiate at single defects display symmetric junction angles. In our samples, there is a degree of anisotropy imposed by the crystal lattice that breaks this symmetry. Therefore we propose that the star-shaped cracks form in our samples due to shrinkage-induced tensile stresses that are set up in “pockets” of reacted materials (Figure 5e), where cracks nucleate on the same single defect that initiated the reaction (Figure 5f).

Rodriguez-Navarro et al. (2012) suggested that the volume change associated with the decarbonation of dolomite could set up stresses sufficient to break apart the unreacted parent crystal. Since we have only used techniques that analyze the surface, we do not know whether the star-shaped cracks extend below the reacted zone. However, for the calcite heated to 700°C, we did observe multiple fragments of unreacted material inside the crumbling sample, suggesting that the reaction-induced stresses had been high enough to at least fracture a mm-sized single crystal. Given the observed break-up of crystals, and assuming that decrepitation and decarbonation-induced cracking are also effective under confinement, we suggest these processes might play a role in grain size evolution in fault zones.

4.3 Implications for natural fault zones

This set of experiments is a simplification of the processes occurring in a natural slipping fault. The most striking differences between our experiments and an actual fault zone are the i) absence of slip, ii) the duration of the thermal cycle and iii) the lack of confinement. First, in a natural fault zone, mechanical wear during slip will lead to grain comminution. A decrease in grain size decreases the temperature at which decarbonation starts (Siman-Tov et al., 2016). Second, regarding the thermal cycle, the heat pulse produced during slip on a fault is inherently shortlived (c.f. Siman-Tov et al., 2016). Because this leaves less time for the reaction to progress, this could result in a smaller extent of decarbonation (Siman-Tov et al., 2016) than what we observe in our experiments at the same temperature. Furthermore, it is likely our samples cooled more slowly than in a real system. If recrystallization takes place, then the final grain size of our samples is an upper bound of that which would form at depth. Third, the effect of confinement is twofold: the stress in a fault can drive compaction and sintering of the porous nanograin structure, which might contribute to the relative weathering-resistance of natural fault mirrors. Additionally, fault systems might be closed systems, i.e. any CO₂ generated during decarbonation would

remain in the system, which would lead to re-carbonation of the oxides to form calcite and Mg-calcite.

In the past years there has been a debate of whether the presence of a fault mirror can be used as an indicator for seismic slip (Fondriest et al., 2013; Siman-Tov et al., 2013), although nanogranular coatings have also been observed in slow slip experiments (Tisato et al., 2012; Siman-Tov et al., 2015; Verberne et al., 2014). Faults obtain their mirror-like appearance from nanometric roughness, and in several slip experiments fault mirrors are correlated with a nanogranular coating, making nano-grains part of the debate on microstructural indicators for seismic slip. Our samples now conclusively indicate that a nano-granular coating is found even on samples that have only been heated, i.e. they have not experienced slip, nor have they experienced a normal load. Hence, slip and normal load are not prerequisite to the formation of nanograins, only heat is sufficient. The easy formation of new nanoparticles in these experiments, also for the fault mirror, thus advocates some caution with the interpretation of natural and experimental microstructures, and calls for new descriptions and criteria to categorize nanograins. Our experiments provide some geometrical constraints: although the nanograins are similar in size and shape, they are uniformly distributed in the heated fault mirror and manually polished sample whereas they line up in the unheated fault mirror sample. Alignment in the Foiana mirror varies from grain to grain, perhaps associated with the local sliding direction on each asperity. It is important to note here that not all natural fault mirrors contain aligned nanoparticles (e.g. Siman-Tov et al., 2013, did not exhibit aligned nanoparticles). Furthermore, within the fault mirrors the nanograins form a compact, resistant layer, which forms the light-reflective surface. The compactness of the layer has been interpreted to be due to sintering (e.g. Siman-Tov et al., 2015). CaO and MgO will form sintered layers at high temperatures. However, upon cooling and reaction with CO₂ to form calcite and Mg-calcite, there will be a substantial increase in volume. The re-carbonation of a sintered layer of oxides would be expected to progress from a discrete number of nucleation points. It therefore seems unlikely that a sintered layer of oxides upon re-carbonation would transform into a homogeneously sintered and compact layer of calcites, implying heat alone will not create a geometry similar to that seen in the fault mirror. Together, the geometrical differences between our heated samples and natural fault mirrors suggests that not all nanograins are the same and it strongly supports the notion that a shear-induced mechanism is necessary to generate the fault mirrors observed in nature. To better distinguish

formation mechanisms we call for a better classification and categorization of nanograins observed in nature and experiments.

Given that fracture theory predicts a limit to how small grains can get by compressive stresses (Kendall, 1978), there are two hypotheses about the formation of nanograins in fault zones: either through decarbonation (e.g. De Paola et al., 2011; Han et al., 2010), or by the pile-up and movement of dislocations (Spagnuolo et al., 2015; Verberne et al., 2014). In the first case it is the high friction at asperities which leads to high temperatures and hence to decomposition of the carbonate and subsequent crystallization of fine CaO and, in the case of dolomite, MgO particles. This process is similar to what happens in our heated samples. As we have seen, the oxide nanoparticles that form from heat cannot be expected to be preserved over geological timescales. Upon cooling and re-equilibration with CO₂ remaining in the system, the CaO and MgO from dolomite can give rise to calcite and Mg-calcite, but not dolomite. Therefore, the presence of dolomite nanoparticles would be a clear sign of dislocation-controlled nanograin formation, whereas Mg-calcite would indicate nanoparticle formation through thermal decomposition (c.f. Green et al., 2015). We have not found any reports of nanograin composition on natural fault mirrors. High velocity experiments on dolomite have shown patches of MgO and Mg-calcite nanoparticles lining some of the fault mirror surfaces (Fondriest et al., 2013; Green et al., 2015), advocating a decarbonation-related mechanism for nanograin formation in these experiments. This poses the question of whether weathering-resistant nanocoatings, similar to natural fault mirrors, are produced in high velocity friction experiments. In calcite samples, calcite nanoparticles can be formed through either route, making them more challenging to distinguish.

For future research, we propose three directions which will shed more light on the formation and nature of the nanogranular coating on carbonate fault mirrors. First, researchers should look specifically for nanograins of dolomite. Two, the weathering resistance of experimentally produced fault mirrors needs further research to understand whether the structures produced in experiments are expected to be preserved in natural outcrops. Third, we suggest friction experiments with controlled mineralogy and subsequent nanoscale reaction experiments, in order to find whether the chemical interaction with clays or other minerals influence the chemical nature and weathering resistance of the fault mirrors that are produced.

5. Conclusions

An ubiquitous feature of naturally formed fault mirror surfaces is that they are covered in a dense, resistant layer of nanograins. We have shown that nanograins form easily on carbonate surfaces that are heated above the decarbonation temperature, decreasing their mirror-like appearance. However, these nanograins, that we presume to be made up of Ca and Mg (in the case of a dolomite parent rock) oxides, react immediately upon exposure to water to form a network of bladed hydroxide crystals, which decreases the reflectivity even more. This implies that the nanograin coating on natural fault mirrors is not simply formed by heat alone (as hypothesized before) and strongly supports the notion that some mechanism related to slip is prerequisite to the formation of a resistant coating. This could either involve a dislocation-mediated break-up of the parent minerals, or the precipitation of chemically resistant nanogranular phases as a consequence of dissolved species in the fluids that percolate through the fault zone. The appearance of dolomite nanograins would be a clear indication of a dislocation-controlled nanograin formation process.

We have also shown that stresses induced by the decarbonation reaction can be large enough to induce fracturing of mm-sized samples, and propose that such a mechanism for grain size reduction should be taken into account as one of the active processes in fault zones at high temperatures.

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