SHEAR HEATING AND CLUMPED ISOTOPE REORDERING IN CARBONATE FAULTS

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ABSTRACT

Natural faults are expected to heat rapidly during seismic slip and to cool quite quickly after the slip event. Here we examine clumped isotope thermometry for its ability to identify short duration elevated temperature events along frictionally heated carbonate faults. Our approach is based on measured Δ_{47} values that reflect the distribution of oxygen and carbon isotopes in the calcite lattice, measuring the abundance of ^{13}C - ^{18}O bonds, which is affected by temperature. We examine three types of calcite rock samples: (1) crushed limestone grains that were rapidly heated and then cooled in static laboratory experiments, simulating the temperature cycle experienced by fault rock during earthquake slip; (2) limestone samples that were experimentally sheared to simulate earthquake slip events; and (3) samples from Fault Mirrors (FMs) collected from principle slip surfaces of three natural carbonate faults. Extensive FM surfaces are believed

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Abbreviations:

FM - Fault mirror.
PSZ - Principal slip zone
KG - Kfar Giladi
BL - Brown Lueders
DG - Dover gray

to form during earthquake slip. Our experimental results show that Δ_{47} values decrease rapidly (in the course of seconds) with increasing temperature and shear velocity. On the other hand, carbonate shear zones from natural faults do not show such Δ_{47} decrease. We suggest that the Δ_{47} response may be controlled by nano-size grains and highly stressed/strained grain boundaries within the carbonate fault zone that can reduce the activation energy for diffusion, and thus lead to an increased rate of isotopic disordering during shear experiments. In our laboratory experiments the high stress and strain on grain contacts and the presence of nanograins thus allows for rapid disordering so that a change in Δ_{47} occurs in a very short and relatively low intensity heating events. In natural faults it may also lead to isotopic ordering after the cessation of frictional heating thus erasing the high temperature signature of Δ_{47} .

Keywords: fault-mirror, shear heating, high-velocity shear, clumped isotope thermometry, calcite, diffusion

1. INTRODUCTION

The present study attempts to resolve two problems that are not obviously related to one another: first, we aim to find a method for recognizing past earthquakes that occurred along carbonate faults, possibly using clumped isotope thermometry; second, we aim to understand the mobilization of stable isotopes within the calcite lattice during short heating durations and its effect on clumped isotopes during such events. To address these issues, we conducted both high-velocity shear experiments and static, fast heating experiments, and measured the stable isotopes distribution as function of the experimental conditions. This approach aims to provide a quantitative thermometer for frictional heating, which has critical implications for the seismic behavior of carbonate faults (Boneh et al., 2013; Di Toro et al., 2011).

Earthquakes nucleate and propagate along faults (Scholz, 2002). Identifying past seismic events on faults contributes to our understanding of the physics of fault slip, sheds light on paleoseismology, and improves present seismic hazard assessments. The common way to identify seismic slip is by finding clues for past high temperatures experienced by the fault principal slip zone (PSZ). Slip motion on an extremely narrow shear zone (the PSZ) is expected to be accompanied by heat production (“shear heating”) due to frictional sliding, and therefore lead to an increase in temperature (McKenzie and Brune, 1972; Rice, 2006). Despite the need to understand thermal history as a recorder of the friction evolution and as a tell-tale signal of past earthquakes, there are very few methods to trace the thermal history in faults post-slip (Rowe and Griffith, 2015). Recent studies reveal possible indicators for temperature increase in sedimentary rocks using thermal maturation of organic molecules (Savage et al., 2014), and in carbonate PSZs by identifying structures related to thermal decomposition (Collettini et al., 2013; Rowe and Griffith, 2015).

Here, we test clumped isotope thermometry as a geochemical indicator for past heating of slip surfaces of carbonate faults, and hence as an indicator for past earthquake occurrences. Carbonate clumped isotope thermometry utilizes the temperature dependent preference of heavy, rare stable isotopes to bind together. This method analyzes the relative abundance of ^{13}C - ^{18}O bonds in the carbonate lattice, as is measured in CO_2 gas that is extracted from the carbonate. The Δ_{47} values reflect the over-abundance of mass 47 isotopologues with respect to that expected from random distribution of ^{13}C and ^{18}O isotopologues (Affek, 2012; Eiler, 2007; Ghosh et al., 2006; Wang et al., 2004). Equilibrium Δ_{47} varies inversely with temperature. As such, the Δ_{47} values reflect the level of order within a carbonate lattice and may be affected by heat induced reorganization of atoms within the lattice.

Several studies have examined experimentally the rate of clumped isotopes reordering by heating to high temperatures at time scales of minutes to days (Henkes et al., 2014; Passey and Henkes, 2012; Stolper and Eiler, 2015). These studies show that Δ_{47} values decrease when calcite is heated, whereas the bulk isotopic composition ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) remains unchanged. The temperature to which the carbonate is heated determines the reaction rate, which increases with temperature, as well as the equilibrium value of Δ_{47} that decreases as a function of temperature. As geologically relevant time scales are usually much longer than those of experiments, Passey and Henkes (2012) derived a first order kinetic model for clumped isotope resetting in the carbonate lattice that focuses on reordering rates derived from long term experiments (10^3 - 10^4 minutes, up to 44 days). More recently, the models also address the non first order kinetics observed in the early phase of heating experiments, in which reordering is faster (Henkes et al., 2014; Stolper and Eiler, 2015). These models allow for the theoretical calculation of expected Δ_{47} changes during short heating experiments (less than several hundred minutes), and may be

applicable for even shorter heating events, in the order of seconds or less, such as those occurring in fault slip. They suggest two different physical approaches to consider the change in reordering rates with time. Henkes et al. (2014) suggest a model involving a decrease in defect concentration with time due to defect annealing at high temperature. Stolper and Eiler, (2015) suggest a model that considers reordering as an isotope exchange reaction between neighboring carbonates within the lattice, with an early phase of fast loss of ^{13}C - ^{18}O bonds, followed by a phase of slower loss due to parallel recovery of ^{13}C - ^{18}O bonds, that is limited by diffusion of carbonate ions to create the relevant neighbors for such recovery. Here we study experimentally the influence of short-term heating (seconds) on clumped isotope reordering in calcite crystals and discuss it in the context of the Henkes et al. (2014) and Stolper and Eiler, (2015) observations and models. By comparing the experimental data to Δ_{47} in PSZ samples from natural faults, we consider the possible effects of grain-size reduction, crystal defects, and high stress and strain on Δ_{47} through reduction of activation energy of diffusion under shear conditions.

A main aim of this paper is to analyze Δ_{47} changes induced by shear heating in faults. We study the region within the fault where shear heating is expected to be most intense. In carbonate faults this region is easily identified as ‘fault mirrors’ (FMs), which are localized regions, that focus most of the slip and most of the shear heating (Fondriest et al., 2013; Siman-Tov et al., 2015, 2013; Smith et al., 2013). Carbonate fault mirrors consist of $\sim 1\ \mu\text{m}$ layer of sintered nanograins and form in the following way: during shear, un-sheared limestone comprising micron size or larger calcite crystals is detached from the bare surfaces of the rock, broken into small fragments, and milled down to nano-size grains (Chester et al., 2005; Reches and Dewers, 2005; Siman-Tov et al., 2013; Storti et al., 2003; Wilson et al., 2005). This comminution process also induces a large number of crystal defects that may form a dense array of grain boundaries

and eventually nanograins (Koch, 1997; Siman-Tov et al., 2013). Under extreme heat and stress conditions, as prevail within the principle slip zone of rapidly sliding faults, the nanograins become sintered together into hard, shiny, very smooth surfaces, termed fault mirrors (FMs, see Siman-Tov et al., 2015, 2013; Smith et al., 2013). The critical velocity for FM formation was observed experimentally to be >0.05 m/s, when using a load of 1-27 MPa and slip displacement >0.02 m (Fondriest et al., 2013; Siman-Tov et al., 2015; Smith et al., 2013). Therefore, FMs were suggested as an indicator for seismic slip in relatively shallow-crust carbonate faults.

Fault mirrors are expected to be well suited for studying the relations between shear heating and clumped isotope in the shallow-crust (<1 km). At this depth, the clumped isotopes values of background rock material most likely reflect the temperature during the original carbonate deposition (at Earth surface conditions) with diagenetic modifications at temperatures relevant to the shallow crust. These would be clearly distinguishable from the expected heating signals of fault mirrors.

2. MATERIAL AND METHODS

We explore the change in Δ_{47} by experiments of either static heating or shear heating in which limestone is sheared under variable slip rates. These two sets of experimental samples (described below) are compared to samples collected from natural FMs that constitute the principle slip zones of natural faults that are thought to have experienced earthquakes.

2.1. ROCK SAMPLES AND GEOLOGICAL SETTINGS

The static heating experiments were conducted using powdered limestone from Kfar Giladi (KG) quarry, northern Israel ($33^{\circ}14'29''\text{N}$, $35^{\circ}33'49''\text{E}$). The quarry is cut by a series of active faults at the margins of the Dead-Sea transform (Nuriel et al., 2012a, 2012b; Siman-Tov et al.,

2013; Weinberger et al., 2009). The KG limestones belong to the Eocene Bar-Kokhba Formation, which is a shelf facies comprised mostly of bio-micritic limestone with nummulites (Nuriel et al., 2012b; Weinberger et al., 2009).

In the shear experiments we used samples of KG limestone, as well as slabs of commercially obtained Brown Lueders (BL) and Dover Gray (DG) limestones. The BL is a fine-grained Permian limestone from Lueders, Texas. It is a bio-micritic rock mostly comprised of calcite with ~15% porosity and is macroscopically homogenous and isotropic (Heard et al., 1972). The DG is a crystalline, low porosity light gray Carboniferous limestone from the Wabaunsee group in Kansas (Moore, 1936).

We analyzed three natural fault surfaces: from the KG quarry (Israel; described above), from the Spoleto thrust (42°44'3"N, 12°45'12"E), and from the Monte Maggio fault (42°45'42"N, 12°56'27"E) both in the Umbria-Marche Apennines (Italy). FM surfaces in KG quarry were sampled from an oblique strike-slip segment (Siman-Tov et al., 2013). The fault strikes NNE-SSW and cuts through the Bar-Kokhba Eocene limestone. The estimated total displacement along this segment is 10-100 m, and fault exhumation is estimated as <100 m (Siman-Tov et al., 2015). Spoleto is a thrust fault that was exhumed from ~1.6 km depth and accumulated 5-10 km of displacement during the Middle Miocene - Lower Pliocene (Collettini et al., 2013; Tesei et al., 2013). Monte Maggio fault is an oblique-normal fault with estimated fault exhumation of ~2 km and a total displacement of ~650 m, which likely accumulated during upper Pliocene to Quaternary (Collettini et al., 2014). The fault cuts through the massive limestones of Calcare Massiccio Formation of Lower Jurassic.

2.2. STATIC HEATING

To investigate the effect of short period heating on Δ_{47} values, we conducted a series of static heating experiments of short duration (seconds) and long duration (72 hours) using KG powder samples. We examined the effects of maximum temperature ($T_{\max}$) and cooling rate on short heating duration samples. Powdered KG limestone ($105 < d < 250 \mu\text{m}$) was vacuum dried at 50 °C and 50-200 mg aliquots were heated inside gold capsules, to which a thermocouple was attached. In general, the capsules were closed but not sealed (see section 1.1.1 in supplementary material; SM) and therefore were exposed to ambient room conditions. Detailed experimental conditions are given in Table 1 and in SM (section 1.1.1, 1.1.2, Table S1, and Figs. S1-S4).

2.3. ROCK SHEAR EXPERIMENTS

2.3.1. EXPERIMENTAL PROCEDURE

The experiments were conducted using a rotary shear apparatus (ROGA) in which two rock blocks are sheared through the rotation of the lower block against a static upper block (Boneh et al., 2013; Reches and Lockner, 2010) (Fig. S5). The setup is capable of applying normal stresses up to 35 MPa, slip velocities of 0.001 to 2 m/s, and unlimited slip distance. Both blocks were ground flat, then roughened with #600 SiC grit and dried for ~24 hr at 100 °C. All experiments were run at room temperature and ambient humidity. Normal load, shear load, slip velocity, fault normal displacement, and block temperature were monitored continuously during the experiment (Table S2).

We report 33 Δ_{47} values of reference and sheared samples that were collected from 12 experimental runs using the three different carbonate rocks. After each set of experiments, the following material was sampled for isotopic analysis from the sheared surface: smeared rock powder that covers the slip surface (gouge), which is the product of wear by scratching,

ploughing and delamination of fault surfaces that are continuously being crushed during slip; delaminated flakes of FMs formed in the experiment; and reference material of undeformed rock.

2.3.2. ROCK TEMPERATURE IN SHEAR EXPERIMENTS

We modeled the 3D heat conduction in the shear experiments to calculate the temperature at the slip surface. The model assumes that all the mechanical work is converted into heat (Rice, 2006), and that conduction is the only mechanism of heat transfer within the rock blocks. The heat source time evolution is the experimental mechanical power density, $PD = \tau(t) \cdot v(t)$ (units of W/m^2), which was calculated from the experimental record of slip velocity, v , and shear stress, τ . The model was validated by temperature measured at two positions embedded within the stationary block (Fig. S6).

The temperature experienced by the experimental fault and its surrounding was simulated using the COMSOL Multiphysics software. The 3D finite-element model of the experimental fault structure considers a boundary condition of a planar heat source in the middle of a 100 μm thick gouge layer bound by two solid rock blocks. This structure follows the post shear structure of the high-velocity experiments that displayed an ultrathin slip surface ($\sim 1 \mu m$) within the gouge layer (Siman-Tov et al., 2015). Variability in mechanical and thermal parameters (specific heat capacity, coefficient of thermal conductivity, rock density) as well as structural and measurement errors produce an error of up to 15% in modeled temperature. More details about the model and its constraints are given in section 1.2.2 of the SM and in Table S3.

2.4. SAMPLING OF NATURAL FAULTS

Three natural fault outcrops were sampled for isotopic analyses. We sampled FM surfaces assuming that these structures were exposed to the maximum temperature increase during the slip

event. The field samples of mirror surfaces were carefully scraped with a scalpel to collect only the PSZ layer of the reflective surfaces, which is less than 10 μm thick. These PSZ samples were compared with reference samples of the non-sheared source rock. The KG reference was an Eocene limestone from Bar-Kokhba Formation. The reference samples for Spoleto and Monte Maggio faults are respective samples of Calcare Massiccio limestone collected in the damage zone far (>10 cm) from the PSZ layer.

2.5. ISOTOPIC ANALYSIS

All three types of samples were analyzed for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} using standard procedures (Ghosh et al., 2006; Huntington et al., 2009). Briefly, ~ 4 mg CaCO_3 was digested overnight in 103% H_3PO_4 at 25 $^\circ\text{C}$. CO_2 was extracted cryogenically on a vacuum line and cleaned by passing it through a GC column (Supelco Q-Plot, 30 m x 0.53 mm, held at -20 $^\circ\text{C}$). Measurements were performed using a Thermo MAT-253 gas source isotope ratio mass spectrometer that was modified to measure masses 44-49 in a dual inlet mode. Each measurement consisted of 90 cycles of sample-standard comparison, with a signal integration time of 8 s.

Δ_{47} is defined as the excess of the mass 47 signal in CO_2 over what is expected based on random distribution of ^{13}C and ^{18}O among all CO_2 isotopologues (Eiler, 2007; Wang et al., 2004):

$$\Delta_{47} = \left[\left(\frac{R_{47}}{R_{47}^*} - 1 \right) - \left(\frac{R_{46}}{R_{46}^*} - 1 \right) - \left(\frac{R_{45}}{R_{45}^*} - 1 \right) \right] \times 1000 \quad (1)$$

where R_{47} , R_{46} , and R_{45} are measured values of $R_i = (\text{mass } i)/(\text{mass } 44)$, and R_i^* are calculated values for isotopologues at random distribution.

Data is reported in the absolute reference frame. Overall standardization is done using CO_2 at equilibrium at several temperatures and tested day-to-day using materials that are traceable to that

reference frame (Zaarur et al., 2013). The typical Yale laboratory uncertainty is $\pm 0.02\text{‰}$ for a non-replicated sample. The uncertainty for our data set is estimated from 5 replicates of 1 sample (# 2055) as $\pm 0.012\text{‰}$ (± 1 SE), which is slightly higher than usual.

$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, are reported versus the VPDB standard reference frame using a pre-calibrated CO_2 tank used as a reference gas, with values of -15.80‰ and -3.64‰ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, respectively. These values are verified using the standard NBS-19 with measured $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of $-2.17 \pm 0.04\text{‰}$ and $+2.11 \pm 0.13\text{‰}$ (1 SD, $n = 12$), respectively, which are comparable to its nominal values of -2.2‰ and $+1.95\text{‰}$ (Zaarur et al., 2013). Oxygen isotopic fractionation factors associated with the acid digestion reaction at 25°C is taken as $^{18}\alpha_{\text{acid}} = 1.01030$ for calcite (Kim et al., 2007).

3. RESULTS

3.1. Δ_{47} VALUES UNDER STATIC HEATING

Samples heated at $T \leq 400^\circ\text{C}$ display Δ_{47} values similar to those of the reference, unheated, samples ($0.64\text{--}0.67\text{‰}$; Fig. 1). In contrast, samples held for a few seconds at temperatures between 500 and $1,000^\circ\text{C}$ show a decrease in Δ_{47} values (Fig. 1, Table S4), to values of $0.24\text{--}0.32\text{‰}$ at $T \geq 800^\circ\text{C}$ (e.g., experiments D102-107, blue circles in Fig. 1), similar to values observed in longer heating (3 min – 44 days) at $T > 500^\circ\text{C}$ (Passey and Henkes, 2012; Stolper and Eiler, 2015), reflecting randomization (or close to it) of the isotopes.

Our observations of very low Δ_{47} values for short heating events suggest that at these high temperatures, short heating is sufficient for randomization of the isotopes. No significant difference was observed in Δ_{47} values between experiments in which cooling was rapid (by dropping the capsules into liquid nitrogen; # D201-D208, green diamonds in Fig. 1), and

experiments in which cooling was slower (# D401-D408, black squares in Fig. 1), suggesting that cooling rates at these short time scales have no effect on the final Δ_{47} value. The maximal temperature in which the sample was held and the time spent at that temperature are the major controlling factors on the Δ_{47} values (Fig. 1). An effect of heating duration was observed in samples heated to 400 °C. The short heating experiments (# D205 and D405) show no change in Δ_{47} value, but Δ_{47} decreased by 0.1 ‰ when the sample was heated for 72 hours. No significant difference is observed between samples heated with or without added water (# D101-D103 and # D106-D107 versus # D104-D105). No difference in Δ_{47} was observed between sealed (# D106-D107) or unsealed capsules (# D102-D103) in the early experiments, so all further experiments were conducted in closed but not sealed capsules.

Although Δ_{47} values decreased with increasing temperature, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values remained unchanged in all short duration (~10s of seconds) heating experiments (Fig. 1), as has also been observed in calcite heating for longer times (Henkes et al., 2014; Passey and Henkes, 2012; Stolper and Eiler, 2015). At 72 hours heating experiments (# D304-D305 in Fig. S3) at $T \geq 600$ °C a decrease in $\delta^{13}\text{C}$ (from -4.5 to -14.6 ‰) and $\delta^{18}\text{O}$ (from -9.5 to -22.5 ‰) was observed, together with observed mass loss resulting from calcite thermal decomposition (Fig. 1). In our experiments, calcite decomposition most likely occurred because the samples were heated at room conditions, unlike previous experiments that were conducted under a CO_2 atmosphere (Henkes et al., 2014; Passey and Henkes, 2012; Stolper and Eiler, 2015). During thermal decomposition of calcite the heavy isotopes are preferentially partitioned into the CO_2 released, leaving more depleted calcite crystals (De Paola et al., 2011). In these experiments Δ_{47} values were surprisingly high (0.50 and 1.07 ‰ at 600 and 800 °C, respectively), likely reflecting fractionation during thermal decomposition or inefficient acid digestion of these samples perhaps

due to the presence of CaO. These samples therefore do not reflect the influence of heating and are not discussed further. In summary, a decrease in Δ_{47} values occurs within seconds in carbonate solids heated to temperatures ≥ 500 °C and thus potentially provide an indicator for very short heating events, such as in earthquakes when fault slip and associated release of heat occurs within a few seconds.

3.2. ISOTOPIC COMPOSITION IN ROCK SHEARING EXPERIMENTS

Three types of limestone (Brown Lueders, Dover Gray, and Kfar Giladi) were used for rock shear experiments at velocities of 0.001-0.63 m/s, at applied normal stress up to 3.1 MPa and slip time up to 1,000 s (Table S2). Values of Δ_{47} determined for 33 samples are listed in Table S5 and plotted in Figs. 2-4. Temperature modeling (see methods section 2.3.2) indicates that the maximal temperature ($T_{\max}$) that the samples were exposed to in these shear experiments was 420 °C (Fig. 4). For the BL limestone (experiments # 1865 and 1873 in Table S5) $\delta^{13}\text{C}$ is 1.04 ± 0.06 ‰, $\delta^{18}\text{O}$ is -4.44 ± 0.18 ‰ and Δ_{47} range between 0.46-0.66 ‰ (Fig. 2, and Table S5). The 2 higher values (0.63 ± 0.02 ‰) correspond to reference and gouge samples, whereas 5 lower values (0.53 ± 0.05 ‰) correspond to the FMs (Fig. 3). For DG (experiment # 2050-2062 and # 2287) $\delta^{13}\text{C}$ is 0.9 ± 0.2 ‰, $\delta^{18}\text{O}$ -2.9 ± 0.6 ‰ and Δ_{47} values range between 0.51-0.71 ‰ (Fig. 2). The 8 higher values (0.67 ± 0.04 ‰) correspond to reference and some gouge samples, whereas the 4 lower values (0.54 ± 0.02 ‰) correspond to other gouge samples and to FM samples (Fig. 3). For KG (experiment # 1840-1855 and # 1880-1892) $\delta^{13}\text{C}$ is -7.3 ± 0.2 ‰, $\delta^{18}\text{O}$ -9.6 ± 0.3 ‰ and Δ_{47} values range between 0.54-0.74 ‰ (Fig. 2), with no obvious correlation with sample types (Fig. 3). Fig. 4 plots all experimental results as function of $T_{\max}$, showing that Δ_{47} drops with increasing $T_{\max}$ but also that this drop in Δ_{47} may start already at low $T_{\max}$ (< 150 °C).

3.3. ISOTOPIC COMPOSITION OF CALCITES IN NATURAL FAULT MIRRORS

The Δ_{47} values in three different limestone faults range from 0.65 to 0.73 ‰ (Fig. 5 and Table S6). No significant difference in Δ_{47} or $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is observed between the slip surfaces and the respective undeformed reference host rock. In the KG quarry the Δ_{47} values for both slip surface and host rock are 0.65 - 0.68 ‰. The values of $\delta^{13}\text{C}$ (-4.5 to -5.9 ‰) and $\delta^{18}\text{O}$ (-8.8 to -9.9 ‰) for both slip surfaces and host rock, are consistent with previous host rocks measurements (Nuriel et al., 2012b). In the Spoleto and Monte Maggio faults (Italy), the Δ_{47} values are 0.71-0.73 ‰, for both fault surfaces and host rock. For Spoleto fault $\delta^{13}\text{C}$ is between 0.1 and 1.0 ‰ and $\delta^{18}\text{O}$ is $\sim$ -4.5 ‰ (Fig. 5). For Monte Maggio fault $\delta^{13}\text{C}$ is $\sim$ 2.0 ‰ and $\delta^{18}\text{O}$ is more variable, between -3.6 ‰ and -5.9 ‰ (Fig. 5). These values are similar to the value typically reported for the limestones of Calcare Massiccio and associated veins (Agosta and Kirschner, 2003; Bachan et al., 2012; Billi et al., 2007).

4. DISCUSSION

4.1. RAPID CLUMPED ISOTOPES REORDERING

The observed decrease in Δ_{47} values by static heating at $T \geq 500$ °C, accompanied by no change in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, indicates internal disordering of ^{13}C - ^{18}O bonds, even at time scales of seconds (Fig. 1). Disordering depends on both time and temperature (Henkes et al., 2014; Passey and Henkes, 2012; Stolper and Eiler, 2015). Hence, the final Δ_{47} value observed in short heating events reflects a combination of the initial Δ_{47} value, the reaction time, and the reaction rate (which depends exponentially on temperature and activation energy; Fig. 6). During long heating events Δ_{47} may reach an equilibrium value that depends on temperature, but is independent of the

initial Δ_{47} value. In short heating events only partial disordering is observed, as samples are usually cooled before reaching equilibrium (Fig. 6).

The change in Δ_{47} may occur either through isotope exchange between neighboring carbonates within the lattice (Stolper and Eiler, 2015) or through diffusion of oxygen atoms (Passey and Henkes, 2012). In either case it is a two-way process so that both disordering and ordering can occur following:

where ordering means formation of ^{13}C - ^{18}O bonds (more clumping, defined as the forward reaction). The back reaction is disordering towards random distribution and lower Δ_{47} values. For convenience, we use here the terminology of Passey and Henkes (2012); a discussion in the terms of the Stolper and Eiler (2015) model is given below.

Although diffusion rate constants do not depend on process direction (Passey and Henkes, 2012), the reaction rate strongly depends on temperature, which in turn defines the equilibrium Δ_{47} value. As initial Δ_{47} values typically reflect mineral formation at low temperatures, heating would lead to net disordering (i.e., the back reaction in Eq. (2)). Furthermore, whereas the reaction at high temperatures is relatively fast, the reaction leading to net ordering at low temperatures is much slower (Fig. 6). In two sets of experiments (# D201-D208 and # D401-D408), the samples were heated within seconds and then cooled at two different rates (Figs. S2 and S4) with no difference in Δ_{47} values. Hence, the cooling in both cases was fast enough to prevent retrograde ordering and preserve the Δ_{47} signal produced at the peak temperature (Fig. 6).

Static heating experiments of longer duration (3 min to 44 days) show decreasing Δ_{47} values as a function of temperature and time (Fig. S7; Henkes et al., 2014 (HS); Passey and Henkes, 2012

(PY); Stolper and Eiler, 2015 (S&E)). To understand the temperature-time behavior with which we can compare our short experiments, we divide the HS & PY data into groups by heating duration: 30-100 min, 100-1,000 min, and longer than 1,000 min and compare it with our and S&E results (Fig. 7). When Δ_{47} is plotted versus maximum heating temperature, the data arrays are described by a combination of exponents that take the form of an error function, in which long heating times allow Δ_{47} to approach equilibrium values at lower temperatures (e.g., ~200 °C at geological time scales versus ~500 °C at laboratory time scales of hours to days). Within a single temperature band (e.g., 425 °C) longer heating duration result in lower Δ_{47} values that are closer to equilibrium at that temperature, relative to short experiments.

Passey and Henkes (2012) derived an approximate model that considers a constant number of ‘equilibrium defects’ but neglects the initial stage of ‘defect annealing’. More complete models that include non first order kinetics were suggested by HS and S&E, with two different physical models to address the high disordering rates at short heating experiments. Our data is consistent with both models; we compare our results to the HS ‘transient defect/equilibrium defect’ model that considers the decrease in C-O bond disordering rate as a result of annealing in transient defects (Henkes et al., 2014). The integrated rate for this model is given by their equation 5:

$$\Delta_{47}(t, T) = \Delta_{47}^{eq}(T) + (\Delta_{47}^{init} - \Delta_{47}^{eq}(T)) e^{-k_c t} e^{\frac{k_d}{k_2} (e^{-k_2 t} - 1)} \quad (3)$$

where $\Delta_{47}^{eq}(T)$ and Δ_{47}^{init} are the equilibrium Δ_{47} value at a given temperature and the initial Δ_{47} value, respectively. T is the temperature in K. k_c , k_d , and k_2 are rate constants describing the reordering behavior due to equilibrium defects, the efficacy of transient defects at inducing reordering, and the loss of transient defects with time, respectively. These reaction rates (k_i)

strongly depend on the activation energies, E_a , and the ambient temperature according to an Arrhenius relation (Henkes et al., 2014):

$$k_i = K_i e^{-\left(\frac{E_a}{R}\right) \frac{1}{T}} \quad (4)$$

where K_i is a constant known as the frequency factor and R is the gas constant. $\Delta_{47}^{eq}(T)$ is the equilibrium curve of Δ_{47} versus the temperature which is calculated as a fourth order polynomial fit to experimental data (Equation 5 in Passey and Henkes, 2012). Using this model and the Arrhenius parameters given in Table B1 in Henkes et al., (2014), we calculate expected Δ_{47} values for different heating durations, with our short heating experimental data being consistent with these theoretical curves for 0.1-10 s (Fig. 7).

4.2. SHEAR INDUCED DISORDERING

The Δ_{47} values of experimentally sheared samples are lower than the reference values of the undeformed rocks, with a significant decrease observed in the FMs formed in the Dover Gray and Brown Lueders experiments (Figs. 2, 3). The shear experiments had a relatively low $T_{\max}$ (up to 420 ± 65 °C; Fig. 4) yet they reduced Δ_{47} signal considerably (Figs. 2, 3). We found that the average $T_{\max}$ required to reduce Δ_{47} in shear experiments is ~ 250 °C, which is significantly lower than $T_{\max}$ required to produce a similar Δ_{47} signal in static heating experiments (≥ 500 °C).

We suggest two possible explanations for the decrease in Δ_{47} values of the sheared samples:

(1) **Thermal Effects:** It is possible that our temperature model for $T_{\max}$ underestimates the actual maximum temperatures on the slip surface because it does not include possible heterogeneity in shear heating. A “hot spot” instability often arises during sliding (Brown and Fialko, 2012) and when this happens it significantly increase local $T_{\max}$ in some places on the slip

surface, while reducing $T_{\max}$ in adjacent locations, a few millimeters away. This instability, well known in engineering, was recently suggested to cause formation of FM patches (Siman-Tov et al., 2015). The spatial fluctuations due to hot spot instability was measured by Brown and Fialko, (2012) to be up to ± 100 °C. Such variability is not sufficient to explain Δ_{47} reduction in shear experiments observed at average $T_{\max} \sim 250$ °C.

(2) **Structural Effects:** Reordering processes may be enhanced at the PSZ because the activation energy (E_a) for diffusion is reduced or because of increased driving forces for diffusion that increases the frequency factor K_i , relative to the bulk rock. The activation energy and the frequency factor values may be changed by the ultra-fine grain-size in the PSZ, the high abundance of defects, and the high stress and strain at grain contacts. Given the exponential dependence of diffusion rates on the activation energy term, we focus on the potential effects of changing it on reordering. Lower activation energy for reordering in the PSZ may considerably enhance Δ_{47} changes both during and after slip and may thus affect natural faults over geological times (see section 4.3).

E_a is expected to be lowered in the PSZ via several processes: Mechanical milling during shear of fault surfaces induces accumulation of defects, increases the relative proportion of grain boundaries, and reduces grain size to the nano-scale (Koch, 1997; Siman-Tov et al., 2013). Atomic diffusion is enhanced both within the bulk of the lattice due to internal defects and on surfaces due to the large number of grain boundaries. A grain size effect on E_a arises in nanograins because they have a much higher free energy than >1 μm crystals, due to their large surface to volume ratio (Guisbiers and Buchaillot, 2008; Sun, 2007).

In addition, we propose, based on previous studies in other stressed materials (e.g. Brune et al., 1995; Muller and Saul, 2004; Shu et al., 2001), that high stress and strain at grain surfaces

within the PSZ may reduce the activation energy for surface diffusion. This effect is significant; in metals a 5% strain was measured to cause a 3 fold reduction in E_a for surface diffusion (e.g. Brune et al., 1995). Thus in a PSZ fault, the structural effect includes high shear stress and strain, nano-size grains, and an increase of defect concentration, the combination of which can lower the activation energy relative to $E_{a,bulk}$. Such reduction may allow rapid reordering kinetics within the fault, even at relatively low temperatures. For example, if $E_{a,PSZ} = 0.5E_{a,bulk}$ and $E_{a,bulk} = 180$ kJ/mol, the structural effect increases the atomic mobility by 15 orders of magnitude at $T = 50$ °C, and by 6 orders of magnitude at $T = 500$ °C. This mechanism may be significant for both co-slip and post-slip clumped isotopes reordering, since it does not require the actual slip motion; once the PSZ material have been milled to nanograins and as long as shear stress is applied on the PSZ, or if shear strain is not relaxed, $E_{a,PSZ} < E_{a,bulk}$ leading to high reordering rates also in the absence of high temperature.

The structural effect may increase reordering rates irrespective of the physical model used to describe the disordering during heating (Henkes et al., 2014; Stolper and Eiler, 2015). The Henkes et al. (2014) model suggests that reordering is driven by defects. As such, an increase of defect concentration by milling directly enhances reordering rates. In addition, high shear stresses and strains may mobilize defects at higher rates and enhance reordering. Stolper and Eiler (2015) suggest a deficit of carbonate pairs that each includes one heavy isotope (namely, neighboring $^{13}C^{16}O_3$ and $^{12}C^{16}O_2^{18}O$) as a reason for the fast reordering in short heating durations, with the formation of such pairs in longer times leading to a decrease in disordering rates. The formation of $^{13}C^{16}O_3$ - $^{12}C^{16}O_2^{18}O$ pairs over time requires long range diffusion of carbonate units which is likely to occur through defects, and therefore may also be enhanced by an increase in defect concentrations in the nano-size grains following shear.

We calculated Δ_{47} using a variety of $E_{a,PSZ}$ values, assuming different heating temperatures and different heating durations (Fig. 8). The Δ_{47} signal measured for the experimentally sheared samples constrain $E_{a,PSZ}$ to be greater than $0.4E_{a,bulk}$. Such a lower $E_{a,PSZ}$ would erase the disordering signal within a few minutes, which is the duration the sample remained under stress after the experiments. We therefore plot the model results for $E_{a,PSZ} = 0.5E_{a,bulk}$ (reduced E_a for k_c and k_d in Equation 3) assuming it is the maximum possible decrease in E_a . As a sensitivity test we add the model results for $E_{a,PSZ} = 0.9E_{a,bulk}$, which show insignificant effect on Δ_{47} values.

In summary, we discussed two possible mechanisms for disordering during shear: 1) reduction of the activation energy or 2) non homogeneous heating. The thermal effect is ignored in the next section in which we discuss post-slip periods, and concentrate on the structural effects for geological time scales.

4.3. REORDERING ALONG NATURAL FAULTS

Reduction in Δ_{47} values is observed in most shear experiments (Fig. 2) yet samples collected from natural carbonate FMs show no difference in Δ_{47} values between FMs and host rock material (Fig. 5). As FMs are the most deformed part of a fault zone the lack of observed change in Δ_{47} in these natural FMs may indicate either that disordering did not occur in the natural faults that we examined, or that the disordering signature was lost in post-slip processes.

It is possible that co-slip temperature conditions in these natural faults did not produce significant clumped isotope disordering, either because T_{max} was not high enough or it was not sustained for long enough time. This is, however, unlikely since at least for the Spoleto fault (Collettini et al., 2013) there is independent evidence for high temperature (>600 °C) and heating duration sufficiently long to allow calcite dissociation. Slip during earthquakes is likely shorter

than in some of our laboratory experiments (a few seconds in nature versus 0.5-60 s in the laboratory). However, extensive FM coverage as found in our sampled faults is believed to form only at high slip velocities and temperatures (Fondriest et al., 2013; Siman-Tov et al., 2015; Smith et al., 2013). It is noteworthy however, that recent studies show the formation of shiny patches also in room temperature experiments: under a normal stress of 50 MPa at low velocity ($v \sim 1 \mu\text{m/s}$), without significant heating during a slip event (Verberne et al., 2014a, 2014b) and therefore no expected isotopic disordering. Yet those experimentally observed low velocity FMs show sub-micron-structures that are different than the high velocity FMs, and also present very small lateral continuity (De Paola et al., 2015; Siman-Tov et al., 2015) which is different than the FM examined here.

Another possible reason for lack of Δ_{47} signal is that coarse sampling may lead to mixing of FM material with less sheared material. Our sampling method was the same in the shear experiments and in natural faults, arguing against a methodological reason for the lack of Δ_{47} decrease in natural faults.

We thus deduce that disordering of clumped isotopes likely occurred during the seismic slip, similar to that in our shear experiments, but was followed by post-slip processes that erased this signal. As the shiny surface characteristic of FM sintered nanograins texture (Siman-Tov et al., 2013) is preserved, it is unlikely that the sheared material has been removed by weathering or altered by recrystallization of the calcite, which would coarsen the grains and alter $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, both of which are not observed.

A post-slip mechanism that may increase the rate of reordering at low temperatures in the FM and increase Δ_{47} values in the natural faults requires a reduction in activation energy at the fault surface ($E_{a,\text{PSZ}} < E_{a,\text{bulk}}$). Such reduction may be the result of nanograin FM texture, high

concentration of crystal defects, and the high shear stress and strain on contacts within the fault PSZ, making the PSZs more reactive than the bulk. This mechanism was discussed above as promoting disordering at relatively low temperatures during shear experiments, but is also relevant for post-slip ordering. Within minutes after the slip event, the PSZ temperature decreases back close to pre-slip ambient temperatures. For the minerals away from the PSZ, with kinetics controlled by $E_{a,bulk}$, more than 100 Ma would be required to reach Δ_{47} equilibrium values at these low temperatures (Fig. 7). In the PSZ, however, where E_a is likely reduced, ordering rates may be faster by orders of magnitude. For example, an increase of Δ_{47} from 0.45‰ to an equilibrium value of 0.65‰ by ordering takes: >100 Ma for $E_{a,PSZ} > 0.8E_{a,bulk}$ but ~100 ka, for $E_{a,PSZ} = \sim 0.7E_{a,bulk}$. These are the time scales that are relevant for the KG fault, in which structural evidence suggests no seismic activity since 93 ka BP (Nuriel et al., 2012a).

We emphasize that the above arguments pertain to the very thin FM within the PSZ, where the intense shear heating takes place within nanograin layer. These arguments do not pertain to measurements made away from PSZs. For example, Swanson et al. (2012) studied Δ_{47} values up to 1 meter away from a detachment fault plane, at a distance where shear heating is unexpected. The low values measured by Swanson et al. (2012) were attributed to mineral precipitation from hot fluids.

In contrast to our observations, a significant reduction in Δ_{47} was found in shear zone samples from the Mormon Peak and the Heart Mountain detachments (Swanson, 2015). These structures were described either as detachments at the base of giant gravity slides (Anders et al., 2006) or as low angle faults (Wernicke et al., 1985). Recent analyses suggest that both structures are slides rather than low angle faults (Anders et al., 2013, 2006; Goren et al., 2010) and as such are suggested to have catastrophically slid for long durations and distances relative to seismic faults

(Anders et al., 2010). Whereas seismic slip on faults lasts seconds, catastrophic slides occur over 10s of minutes to hours (Goren et al., 2010). Such slides slip for a distance of a few kilometers in a single event, whereas faults slip only a couple of meters per event. The temperatures generated in catastrophic gravity sliding events are much higher and maintained for a longer time so that heat can be transported to a greater distance from the slip surface. These unique thermal conditions are evident in the formation of a marble band and as indicators for carbonate decomposition along the Heart mountain detachment plane (Anders et al., 2010; Goren et al., 2010). The preservation of disordered Δ_{47} signature is likely due to the higher disordering intensity that occurred in this event. Furthermore, our hypothesis for rapid ordering in the PSZ is consistent with the distribution of Δ_{47} signal in the Heart Mountain detachment. A marble layer located away from the principal slip zone has generally lower Δ_{47} values than the gouge layer of the PSZ (Swanson, 2015). It is likely that temperatures were very high all around the detachment fault, leading to a decrease in Δ_{47} , but ordering rates during and after cooling were much faster for the small grain size in the gouge zone compared to the large marble crystals. Direct comparison between simple seismically active faults and these two detachments is thus hampered by their different thermal distribution, the different fault structure (Anders et al., 2013), and also by the proximity of Heart Mountain and Mormon Peak detachments to volcanic sources and associated hydrothermal fluids (Aharonov and Anders, 2006; Anders et al., 2006).

In summary, we suggest that in addition to thermal conditions, the special structure of the PSZ may govern the rate of reordering. Nanograins and severely damaged and strained crystals, allow for faster reordering relative to undamaged crystal lattice, at both high and low temperatures. Thus although the structure of PSZ allows relatively fast disordering to occur, so that even short

shear heating events produce a signal, the same PSZ structure also allows rapid ordering and erasure of this signal.

5. CONCLUSIONS

Reorganization of carbon and oxygen atoms in a calcite lattice leads to disordering and ordering reactions that are recorded as a change in calcite Δ_{47} , with typically fast disordering at high temperatures and slow ordering at low temperatures. The extent of change depends on both the temperature and the duration of heat exposure. Short heating, in order of seconds, of coarse (105-250 μm) calcite grains leads to some decrease in Δ_{47} at temperatures above 500 °C and a significant decrease above 700 °C. Heating during shear, however, led to a significant decrease already at lower temperatures (on average at 250 °C) in the principle slip zone that formed during slip experiments. We suggest that the grinding of calcite to nanograins, the large amount of lattice defects, and the high shear stress and strain on the grain contacts may reduce the activation energy for these reactions and therefore enhances reordering in the lattice. Such increased rate of reordering may reduce the temperature at which disordering occurs in short heating events, but also may reduce the time required for ordering at low temperatures in geological settings. This is consistent with disordering observed in laboratory produced fault mirrors, but this disordering is erased in natural systems by ordering over a time scales shorter than a million years. Thus, owing to its rapid signal decay, Δ_{47} may be a promising field marker for young seismic events. To establish the validity of this hypothesis and broaden the impact of our experimental data, better constraints on the effect of grain-size, defect concentration, and applied shear stresses and strains are needed, and more natural fault systems should be studied.

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531 REFERENCES

- 532 Affek, H.P., 2012. Clumped isotope paleothermometry: Principles, applications, and challenges.
 533 In: Ivany, L.C., Huber, B. (Eds.), *Reconstructing Earth's Deep-Time Climate – The State of*
 534 *the Art in 2012*. In: *Paleontological Society Papers*. 18, 101–114.
- 535 Agosta, F., Kirschner, D.L., 2003. Fluid conduits in carbonate-hosted seismogenic normal faults
 536 of central Italy. *Journal of Geophysical Research* 108, 2221. doi:10.1029/2002JB002013
- 537 Aharonov, E., Anders, M.H., 2006. Hot water: A solution to the Heart Mountain detachment
 538 problem? *Geology* 34, 165–168. doi:10.1130/G22027.1
- 539 Anders, M.H., Christie-blick, N., Walker, C.D., 2006. Distinguishing between Rooted and
 540 Rootless Detachments : A Case Study from the Mormon Mountains of Southeastern Nevada.
 541 *The Journal of Geology* 114, 645–664.
- 542 Anders, M.H., Fouke, B.W., Zerkle, A.L., Tavarnerelli, E., Alvarez, W., Harlow, G.E., 2010. The
 543 Role of Calcining and Basal Fluidization in the Long Runout of Carbonate Slides: An
 544 Example from the Heart Mountain Slide Block, Wyoming and Montana, U.S.A. *Journal of*
 545 *Geology* 118, 577–599. doi:Doi 10.1086/656383
- 546 Anders, M.H., Schneider, J.R., Scholz, C.H., Losh, S., 2013. Mode I microfracturing and fluid
 547 flow in damage zones: The key to distinguishing faults from slides. *Journal of Structural*
 548 *Geology* 48, 113–125. doi:10.1016/j.jsg.2012.11.010
- 549 Bachan, A., van de Schootbrugge, B., Fiebig, J., McRoberts, C.A., Ciarapica, G., Payne, J.L.,
 550 2012. Carbon cycle dynamics following the end-Triassic mass extinction: Constraints from
 551 paired $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ records. *Geochemistry, Geophysics, Geosystems* 13, Q09008.
 552 doi:10.1029/2012GC004150
- 553 Billi, A., Valle, A., Brilli, M., Faccenna, C., Funiciello, R., 2007. Fracture-controlled fluid
 554 circulation and dissolutional weathering in sinkhole-prone carbonate rocks from central
 555 Italy. *Journal of Structural Geology* 29, 385–395. doi:10.1016/j.jsg.2006.09.008
- 556 Boneh, Y., Sagy, A., Reches, Z., 2013. Frictional strength and wear-rate of carbonate faults
 557 during high-velocity, steady-state sliding. *Earth and Planetary Science Letters* 381, 127–137.
 558 doi:10.1016/j.epsl.2013.08.050
- 559 Brown, K.M., Fialko, Y., 2012. “Melt welt” mechanism of extreme weakening of gabbro at
 560 seismic slip rates. *Nature* 488, 638–41. doi:10.1038/nature11370
- 561 Brune, H., Bromann, K., Röder, H., Kern, K., Jacobsen, J., Stoltze, P., Jacobsen, K.W., Nørskov,
 562 J.K., 1995. Effect of strain on surface diffusion and nucleation. *Physical Review B* 52,
 563 1314383–1325067. doi:10.1103/PhysRevB.52.R14380

- 564 Chester, J.S., Chester, F.M., Kronenberg, A.K., 2005. Fracture surface energy of the Punchbowl
565 fault, San Andreas system. *Nature* 437, 133–6. doi:10.1038/nature03942
- 566 Collettini, C., Carpenter, B.M., Viti, C., Cruciani, F., Mollo, S., Tesei, T., Trippetta, F., Valoroso,
567 L., Chiaraluce, L., 2014. Fault structure and slip localization in carbonate-bearing normal
568 faults: An example from the Northern Apennines of Italy. *Journal of Structural Geology* 67,
569 154–166. doi:10.1016/j.jsg.2014.07.017
- 570 Collettini, C., Viti, C., Tesei, T., Mollo, S., 2013. Thermal decomposition along natural carbonate
571 faults during earthquakes. *Geology* 41, 927–930. doi:10.1130/G34421.1
- 572 De Paola, N., Chiodini, G., Hirose, T., Cardellini, C., Caliro, S., Shimamoto, T., 2011. The
573 geochemical signature caused by earthquake propagation in carbonate-hosted faults. *Earth*
574 *and Planetary Science Letters* 310, 225–232. doi:10.1016/j.epsl.2011.09.001
- 575 De Paola, N., Holdsworth, R.E., Viti, C., Collettini, C., Bullock, R., 2015. Can grain size
576 sensitive flow lubricate faults during the initial stages of earthquake propagation? *Earth and*
577 *Planetary Science Letters* 431, 48–58. doi:10.1016/j.epsl.2015.09.002
- 578 Di Toro, G., Han, R., Hirose, T., De Paola, N., Nielsen, S., Mizoguchi, K., Ferri, F., Cocco, M.,
579 Shimamoto, T., 2011. Fault lubrication during earthquakes. *Nature* 471, 494–8.
580 doi:10.1038/nature09838
- 581 Eiler, J.M., 2007. “Clumped-isotope” geochemistry—The study of naturally-occurring, multiply-
582 substituted isotopologues. *Earth and Planetary Science Letters* 262, 309–327.
583 doi:10.1016/j.epsl.2007.08.020
- 584 Fondriest, M., Smith, S.A.F., Candela, T., Nielsen, S.B., Mair, K., Di Toro, G., 2013. Mirror-like
585 faults and power dissipation during earthquakes. *Geology* 41, 1175–1178.
586 doi:10.1130/G34641.1
- 587 Ghosh, P., Adkins, J., Affek, H.P., Balta, B., Guo, W., Schauble, E.A., Schrag, D., Eiler, J.M.,
588 2006. ^{13}C – ^{18}O bonds in carbonate minerals: A new kind of paleothermometer. *Geochimica*
589 *et Cosmochimica Acta* 70, 1439–1456. doi:10.1016/j.gca.2005.11.014
- 590 Goren, L., Aharonov, E., Anders, M.H., 2010. The long runout of the Heart Mountain landslide:
591 Heating, pressurization, and carbonate decomposition. *Journal of Geophysical Research* 115,
592 B10210. doi:10.1029/2009JB007113
- 593 Guisbiers, G., Buchaillot, L., 2008. Size and shape effects on creep and diffusion at the
594 nanoscale. *Nanotechnology* 19, 435701. doi:10.1088/0957-4484/19/43/435701
- 595 Heard, H.C., Borg, I.Y., Carter, N.L., Raleigh, C.B., 1972. Flow and fracture of rocks. American
596 Geophysical Union, Washington DC.

597 Henkes, G.A., Passey, B.H., Grossman, E.L., Shenton, B.J., Pérez-Huerta, A., Yancey, T.E.,
598 2014. Temperature limits for preservation of primary calcite clumped isotope
599 paleotemperatures. *Geochimica et Cosmochimica Acta* 139, 362–382.
600 doi:10.1016/j.gca.2014.04.040

601 Huntington, K.W., Eiler, J.M., Affek, H.P., Guo, W., Bonifacie, M., Yeung, L.Y., Thiagarajan,
602 N., Passey, B., Tripathi, A., Daëron, M., Came, R., 2009. Methods and limitations of
603 “clumped” CO₂ isotope (Delta47) analysis by gas-source isotope ratio mass spectrometry.
604 *Journal of mass spectrometry : JMS* 44, 1318–1329. doi:10.1002/jms.1614

605 Kim, S.T., O’Neil, J.R., Hillaire-Marcel, C., Mucci, A., 2007. Oxygen isotope fractionation
606 between synthetic aragonite and water: Influence of temperature and Mg²⁺ concentration.
607 *Geochimica et Cosmochimica Acta* 71, 4704–4715.

608 Koch, C.C., 1997. Synthesis of nanostructured materials by mechanical milling: problems and
609 opportunities. *Nanostructured Materials* 9, 13–22. doi:10.1016/S0965-9773(97)00014-7

610 McKenzie, D., Brune, J.N., 1972. Melting on fault planes during large earthquakes. *Geophysical*
611 *Journal of the Royal Astronomical Society* 29, 65–78.

612 Moore, R.C., 1936. Stratigraphic classification of Pennsylvanian rocks of Kansas. *Kansas Geol.*
613 *Survey Bull.* 22, 1–256.

614 Muller, P., Saul, A., 2004. Elastic effects on surface physics. *Surface Science Reports* 54, 157–
615 258. doi:10.1016/j.surfrep.2004.05.001

616 Nuriel, P., Rosenbaum, G., Zhao, J.-X., Feng, Y., Golding, S.D., Villemant, B., Weinberger, R.,
617 2012a. U-Th dating of striated fault planes. *Geology* 40, 647–650. doi:10.1130/G32970.1

618 Nuriel, P., Weinberger, R., Rosenbaum, G., Golding, S.D., Zhao, J., Tonguc Uysal, I., Bar-
619 Matthews, M., Gross, M.R., 2012b. Timing and mechanism of late-Pleistocene calcite vein
620 formation across the Dead Sea Fault Zone, northern Israel. *Journal of Structural Geology* 36,
621 43–54. doi:10.1016/j.jsg.2011.12.010

622 Passey, B.H., Henkes, G. a., 2012. Carbonate clumped isotope bond reordering and
623 geospeedometry. *Earth and Planetary Science Letters* 351-352, 223–236.
624 doi:10.1016/j.epsl.2012.07.021

625 Reches, Z., Dewers, T., 2005. Gouge formation by dynamic pulverization during earthquake
626 rupture. *Earth and Planetary Science Letters* 235, 361–374. doi:10.1016/j.epsl.2005.04.009

627 Reches, Z., Lockner, D.A., 2010. Fault weakening and earthquake instability by powder
628 lubrication. *Nature* 467, 452–5. doi:10.1038/nature09348

629 Rice, J.R., 2006. Heating and weakening of faults during earthquake slip. *Journal of Geophysical*
630 *Research* 111, B05311. doi:10.1029/2005JB004006

- 631 Rowe, C.D., Griffith, W.A., 2015. Do faults preserve a record of seismic slip: A second opinion.
632 Journal of Structural Geology 78, 1–26.
- 633 Savage, H.M., Polissar, P.J., Sheppard, R., Rowe, C.D., Brodsky, E.E., 2014. Biomarkers heat up
634 during earthquakes: New evidence of seismic slip in the rock record. *Geology* 42, 99–102.
635 doi:10.1130/G34901.1
- 636 Scholz, C.H., 2002. The mechanics of earthquakes and faulting, 2nd ed. Cambridge University
637 Press.
- 638 Shu, D.J., Liu, F., Gong, X.G., 2001. Simple generic method for predicting the effect of strain on
639 surface diffusion. *Physical Review B* 64, 245410. doi:10.1103/PhysRevB.64.245410
- 640 Siman-Tov, S., Aharonov, E., Boneh, Y., Reches, Z., 2015. Fault mirrors along carbonate faults:
641 Formation and destruction during shear experiments. *Earth and Planetary Science Letters*
642 430, 367–376. doi:10.1016/j.epsl.2015.08.031
- 643 Siman-Tov, S., Aharonov, E., Sagy, A., Emmanuel, S., 2013. Nanograins form carbonate fault
644 mirrors. *Geology* 41, 703–706. doi:10.1130/G34087.1
- 645 Smith, S.A.F., Di Toro, G., Kim, S., Ree, J.H., Nielsen, S., Billi, A., Spiess, R., 2013. Coseismic
646 recrystallization during shallow earthquake slip. *Geology* 41, 63–66. doi:10.1130/G33588.1
- 647 Stolper, D.A., Eiler, J.M., 2015. The kinetics of solid-state isotope-exchange reactions for
648 clumped isotopes: a study of inorganic calcites and apatites from natural and experimental
649 samples. *American Journal of Science* 315, 363–411. doi:10.2475/05.2015.01
- 650 Storti, F., Billi, A., Salvini, F., 2003. Particle size distributions in natural carbonate fault rocks:
651 insights for non-self-similar cataclasis. *Earth and Planetary Science Letters* 206, 173–186.
- 652 Sun, C.Q., 2007. Size dependence of nanostructures: Impact of bond order deficiency. *Progress*
653 *in Solid State Chemistry* 35, 1–159.
- 654 Swanson, E., 2015. Structural and clumped - isotope constraints on the mechanisms of
655 displacement along low - angle detachments (Chapter 5). PhD thesis, California Institute of
656 Technology, Pasadena, CA.
- 657 Swanson, E.M., Wernicke, B.P., Eiler, J.M., Losh, S., 2012. Temperatures and fluids on faults
658 based on carbonate clumped-isotope thermometry. *American Journal of Science* 312, 1–21.
659 doi:10.2475/01.2012.01
- 660 Tesei, T., Collettini, C., Viti, C., Barchi, M.R., 2013. Fault architecture and deformation
661 mechanisms in exhumed analogues of seismogenic carbonate-bearing thrusts. *Journal of*
662 *Structural Geology* 55, 167–181. doi:10.1016/j.jsg.2013.07.007

663 Verberne, B.A., Plümper, O., de Winter, D.A.M., Spiers, C.J., 2014a. Superplastic nanofibrous
664 slip zones control seismogenic fault friction. *Science* 346, 1342–4.
665 doi:10.1126/science.1259003

666 Verberne, B.A., Spiers, C.J., Niemeijer, A.R., De Bresser, J.H.P., De Winter, D.A.M., Plümper,
667 O., 2014b. Frictional properties and microstructure of calcite-rich fault gouges sheared at
668 sub-seismic sliding velocities. *Pure and Applied Geophysics* 171, 2617–2640.
669 doi:10.1007/s00024-013-0760-0

670 Wang, Z., Schauble, E. a., Eiler, J.M., 2004. Equilibrium thermodynamics of multiply substituted
671 isotopologues of molecular gases. *Geochimica et Cosmochimica Acta* 68, 4779–4797.
672 doi:10.1016/j.gca.2004.05.039

673 Weinberger, R., Gross, M.R., Sneh, A., 2009. Evolving deformation along a transform plate
674 boundary: Example from the Dead Sea Fault in northern Israel. *Tectonics* 28, TC5005.
675 doi:10.1029/2008TC002316

676 Wernicke, B., Walker, J.D., Beaufait, M.S., 1985. Structural discordance between neogene
677 detachments and frontal sevier thrusts, central Mormon Mountains, southern Nevada.
678 *Tectonics* 4, 213–246. doi:10.1029/TC004i002p00213

679 Wilson, B., Dewers, T., Reches, Z., Brune, J., 2005. Particle size and energetics of gouge from
680 earthquake rupture zones. *Nature* 434, 749–752.

681 Zaarur, S., Affek, H.P., Brandon, M.T., 2013. A revised calibration of the clumped isotope
682 thermometer. *Earth and Planetary Science Letters* 382, 47–57.
683 doi:10.1016/j.epsl.2013.07.026

684

FIGURE CAPTIONS

Fig. 1. Stable isotopes response to elevated temperatures in static heating experiments. Carbonate powder was heated for periods of: <26 s (diamonds and squares depict different cooling rates), ~30 s (circles), and 72 hours (stars) at temperatures between 100-972 °C (Table 1). Samples that did not experience thermal decomposition show no change in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, whereas a decrease in Δ_{47} is observed at high temperatures (see Table 1 for details).

Fig. 2. Isotopic data for rock samples in shear experiments. Three different limestone types were sheared: Kfar Giladi (KG, red circles), Dover Grey (DG, blue squares), and Brown Lueder (BL, green diamonds). Shear velocities ranged between 0.001-0.63 m/s, normal stress ranged between 0.4-3.1 MPa, and slip time was between 0.5-1,000 s. Δ_{47} values (A) decrease with increasing shear velocity, whereas $\delta^{18}\text{O}$ (B) and $\delta^{13}\text{C}$ (C) values do not change.

Fig. 3. Δ_{47} in shear experiments depicted by material type. Reference samples were taken far from the experimental slip surface. Powder samples are pulverized material formed by shear and collected from the slip surface. Fault Mirror (FM) samples were scratched from FM surfaces formed in shear experiments. Small symbols are data for individual samples; large symbols (with error bars) are the average (± 1 standard deviation) for each material and limestone type. In general, Δ_{47} values of sheared materials (powder or mirror) are lower than the reference, with lowest Δ_{47} values observed in Fault Mirrors.

Fig. 4. Δ_{47} values in shear experiments (blue squares, green diamonds, red circles) plotted versus the estimated maximum temperature. Samples with similar maximum temperatures (within a range of 30 °C) were averaged (large symbols).

Fig. 5. Isotopic composition of natural faults at three sites: Kfar Giladi (red circles), Spoleto (blue squares), and Monte Maggio (green diamonds), examining differences between host rock away from the fault surface (Reference), the Fault Mirror surface (up to a few micron deep), and Striated Surface (only in Kfar Giladi; these are non FM, rough surfaces, with lineation indicating slip direction). $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are consistent with previous measurements at all sites (blue strip reflects the range observed by Nuriel et al. (2012) in Kfar Giladi; red strip is the range observed in the Calcare Massiccio host rock by Bachan et al. (2012) and Billi et al. (2007) in Spoleto and Monte Maggio). No significant differences are observed between Fault Mirrors and Reference Δ_{47} , $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values.

Fig. 6. Schematic description of the clumped isotopes reordering (disordering and ordering) and the path of Δ_{47} evolution during heating and cooling of a calcite sample (black dashed line). When a calcite sample is subjected to high temperature, Δ_{47} will decrease from its initial value by the disordering reaction (green curve). Given sufficient time at high temperature it will reach a 'high-temperature equilibrium' value. If, however, the heating event is short Δ_{47} would decrease only to a 'lower value' but will not reach equilibrium. After cooling, Δ_{47} would follow the ordering curve (blue curve). The reaction rate constants are independent of the reaction direction (disordering or ordering) but temperature strongly affects the reaction rates. Therefore the ordering reaction at low temperature is much slower than disordering so that a sample will undergo only partial ordering but will not reach the 'low temperature equilibrium'.

Fig. 7. The effect of temperature and time during static heating of calcite, comparing the short heating events (1-10 seconds) in this study (blue stars; TS) with longer heating in three previous studies (Henkes et al., 2014 (HS); Passey and Henkes, 2012 (PY); Stolper and Eiler, 2015 (S&E)). Δ_{47} is plotted versus the maximum temperature experienced by each sample with colored

curves reflecting the approach to equilibrium (black dashed line depicts equilibrium) at different time scales. Data from longer heating experiments (HS and PY) are classified by heating duration: shorter than 100 min (purple squares), between 100-1,000 min (green circles), and longer than 1,000 min (orange diamonds). Data for each time group plots along an error function type shape for the relevant time scale, with higher temperature required for disordering at shorter heating events. The error function shape curves (colored solid lines) depict the theoretical kinetics of clumped isotopes reordering (Eq. (3)) for different heating durations; we used the coefficients derived by Henkes et al. (2014) to fit Δ_{47} in Brachiopod shells heated between 30 min and four days (red dots). The S&E data are for static heating experiments, for duration of 3 min to 21 days, measured in another laboratory and fits well the same general trend (black asterisks).

Fig. 8. Δ_{47} values in shear experiments (blue squares, green diamonds, red circles) and static heating experiments (blue stars) from this study plotted versus the estimated maximum temperature. Solid and dashed lines are calculated from theory. The maximum temperature was calculated by a 3D model (described in section 2.3.2 and SM). Samples with similar maximum temperatures (within a range of 30 °C) were averaged (large symbols). Lines depict the theoretical kinetics of the approach to equilibrium (black dashed curve) of clumped isotopes reordering for three different activation energies, $E_{a,bulk}$ (the original E_a value estimated by Henkes et al., 2014), and exemplified for possible reduced activation energy: 90% $E_{a,bulk}$ (dashed line) and 50% $E_{a,bulk}$ (dotted line) and two heating durations ($t = 1$ s in orange and $t = 1,000$ s in green). The mechanisms for reduction in $E_{a,bulk}$ in our experiments are discussed in the text. The static heating results fit the predicted Δ_{47} values for heating duration of <1 s. Most analyses of sheared samples can be explained by a 50% reduction in $E_{a,bulk}$ in Eq. (3) ($0.5E_{a,bulk}$). Δ_{47} values are higher than the equilibrium values at the maximum temperature of exposure during the

752 experiment, suggesting that the sheared samples have undergone only partial disordering and
753 have not reached equilibrium.

Figure 1

- Heating for ~30 s at $T > 800^\circ\text{C}$
- ◇ Fast (2-26 s) heating followed by quenching
- ★ Heating for 72 hr followed by quenching
- Fast (4-25 s) heating followed by slow cooling

Figure 2

○ Kfar Giladi ◇ Brown Lueder □ Dover gray

Figure 3

Figure 4

Figure 6

Figure 7

Figure 8

Table 1

Table 1. Experimental conditions of static heating.

Series	Sample	Weight ^a	T _{max} ^b	Heating time ^c	Time at T _{max} ^d	Cooling method ^e
		(mg)	(°C)	(s)		
1	D101-D107	100-210	800-1000	25-78	~30 s	Quenching in air, 10 min Model cooling ~30 min
2	D201-D208	50	100:100:800	2-26	<1 s	Quenching in LN ₂ , <5 s
3	D301-D305	50	25, 200:200:800	10-100	72 hr	Quenching in LN ₂ , <5 s
4	D401-D408	50	100:100:800	4-25	<1 s	Model cooling 5-40 s

^a Powder weight before heating the sample.

^b The maximum temperatures recorded by a thermocouple attached to the gold capsule. 100:100:800 indicates that each of the sample was heated to a different target T_{max} between 100 °C and 800 °C in temperature spacing of 100 °C.

^c Time required to reach T_{max} from the initial (room) temperature.

^d The time duration that the sample was held at T_{max}. For series 2 and 4 this time is <1 s as the sample was cooled immediately upon reaching T_{max}.

^e The time required to cool below 200 °C is given following the cooling method. The model cooling paths are different for series 1 and 4, since a portion of the model parameters differ between the two calculations (see supplementary material for greater information). LN₂ denotes liquid nitrogen.