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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 such 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 an 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 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, the high abundance of defects, 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}.

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).

Abbreviations: FM, Fault mirror; PSZ, Principal slip zone; KG, Kfar Giladi; BL, Brown Lueders; DG, Dover gray.

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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 ($\delta^{18}O$ and $\delta^{13}C$) 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 min, 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; this process 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 these 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 therefore most shear heating (Fondriest et al., 2013; Siman-Tov et al., 2015, 2013; Smith et al., 2013). Carbonate fault mirrors consist of ~1 μm 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 occur 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 retain the temperature during the original carbonate deposition (at Earth surface conditions) with diagenetic modifications at the relatively low 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°14′29″N, 35°33′49″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 homogeneous 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.