



Resilience of clumped C-O isotopes of calcite to mechanical twinning and dislocation slip

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Clumped isotopes offer constraints on paleotemperature of carbonate mineral precipitation in near-surface marine environments and of diagenetic burial and deformation of rocks in the subsurface. Isotopic ordering of C and O within carbonate groups of calcite may reflect equilibrium conditions during mineral nucleation and growth, whereas diffusional exchange between carbonate ions, mechanical twinning, and shear through the motion of line defects may reorder or reset clumped C-O isotopes. Previous studies have shown that clumped isotopes of calcite are altered by solid-state diffusion at temperatures as low as 100°C given sufficient geologic time. C-O isotopes of limestones may also be reordered over short times of deformation experiments when frictional heating is significant. Some natural carbonate shear zones deformed by dislocation creep accommodated by dynamic recrystallization exhibit altered C-O clumped isotopes, which may record the deformation temperature. Other shear zones show little evidence of clumped isotope change, and the effects of deformation and recovery mechanisms on mobilization of C and O to and from carbonate anions have not been identified.

We measured clumped C-O isotopes of calcite single crystals subjected to triaxial shortening parallel and perpendicular (and at 22° and 68°) to their *c*-axes at temperatures of 20, 200, and 400°C, confining pressures of 150 and 200 MPa, and a strain rate of 10^{-5} s^{-1} to test for isotopic reordering due to mechanical twinning and dislocation slip in the absence of recrystallization. Deformation mechanisms and crystallographic orientations of the deformed specimens were defined by optical and scanning electron microscopy, and electron backscattered diffraction (EBSD). Clumped isotope mass 47 values (Δ_{47} due to associated ^{13}C and ^{18}O) of CO_2 (upon carbonate acid digestion at 90°C and manual line preparation) were measured by gas source mass spectrometry.

Crystals shortened perpendicular to *c* and the mirror plane deformed by extensive *e*-twinning with lesser amounts of *r*-slip near sample-piston boundaries where strains are inhomogeneous. Crystals shortened parallel to *c* deformed primarily by dislocation slip on the *r*-plane with some *f*-slip suggested by microstructures and crystallographic rotations; mechanical *e*-twins are restricted to sample ends where strains were affected by rigid-piston boundary conditions. None of the deformed samples display newly recrystallized grains.

Multiple clumped isotope measurements were made within domains of each deformed crystal (9 mm diam, ~16 mm long), defined by their microstructures and crystallographic orientations. Triplicate measurements of clumped C-O isotope (Δ_{47}) values are in good agreement (± 0.02) within each domain and with the original clumped isotope measurements of undeformed crystals, irrespective of their formation temperatures (indicated by $\Delta_{47} = 0.38, 0.51, \text{ and } 0.53$) or intracrystalline deformation mechanisms. We conclude that neither mechanical twinning (on the *e*-plane) nor dislocation slip (on the *r*- or *f*-planes) affect C-O isotope ordering, and that deformation events will alter clumped isotopic compositions only when temperatures are sufficiently high for diffusional C-O reordering or reset by dynamic recrystallization. These results also reveal that the Ca-O bonds alone are broken and re-established during twinning and slip, and that strongly bonded carbonate groups maintain their integrity during twinning and slip.