The geology, physics and chemistry of earthquakes hosted in carbonate-built rocks



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2) Experimental results

Observations regarding friction in carbonates at seismic slip rates

3) Processes at seismic slip initiation

Fast moving dislocations and flash weakening in calcite

4) Processes during and at the end of seismic slip

Grain Boundary Sliding and superplastic behavior

Why carbonates?

Epicenters overlap with thick sequences (4-10 km) of carbonate- built (calcite and dolomite) rocks (case for Italy and Greece).



Why carbonates?

Carbonate-built fault zone exhumed from 2-3 km depth

(Campo Imperatore Fault Zone, Italy).





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Mirror-like surfaces (Campo Imperatore Fault Zone, Italy).



Demurtas et al., JSG 2016

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Demurtas et al., JSG 2016

Great earthquakes: Slip-up-to-thetrench in carbonate biogenic oozes in megathrusts earthquakes

Courtesy of C. Agnini 1005 0 - 50 m 50 - 100 m 5 um 100 - 200 n 200 - 300 n 300 - 500 m 300 - 500 r 500 - 1,000 r 500 - 1000 100°W 120°W Friction test Site U1412 sample 0 m location silty clays 100 m 200 m biogenic oozes

Vannucchi et al., Nat. Geos. 2017



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What happens in a fault patch at the passage of the EQ rupture front?



Both result in mechano-chemical reactions (CO_2 emission, etc.) and control the frictional evolution at a fault patch.





SHIVA owns an environmental/vacuum chamber equipped with a mass spectrometer. Fluid pressurizing system.









CALCITE One breakdown reaction DOLOMITE Two breakdown reactions



T = 550°C MgCa(CO₃)₂→ MgO+(Ca,Mg)CO₃+CO₂

T = 800°C $CaCO_3 \rightarrow CaO+CO_2$



100 μm

Slipping zone

Slipping zone

Ca

Fluid pressure vessel



Cohesive calcite-built rocks: thermo-mechanical pressurization contribution to weakening negligible.



- τ_{ss} similar under room humidity, drained and undrained conditions;
- Negligible shortening in all conditions;
- Small measured pore fluid overpressure

Gouge holder



Stationary side (normal stress)

Rotary side

Designed by S. Nielsen Smith et al., Geology , 2013 Non-cohesive calcite-bearing rocks. Friction: strong velocity-dependence.







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Flash heating (and weakening):

- short duration (<< 1 ms) asperity-scale process
- high "local" temperatures (T > 800 °C)
- low friction at low "bulk" T (< 100 °C)



Short slip experiments on cohesive Carrara marble (99 % calcite)





Spagnuolo et al., Nat.Sci.Rep. 2015

Short slip experiments on cohesive Carrara marble (99 % calcite)





Spagnuolo et al., Nat.Sci.Rep. 2015

Experiments in vessel to determine gas emission during slip. Mass spectrometer with cable inserted in vessel.





Spagnuolo et al., Nat.Sci.Rep. 2015

Slip resulted in emission of:

- CO_2 for slip = 1.5 mm.
- CO_2 , H_2 and C_xH_y (methane) for larger slips.

These chemical species were not detected in tests without rock samples.







- Samples recovered with gloves and covered with Pt for FIB-SEM and TEM investigations.
- No graphite in starting Carrara marble

- Focused Ion Beam SEM.
- Electron transparent foils investigated with HRTEM



Spagnuolo et al., Nat.Sci.Rep., 2015

Nanograins beneath slip surface. Nanograins domains limited by fractures and bent cleavages surfaces (mosaic-like structure).











Slip = 1.5 mm

Inter-cleavage crystal domains with high dislocation density

Polycrystalline mosaicism nanostructure

Amorphous carbon-phase in the slipping zone (EDS analysis)



Slip = 5 mm Pt-layer a-C **Platinum** (g) C-Ka units) Amorph. carbon (a-C) (arb Ca-Ka, 0-Kα, ntensity Ca-Ka, ★ Calcite 0 2 4 Energy (keV) Calcite 500 nm HAADF-STEM Spagnuolo et al., Nat.Sci.Rep. 2015



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3) **Dislocations avalanches:** kinetic energy converted into heat and (nanoscale) T and P increase in the lattice (possibly several 1000 K and GPa, respectively). Effects:

- Release of CO₂
- Grain size reduction
- Formation of amorphous carbon at asperity contacts and flash weakening (friction coefficient ~0.15: Yu et al., Surf. Coat. Tech., 2007)



Estimate of T increase due to fast moving dislocations:

$$\Delta T \leq \frac{k_s l v_{\rm dis}}{16\pi\lambda} \left(\frac{2\lambda}{C_{\rm p} v_{\rm dis} b}\right)^{\frac{1}{2}}$$

 $k_s = \frac{\pi G b}{4a} (\delta x)^{-\frac{1}{2}}$ Hall-Petch shear stress intensity for pile up

$$G$$
 shear modulus calcite (35 GPa)

$$\lambda$$
 thermal conductivity calcite (5.54 N s⁻¹ K⁻¹)

$$\rho$$
 calcite density (2700 kg m⁻³)

a

Sx

 v_{dis}

$$= 2(1-v)(2-v)$$
 with v the Poisson ratio

velocity of dislocations, estimated from dislocation density, $\rho_{dis} = 10^{12} - 10^{14} \text{ m}^{-2}$ and bulk strain rate 10^4 s^{-1} :

$$\gamma = b \rho_{dis} v_{dis}$$

Armstrong & Elba, 1989



e.g. Tisato et al., JSG 2012



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Dolomite- and calcite-built rocks have similar "frictional" strength at steady-state.





Dolomite- and calcite-built rocks have small to negligible shear stress dependence with normal stress, especially at large slip rates and normal stresses. **Typical of crystal-plastic processes**.

Shear stress vs. normal stress





Slip surface Slipping zone (very porous)



Calcitic Marble

Dolomitic Marble

Slip = 5 m σ_n = 10 MPa V = 1 m/s acc. = 6.5 m/s²



Microstructural similarities are impressive

Deformation mechanism: superplastic flow of calcite by grain boundary sliding aided by diffusion creep



Superplastic behavior: grain boundary sliding aided by diffusion creep





$$\tau_{ss} = \left(\frac{\dot{\varepsilon} \, d^3 \, exp^{H} \, /_{RT}}{A}\right)^{1/n}$$

- $\dot{\mathcal{E}}$ = strain rate
- *H* = apparent activation energy
- A = pre-exponential factor
- d = grain size
- n = stress exponent

Rough extrapolation: no steady-state strain rate and temperatures; strain rates not well constrained

Grain size dependent: GBS & diffusion creep

De Paola et al., 2015 Green et al., 2015





Calcitic Marble

$$\tau_{ss} = \left(\frac{\dot{\varepsilon} d^3 exp^{H} /_{RT}}{A}\right)^{1/n}$$

Schmidt et al., 1977

T = 850° C 20 < d < 200 nm $100 < \dot{\mathcal{E}} < 10000 \text{ s}^{-1}$



$$\tau_{ss} = \left(\frac{\dot{\varepsilon} \,\mu \, d^3 \, exp^{H^*}/_{RT}}{2\varepsilon_0 \, \Omega}\right)^{1/n}$$

Davis et al., 2008

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H *= 280 KJ mole<sup>-1</sup>
n ~ 1.3
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Grain size and T-dependent process may explain rapid shear stress recovery during cooling at slip deceleration



Mirror-like, sliding surface in calcitic marble: foam-like microstructures also formed by sintering at the end of slip (FE-SEM image).

1 μm



Microporous fabric: pore-controlled advective process* (possibly vapor transport) propelled by CO₂ gas exhaust due to decarbonation.

Fast element migration:

- efficient mass transfer for grain boundary sliding during slip;
- rapid sintering of nanograins into a foamlike surface at end of slip.



^{*}permeability < 10⁻¹⁷m² in rexx calcite gouges (Rempe PhD Thesis).

Do these processes occur in nature?

Exp. and natural microstructures are very similar: mirror-like surfaces, truncated clasts....



Nature (Foiana Fault zone, Fondriest et al., Geology 2013)

Experiment

Exp. and natural microstructures are similar: possible re-crystallized calcite, foliated cataclasites, etc.



Conclusions

- 1. Destructive (also megathrust) earthquakes occur in faults cutting carbonates.
- 2. The passage of the seismic rupture front induces abrupt slip accelerations and temperature-dependent fault weakening.
- 3. At slip initiation, formation of amorphous carbon at the asperity contacts may contribute to "flash weakening".
- 4. With progressive seismic slip and bulk temperature increase, grain size dependent processes reduce fault strength.