SUPPLEMENTARY INFORMATION

Seismic fault weakening via CO₂ pressurization enhanced by mechanical deformation of dolomite fault gouges

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MATERIALS AND METHODS

Sample Preparation

A commercial dolomite powder with high purity (SD200, SungSin) was used in this study. The mean particle size of the powder was ~10 μm . The sample was mechanically deformed using a high-energy ball mill system (E_{max} , Retsch GmbH, Germany) consisting of oppositely rotating jar and turning discs that generate high impact energy (Fig. S1).

Wet milling was performed by loading the dolomite powder, distilled water, and 1-mm sized zirconia (ZrO_2) balls with a volume ratio of 2:3:4 into a 50-mL zirconia jar. The rotation speed was fixed at 1500 rpm and the grinding time was varied from 10 to 480 min. Additionally, during grinding, the temperature of the milling jar was controlled using a water cooling system.

The maximum temperature of the outer surface of grinding jar was below 50 °C. The sample was naturally dried at ambient conditions after grinding for 1–2 days

Figure S1. Schematic view of the motion of the balls and dolomite powder in a zirconia jar during high-energy ball milling.

Characterization methods

X-ray diffraction analysis

The X-ray diffraction (XRD) analysis was performed using the Rigaku SmartLab X-ray diffractometer at the Korea Institute of Geoscience and Material Resources. Cu-K α radiation was used with a tube voltage of 40 kV and current of 30 mA. The 2θ scan range was 3°–90° at an interval of 0.02°.

Brunauer–Emmett–Teller specific surface area analysis

The specific surface area of the dolomite sample was measured using a specific surface area analyzer (Micromeritics ASAP-2420) at the Jeonju Center of Korea Basic Science Institute. Before the experiment, the water adsorbed on the dolomite particle surface was

removed by heating at 300 °C for 2 h. Subsequently, the Brunauer–Emmett–Teller (BET) method involving nitrogen adsorption at 77 K was used.

Laser diffraction particle size analysis

The particle size was determined using a laser diffraction particle size analyzer (Mastersizer 3000, Malvern Panalytical, UK) at the Korea Institute of Geoscience and Material Resources. Dolomite in an aqueous colloid solution was dispersed for 10 min using a 28 kHz ultrasonic dispersing machine.

Scanning electron microscopy

Scanning electron microscopy was performed using a high-resolution scanning electron microscope (HR FE-SEM, TESCAN-MIRA3) at Kongju National University. The sample was coated with platinum (Pt) using an ion coating machine and an accelerating voltage of 10.0 kV.

Thermogravimetry and differential thermal analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed using the SDT Q600 (TA Instruments, USA) at Kangwon National University. The maximum temperature in the alumina sample holder was set to 1000 °C and a heating rate of 10 °C/min was applied. The measurements were performed under the flow of N₂ gas at a flow rate of 100 mL/min.

²⁵Mg solid-state nuclear magnetic resonance (NMR) spectroscopy

^{25}Mg magic angle spinning (MAS) NMR spectra were obtained after single-pulse excitation with a 90° ($\pi/2$) pulse length of 6 μs at a spin rate of 13 kHz at ambient temperature ($\sim 25^\circ\text{C}$) with a 4-mm HFX MAS probe using a 600 MHz (^1H NMR frequency) solid state NMR spectrometer (Agilent, USA). The ^{25}Mg chemical shift was calibrated using an external reference (MgO powder, 26.7 ppm) with respect to the MgCl_2 solution (0 ppm).

RESULT OF LASER DIFFRACTION PARTICLE SIZE ANALYSIS

Figure S2 shows the evolution of the dolomite's particle size upon grinding, as measured by the laser diffraction particle size analysis. In the volume frequency, particles ranging from several to tens of microns are generally observed, but particles smaller than 1 micrometer also exist. Upon grinding, the decrease in the particle size was abruptly observed until 30 minutes of grinding and became gradual until 120 minutes of grinding. As the grinding proceeded longer than 120 minutes, particles of several micrometers in size partly appeared again, indicating agglomeration due to the high-surface energy of the ultrafine particles

Figure S2. Variation in volumetric particle size distribution of dolomite upon grinding, measured using laser diffraction particle size analysis.

NUMERICAL METHODS

Model setup

We defined an anti-symmetric domain along the plane, $z = 0$, which indicates the center of the shear zone with a thickness of 0.01 m. The one-dimensional domain was uniformly gridded using 1200 finite elements. In the shear zone (yellow region in Fig. S3b), low-crystalline ($E_a = 220$ kJ/mol) and high-crystalline ($E_a = 320$ kJ/mol) dolomite elements were discretely assigned to 30 meshes. Thereafter, we varied the ratio of low-crystalline to high-crystalline dolomite in the shear zone from 0% (i.e., pure high-crystalline dolomite) to 50% (i.e., completely low-crystalline dolomite) by randomly distributing the low-crystalline phase in the meshed grid (Fig. S3a). For instance, four amongst 30 meshes in the shear zone were assigned to low-crystalline dolomite with $E_a = 220$ kJ/mol for the case of ~13% low-crystalline phase. In the surrounding zone (brown region), only crystalline dolomite was assigned to the meshes. The seismic slip velocity, V , in the shear zone decreased linearly from 0.5 to 0 m/s (Fig. S3c and Eq. S1), causing shear stress and dissipative frictional heating. The ambient normal stress, σ_n , was 180 MPa. Additionally, Dirichlet boundary conditions were applied, i.e., a temperature, $T = 210$ °C, and a pore pressure, $P_p = 70$ MPa, were applied to the top boundary ($z = 0.2$ m). Reflective boundary conditions, i.e., $\partial T / \partial z = 0$ and $\partial P_p / \partial z = 0$ were assigned to the bottom boundary ($z = 0$). The depth of our model is 7 km with an initial temperature of 210 °C. The initial hydrostatic pore pressure is defined as 70 MPa.

$$v(z)[\text{m/s}] = \begin{cases} 100 \times z & (0 \leq z \leq 0.005) \\ 0.5 & (z \geq 0.005) \end{cases} \quad (\text{S1})$$

Figure S3. Schematic diagram of the one-dimensional numerical modeling of the thermomechanical interactions of shear heating, CO₂ emission, and pore pressure. (a) In the shear zone, we distributed low-crystalline dolomite in uniformly meshed grids. For pure low-crystalline dolomite, 15 of 30 elements in the shear zone contain the phase with $E_a = 220$ kJ/mol. For pure high-crystalline dolomite, we added the phase with $E_a = 320$ kJ/mol to all elements. (b) The yellow and brown regions are the shear zone and surroundings, respectively. (c) Differential seismic slip occurs at the top of the shear zone. The normal stress is uniform in the whole domain.

Governing equations

The thermal decomposition and CO₂ emission of dolomite can be described with the following chemical reaction:

The reaction kinetics of CO₂ emission were quantified using the Arrhenius relationship, $v = A \exp(-E_a/RT)$, where v , A , E_a , R , and T are the reaction rate coefficient, kinetic constant, activation energy, universal gas constant, and absolute temperature, respectively (see Table S1). In our modelling, normal stress and ambient temperature are ~180 MPa and 210 °C, respectively. Under these conditions, the state of CO₂ is supercritical (Sulem and Famin, 2009). We defined the mass of CO₂ per unit volume as m_f . The time derivative of m_{CO_2} can be expressed as:

$$\frac{\partial m_f}{\partial t} = \frac{\partial m_d}{\partial t} - \frac{\partial q_f}{\partial z}, \quad (S3)$$

where $q_f = -\frac{\rho_f k_f}{\eta_f} \frac{\partial P_p}{\partial z}$, z , m_d , and q_f represent the spatial coordinate, mass of CO₂ released owing to thermal decomposition, and CO₂ flux, respectively. Further, ρ_f , η_f , k_f , and P_p represent the density and viscosity of CO₂, permeability, and pore pressure, respectively. Based on Sulem and Famin (2009) and Platt et al. (2015),

$$\frac{\partial m_f}{\partial t} = n \frac{\partial \rho_f}{\partial t} + \rho_f \frac{\partial n}{\partial t}, \quad (S4)$$

where n and ρ_{CO_2} represent the porosity and density of CO₂, respectively, and $\frac{\partial \rho_f}{\partial t}$ can be expressed as:

$$\frac{\partial \rho_f}{\partial t} = \rho_f \beta_f \frac{\partial P_p}{\partial t} - \rho_f \lambda_f \frac{\partial T}{\partial t}, \quad (S5)$$

where β_f and λ_f are the compressibility and thermal expansivity of the pore fluid, respectively; T represents temperature; and $\frac{\partial n}{\partial t}$ is related to the pore pressure, temperature, and thermal decomposition as:

$$\frac{\partial n}{\partial t} = n \beta_n \frac{\partial P_p}{\partial t} + n \lambda_n \frac{\partial T}{\partial t} + \frac{\zeta}{\rho_{CaMg(CO_3)_2}} \frac{\partial m_d}{\partial t}, \quad (S6)$$

where $\zeta = \frac{1}{2} \left(\frac{M_{\text{CaMg}(\text{CO}_3)_2}}{M_{\text{CO}_2}} - \frac{\rho_{\text{CaMg}(\text{CO}_3)_2}}{\rho_{\text{CaO}}} \frac{M_{\text{CaO}}}{M_{\text{CO}_2}} - \frac{\rho_{\text{CaMg}(\text{CO}_3)_2}}{\rho_{\text{MgO}}} \frac{M_{\text{MgO}}}{M_{\text{CO}_2}} \right)$, and ρ_X and M_X refer to the density and molar mass of component X, respectively. The temporal change in the pore pressure could be derived using Eq. (S3)–(S6):

$$\frac{\partial P_p}{\partial t} = \frac{k_f}{n(\beta_f + \beta_n)\eta_f} \frac{\partial^2 P_p}{\partial z^2} + \frac{\lambda_f - \lambda_n}{\beta_f + \beta_n} \frac{\partial T}{\partial t} + \frac{1 - \rho_f \zeta / \rho_{\text{CaMg}(\text{CO}_3)_2}}{n(\beta_f + \beta_n)} (1 - n) A \exp\left(-\frac{E_a}{RT}\right) \quad (\text{S7})$$

The temperature evolution during the thermal decomposition could be determined as follows:

$$\frac{\partial T}{\partial t} = \frac{k_T}{\rho C} \frac{\partial^2 T}{\partial z^2} + \frac{\mu}{\rho C} \left(\sigma_n - \frac{1}{0.005} \int_0^{0.005} P_p(y, t) dy \right) \frac{\partial v}{\partial z} - \frac{(1-n) E_a \rho_{\text{CaMg}(\text{CO}_3)_2}}{\rho C M_{\text{CaMg}(\text{CO}_3)_2}} A \exp\left(-\frac{E_a}{RT}\right) \quad (\text{S8})$$

The first, second, and third terms on the right-hand side of Eq. (S8) describe the effects of thermal diffusion, shear heating, and endothermic CO₂ emission, respectively. The values of these parameters are listed in Table S1. The Eq. (S7) and Eq. (S8) were discretized using a finite element method with a linear shape function. The left-hand side of the equations, which are the time derivatives of pore pressure and temperature, were approximated by a backward difference method. The third and fourth terms of the right-hand side act as source functions, which are updated each time step. Eq. (S7) and Eq. (S8) were coupled via a sequential calculation following 2nd order Runge-Kutta time-stepping method, and the time-steps were shorter than 0.0001 s for all the runs.

Selection of activation energy for numerical modelling

Previous laboratory experiments studies have suggested a greatly varied activation energy for dolomite decomposition from 97 to 333 kJ/mol (Olszak-Humienik and Jablonski, 2015, Gunasekaran and Anbalagan 2007, DeAngelis et al., 2007). To obtain the suitable activation energies for numerical modeling, we performed a parametric simulation with varying activation energy to find the best-fit activation energies for explaining thermal

behavior of dolomite up on grinding in our laboratory experiments. We assumed that the reaction rate coefficient is $2.95 \cdot 10^{15} \text{ s}^{-1}$ derived from calcium carbonate (Dollimore et al., 1996)

In our laboratory experiments, the samples without and with ball-mill pulverization showed high- and low-temperature decarbonation at ~ 700 and ~ 400 °C, respectively. We determined the temperature (Fig. S4) and pore pressure (Fig. S5) evolution of the uniform-activation-energy (180–330 kJ/mol) cases to assign suitable activation energy values for numerical simulations. The cases with $E_a = 320$ kJ/mol and $E_a = 220$ kJ/mol, which were adopted for the high- and low-crystalline phases in the numerical models, respectively, showed stable decarbonation temperatures at ~ 700 and ~ 400 °C, respectively. Additionally, the level of saturated pore pressure was independent of E_a even though lower E_a values resulted in quicker saturation (Fig. S5).

Figure S4. Temperature evolution during seismic slip within 10 s for the uniform-activation-energy (180–330 kJ/mol) cases.

Figure S5. Pore pressure evolution during seismic slip within 10 s for the uniform-activation-energy (180–330 kJ/mol) cases.

Effective shear strength of fault

Temporal change of shear strength of fault τ is calculated following:

$$\tau(t) = \mu \times (\sigma_n - P_p(t)) \quad (S9)$$

Compressibility of pore and permeability

We followed Sulem and Famin (2009) and Wibberley and Shimamoto [2005] to calculate compressibility of pore β_n and permeability k_f

$$\beta_n = \frac{1}{n} \left(2.5 \cdot 10^{-4} \exp \left(-1.38 \cdot (\sigma_n - P_p) \right) - (1 + n) \cdot 1.25 \cdot 10^{-4} \right) [1/\text{MPa}] \quad (S10)$$

$$k_f = k_{f_0} \left(\frac{1 - n_0}{1 - n} \right)^2 \left(\frac{n}{n_0} \right)^3 \quad (S11)$$

We note that we applied the same values of k_{f_0} and n_0 to both of shear zone and the surroundings following Sulem and Famin (2009).

Contributions to pore pressure change

In Fig. S6, we plotted the averaged values over the shear zone of the first, second, and third terms in the Eq. (S7) to show their quantitative contributions to pore pressure change. For the pure high-crystalline case (i.e., 100% 320 kJ/mol phase; Fig. S6a), we found that the effect

of thermal expansion contrast between pores and pore fluid (blue line) is restricted in the beginning stage. On the other hand, the effect of CO₂ emission (red line) on pore pressure change has one peak at 1.7 s and then decreases gradually. For the mixture of low-and high-crystalline dolomite case (i.e., 87.5%:12.5% = 320 kJ/mol:220 kJ/mol), two peaks of CO₂ emission (red lines in Fig. S6b), which are respectively from 220 kJ/mol and 320 kJ/mol phases. are shown. It is consistent with two-stage thermal pressurization at low and high temperatures in high-energy ball mill experiments. For the pure low-crystalline dolomite case (i.e., 50%:50% = 320 kJ/mol:220 kJ/mol; Fig. S6c), the overall pattern is similar with that of the pure high-crystalline case. However, the faster and stronger emission of CO₂ than the high-crystalline case is shown since the activation energy is lower than the pure high-crystalline case.

Figure S6. Contributions to pore pressure change from the diffusion (grey lines), thermal expansion contrast between pores and pore fluid (blue lines), and the effect of CO₂ emission (red lines) in (a) pure high-crystalline dolomite (100% 320 kJ/mol phase), (b) mixture of low- and high-crystalline dolomite (12.5% 220 kJ/mol phase), and (c) pure low-crystalline dolomite (50% 220 kJ/mol phase).

Table S1. Variable descriptions and values.

Descriptions	Symbols	Values
Density of dolomite	$\rho_{\text{CaMg}(\text{CO}_3)_2}$	2.84 [g/cm ³]
Density of CaO	ρ_{CaO}	3.34 [g/cm ³]
Density of MgO	ρ_{MgO}	3.58 [g/cm ³]
Density of super critical CO ₂	ρ_f	*Depending on P _p and T [kg/m ³]
Molar mass of dolomite	$M_{\text{CaMg}(\text{CO}_3)_2}$	184.4008 [g/mol]
Molar mass of CaO	M_{CaO}	56.0774 [g/mol]
Molar mass of MgO	M_{MgO}	40.3044 [g/mol]
Molar mass of CO ₂	M_{CO_2}	44.0095 [g/mol]
Viscosity of pore fluid	η_f	*Depending on P _p and T [Pa·s]
Compressibility of pore fluid	β_f	*Depending on P _p and T [1/MPa]
Thermal expansivity of pore fluid	λ_f	*Depending on P _p and T [1/°C]
Compressibility of pore	β_n	Eq. S9 [1/MPa]
Thermal expansivity of the pore	λ_n	2.4×10^{-5} [1/°C]
Reference permeability	k_{f_0}	10^{-19} [m ²]
Reference porosity	n_0	0.03
Permeability	k_f	Eq. S11 [m ²]
Specific heat	ρC	2.7 [MPa/°C]
Thermal diffusivity	$k_T/(\rho C)$	0.7 [mm ² /s]
Reaction rate coefficient	A	$\dagger 2.95 \times 10^{15}$ [1/s]
Universal gas constant	R	8.31447 [J/K/mol]
Friction coefficient	μ	0.1

*National Institute of Standards and Technology (<http://webbook.nist.gov/chemistry/>)

†Dollimore et al., 1996

REFERENCES CITED

DeAngelis, M.T., Labotka, T.C., Cole, D.R., Fayek, M., and Anovitz, L.M., 2007, Experimental investigation of the breakdown of dolomite in rock cores at 100 MPa, 650–750 °C: *American Mineralogist*, v. 92, no. 4, p. 510-517.

- Dollimore, D., Tong, P., and Alexander, K.S., 1996, The kinetic interpretation of the decomposition of calcium carbonate by use of relationships other than the Arrhenius equation: *Thermochimica Acta*, v. 282-283, p. 13-27.
- Gunasekaran, S., and Anbalagan, G., 2007, Spectroscopic study of phase transitions in dolomite mineral: *Journal of Raman Spectroscopy*, v. 38, no. 7, p. 846-852.
- Olszak-Humienik, M., and Jablonski, M., 2015, Thermal behavior of natural dolomite: *Journal of Thermal Analysis and Calorimetry*, v. 119, no. 3, p. 2239-2248.
- Platt, J.D., Rudnicki, J.W., and Rice, J.R., 2014, Stability and localization of rapid shear in fluid-saturated fault gouge: 2. Localized zone width and strength evolution: *Journal of Geophysical Research: Solid Earth*, v. 119, no. 5, p. 4334-4359.
- Sulem, J., and Famin, V., 2009, Thermal decomposition of carbonates in fault zones: Slip-weakening and temperature-limiting effects: *Journal of Geophysical Research: Solid Earth*, v. 114.
- Wibberley, C.A.J., and Shimamoto, T., 2005, Earthquake slip weakening and asperities explained by thermal pressurization: *Nature*, v. 436, no. 7051, p. 689-692.