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Earthquakes produce carbon dioxide in crustal faults

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1 **Fourier transform infrared (FTIR) micro-analysis of pseudotachylytes (i.e. friction-**
2 **induced melts produced by seismic slip) from the Nojima fault (Japan) reveals that**
3 **earthquakes almost instantaneously expel 99 wt% of the wall rock CO₂ content.**
4 **Carbon is exsolved because it is supersaturated in the friction melts. By extrapolation**
5 **to a crustal-scale fault rupture, large events such as the M7.2 Kobe earthquake (1995)**
6 **may yield a total production of 1.8 to 3.4 × 10³ tons CO₂ within a few seconds. This**
7 **extraordinary release of CO₂ can cause a flash fluid pressure increase in the fault**
8 **plane, and therefore enhance earthquake slip or trigger aftershocks; it may also**
9 **explain the anomalous discharge of carbon monitored in nearby fault springs after**
10 **large earthquakes. Because carbon saturation in silicate melts is pressure-dependent,**
11 **FTIR can be used as a new tool to constrain the maximum depth of pseudotachylyte**
12 **formation in exhumed faults.**

13

14 **Keywords:** pseudotachylyte, infrared spectroscopy, fluids, CO₂ exsolution, earthquake, slip
15 weakening, Nojima fault.

16

17 **Introduction**

18 An earthquake occurs because the shear resistance of a slipping fault becomes weaker with
19 increasing slip [1]. The fault rocks are crushed by friction and may even melt if the heat
20 generated is large enough [2]. Knowing how much energy is released as frictional heat, or
21 converted into fractures and elastic waves, is essential for assessing how tectonic stress
22 relaxation generates near-fault acceleration and surface damage, and how much stress is left

23 for future rupture of the Earth's crust. However, the production of heat is poorly
24 constrained in the energy budget of earthquakes because the magnitude of fault weakening
25 and its mechanism are not well known. In most theoretical or experimental mechanisms
26 proposed to explain slip weakening, the lubricating agent is a fluid medium (either aqueous,
27 melt or slurry) trapped within the fault plane and put under pressure by thermal or dynamic
28 effects [3-8]. The efficiency of these slip-weakening mechanisms depends largely on the
29 quantity of fluid involved and the pressurization achieved, which are difficult to assess.
30 Therefore, determining the magnitude of coseismic shear stress reduction and the energy
31 balance of earthquakes is still a major issue in seismology.

32 To constrain the fluid budget of a slipping fault and improve our understanding of
33 weakening processes, we have analyzed the water and carbon dioxide content of
34 pseudotachylytes (i.e. melts produced by friction during earthquakes) using a Fourier
35 transform infrared microspectrometer (micro-FTIR). FTIR is a conventional tool for the
36 study of volatile species in magmatic melts [9], albeit never applied to friction melts so far.
37 We show that pseudotachylytes may be used to infer the fluid concentration in fault rocks
38 at the time of seismic slip, providing new insights on earthquake mechanics.

39 The studied example is the Nojima fault (Fig. 1) that was activated on a dextral, 10.5 km-
40 long surface rupture [10] by the Kobe (Hyogo-ken Nanbu) earthquake ($M_{\text{JMA}} = 7.2$, $M_{\text{W}} =$
41 6.9 , focal depth = 16 km, January 17th, 1995), killing more than 6400 people. Immediately
42 after the shake, the HCO_3^- concentration increased by 30 wt% in nearby springs [11]. This
43 unexplained carbon discharge, together with other coseismic geochemical anomalies,
44 decreased gradually to normal values in the following ten months [12-15]. One year after
45 the earthquake, the Geological Survey of Japan drilled a borehole (Fig. 1) that reached the

46 upper boundary of the 83° dipping fault at 623.1 m depth within Cretaceous granodiorites
47 [16]. The fault core consists in a 30 cm-thick cataclasite composed of quartz, albite and K-
48 feldspar clasts derived from the granodiorite protolith, crushed together with secondary
49 clays, zeolites and carbonates [16, 17]. The carbonates have a biogenic isotopic signature as
50 well as present-day pore fluids in the fault, which suggests a superficial or sedimentary
51 source for the alteration fluids in general and the carbon in particular [18-20]. Because of
52 hydrothermal alteration, the cataclasite is enriched in SiO₂, CaO and depleted in MgO,
53 Fe₂O₃, Na₂O, K₂O relative to the granodiorite protolith. The cataclasite also contains 3.5 to
54 10 wt% equivalent CO₂ with an average at 7.6 wt%, and 1 to 5 wt% H₂O with an average at
55 2.7 wt% (mean of 5 measurements taken from Figure 7 in [17]). This study focuses on two
56 millimetre-thick pseudotachylytes (Fig. 2a) embedded in the cataclasite layers at 624.59 m
57 within the Nojima fault core [17]. The texture of these pseudotachylytes has already been
58 investigated in detail [21, 22] and is only summarized briefly. The dark layer of
59 pseudotachylyte (PT1) contains fragments of cataclasite (isolated or aggregated quartz,
60 albite and calcite clasts with molten rims) in a brown matrix. These fragments, and the
61 fresh PT1 – cataclasite interface devoid of shear localization structures, indicate that the
62 cataclasite is the precursory of PT1. A second, clearer pseudotachylyte (PT2), containing
63 plastically deformed fragments of PT1 and fewer mineral remnants in a transparent matrix
64 (Fig. 2a), re-melted the dark layer. The random occurrence of fluid-filled vesicles in the
65 two matrixes, and the homogeneous aspect of these matrixes under the SEM [21] suggest
66 that the two pseudotachylytes are made of undevitrified glass [22]. The composition of the
67 vesicles (84 mol% H₂O; 15.3 mol% CO₂; 0.7 mol% NaCl) attest to the supersaturation of
68 H₂O and CO₂ in the melts [22]. In addition, the molten rims of clasts in the two

69 pseudotachylytes indicate that melting reached a minimum temperature of 1200 °C [22],
70 which is consistent with melting temperatures estimated from other pseudotachylyte
71 samples in the Nojima fault [23]. The two matrixes have a dacite composition (~68 wt%
72 SiO₂, 3 wt% Na₂O + K₂O) similar to the bulk composition of the cataclasite. Calcite
73 fragments in the melts, and the fact that both matrixes contain up to twice the CaO content
74 of the granodiorite protolith (4.06 wt%), imply that the precursory cataclasite was already
75 carbonate-rich before melting. Carbonate precipitation continued between and after the
76 melting events [24]. Pseudotachylytes were quenched at ambient temperatures of 150 – 350
77 °C and a depth range of 4 – 15 km [22, 25, 26]. These pseudotachylytes formed well after
78 the cooling of the granodiorite basement (74 Ma [27]), and were then uplifted with the
79 basement by a left-lateral thrust motion of the fault, mostly before the Eocene [26].
80 Exhumation is still occurring in the present even though the fault has shifted to a right-
81 lateral thrust movement since the Plio-Pleistocene [28]. It is therefore likely that these
82 exhumed pseudotachylytes represent slipping processes similar to those occurring today
83 between the Kobe earthquake hypocenter and the surface. The multiple occurrence of
84 pseudotachylytes within carbonate-bearing cataclasites on surface exposures of the Nojima
85 fault [23], and on other faults along the Median Tectonic Line running through Japan,
86 suggests that the lateral extent of melts is large, and/or that friction melting is a widespread
87 phenomenon along those faults.

88

89 **Analytical methods and results**

90 Infrared spectra were measured on a JASCO, FTIR 620plus, IRT 30 apparatus, equipped
91 with an automatic XY mapping stage moving the sample at 50 μm steps on X and Y under
92 the microscope. Spectra were acquired by collecting 50 scans in the range 6000 – 700 cm^{-1}
93 with a 4 cm^{-1} resolution and a 50 \times 50 μm aperture. Every ten spectra during the mapping,
94 the automatic stage moved to a position beyond the sample in order to take a background
95 air spectrum. All the spectra were automatically corrected from background by the JASCO
96 Spectra Manager software, and then corrected using the same linear baseline in the range
97 5000 – 1300 cm^{-1} . The thickness of the wafer was measured using a laser scanning confocal
98 microscope (KEYENCE VK-8500) at the centre and corners of each of the mapped areas,
99 and was found to be $63 \pm 3 \mu\text{m}$. Absorbance peaks were converted into volatile
100 concentrations following the conventional procedure for SiO_2 -rich melts [9], assuming a
101 glass density of 2.7 $\text{g}\cdot\text{cm}^{-3}$. The total error on concentration estimates is 5 to 10 % [9].
102 Concentration maps were built using the JASCO Spectra Manager software.
103 Four areas were analyzed by FTIR in the sample (Fig. 2). Each 50 \times 50 μm pixel
104 corresponds to an infrared spectrum, and hence to a couple of H_2O and CO_2 concentrations
105 (typical FTIR spectra provided in Fig. 3). The measured concentrations include the fraction
106 of H_2O and CO_2 dissolved in the glass and the fraction trapped in fluid inclusions. Water is
107 observed entirely as molecular H_2O (no dissolved OH). The two pseudotachylytes display a
108 similar water content of about 2 wt% H_2O (Fig. 2b), except in cracks. There is, however, an
109 extremely sharp contrast of molecular CO_2 concentration between the dark older PT1
110 containing up to 5000 ppm CO_2 , and the clear younger PT2 nearly devoid of CO_2 (Fig. 2c).
111 The presence of water and carbon dioxide dissolved as molecular species, not as ionic

112 species, is typical of dacite type, silica-rich melts [29]. In addition, CO_3^{2-} is detected as
113 secondary carbonate minerals (mostly calcite) precipitated in microcracks or as mineral
114 fragments in the glass (Fig. 2d). PT1 contains 1 wt% CO_3^{2-} or 0.7 wt% equivalent CO_2
115 (average of all the spectra measured on PT1). Because PT2 is younger and less fractured
116 than PT1, it contains only 0.3 wt% CO_3^{2-} or 0.2 wt% equivalent CO_2 in average.
117 FTIR data are also reported in an H_2O - CO_2 diagram before (Fig. 4a) and after filtering (Fig.
118 4b) in order to consider only pure matrix glass without carbonates. PT1 contains 1.5 – 2.8
119 wt% H_2O and 1000 – 5000 ppm CO_2 , whereas PT2 contains 1 – 2.8 wt% H_2O and 0 – 500
120 ppm CO_2 away from its contact with PT1.

121

122 **Discussion and conclusion**

123 **1. Budget of volatile exsolution by friction melting**

124 Our results show that friction melting causes carbon devolatilization of the fault rocks.
125 Because PT1 contains up to 0.7 wt% equivalent CO_2 as crystallized carbonates (i.e. 1 wt%
126 CO_3^{2-} , Fig. 2d), some carbonates may postdate the first melting event such that the
127 cataclasite possibly contained less carbon before PT1 formation than it does now, i.e. only
128 2.8 – 6.9 – 9.3 wt% equivalent CO_2 (minimum – average – maximum of Tanaka's et al.
129 measurements [17], minus 0.7 wt%). In order to set a lower bound to our quantification of
130 CO_2 loss, we therefore assume the precursory cataclasite to have contained no more than
131 2.5 – 3.5 wt% equivalent CO_2 before PT1. Even though, PT1 (1.5 – 2.8 wt% H_2O , 1000 –
132 5000 ppm CO_2) contains as much H_2O as the parent cataclasite, but about ten times less
133 CO_2 . Likewise, PT2 (at 1 – 2.8 wt% H_2O , 0 – 500 ppm CO_2 away from its contact with

134 PT1) contains as much H₂O as PT1 from which it melted, but ten times less CO₂ (for a
135 minimum estimate of the CO₂ loss, we neglect the carbonates precipitated after PT1 and
136 before PT2). Therefore, each fusion expels at least 90 wt% of the CO₂ dissolved or trapped
137 as carbonates in the protolith, because carbon is supersaturated in the molten phase. Only 1
138 wt% of the initial CO₂ content is kept in the fault plane after the two melting events, while
139 the remaining 99 % are exsolved as fluid CO₂.

140 Assuming a rock density of 2.7 g.cm⁻³, the fusion of 10⁻³ m³ (i.e. 1 mm thickness × 1 m² of
141 fault plane) of cataclasite (at 2.5 – 3.5 wt% CO₂) into PT1 (at 1000 – 5000 ppm CO₂) yields
142 56 to 95 g CO₂. Likewise, the re-fusion of 10⁻³ m³ of PT1 into PT2 (at 0 – 500 ppm CO₂)
143 releases 1.4 to 14 g CO₂ in 1 m² of fault plane. Frictional melting is therefore an
144 unexpected and significant source of CO₂ in the Nojima fault.

145

146 **2. Degassing behaviour of friction melts**

147 FTIR data yield constraints on the ambient pressure during friction melting, because H₂O
148 and CO₂ saturation in silicate melts is pressure-dependent. Spectra measured in PT1 define
149 a trend in the high CO₂ field, whose slope indicates that the supersaturated melts were
150 quenched while degassing an 80 mol% H₂O and 20 mol% CO₂ fluid mixture (Fig. 4b),
151 consistent with the measured composition of fluid inclusions [22]. The lower end of the
152 degassing trend (2 wt% H₂O, 1000 ppm CO₂) is the closer to the composition of the pure
153 matrix glass without fluid inclusions. Considering the ~1200 °C temperature of melting, a
154 maximum pressure of 300 MPa may then be estimated for the formation of the PT1 glass
155 using the VolatileCalc software [30], or a 11 km depth assuming a 2.7 g.cm⁻³ rock density.

156 Spectra acquired in PT2 lie in the low CO₂ range (Fig. 4b). The low slope of PT2 degassing
157 path suggests that the glass exsolved a much higher proportion of H₂O relative to CO₂ than
158 PT1 (≥ 97 mol% H₂O, ≤ 3 mol% CO₂). If PT2 ever reached equilibrium saturation, it is
159 again in the lower end of the degassing path at less than 2 wt% H₂O and 200 ppm CO₂, or a
160 130 MPa maximum pressure (5 km). The consistency of these depths with independent
161 depth estimates [25, 26] implies that PT1 and PT2 nearly reached equilibrium volatile
162 saturation. Our results suggest that the two melting events occurred at different depths, and
163 therefore were separated by a large time span. FTIR mapping is a new method that provides
164 depth constraints on the formation of individual layers of glassy pseudotachylyte in
165 exhumed faults, without any assumption on the geotherm.

166 In addition, the solubility laws of volatiles in silicate melts may be used to explain the
167 degassing pattern during friction melting. In doing so, we assume that that H₂O and CO₂
168 exsolution in pseudotachylytes is ruled by local liquid-gas equilibrium as a first
169 approximation, keeping in mind that true equilibrium was probably not achieved within the
170 short time lapse of heating and quenching. Under this assumption, CO₂ exsolves faster than
171 H₂O due to the low solubility of carbon compared to H₂O. Consequently, a silicate melt
172 degassing in an open system (i.e. the exsolved fluid mixture is removed from the melt)
173 follows a steep path in the H₂O-CO₂ space, because CO₂ is almost entirely lost before H₂O
174 supersaturation begins. On the other hand, a magma degassing in a closed system (in which
175 the exsolved fluid stays in contact with the melt) follows a gently sloping path in the H₂O-
176 CO₂ space, because the partial pressure of CO₂ gradually increases in the exsolved phase
177 and hampers further CO₂ degassing. Accordingly, FTIR data reveal that each
178 pseudotachylyte degassing proceeds in two stages: 1) Loss of 90 wt% CO₂ without

179 significant H₂O loss from the cataclasite to PT1, and from PT1 to PT2 (dashed arrows in
180 Fig. 4b). This degassing path is consistent with an open system that prevails as long as the
181 melt viscosity is low enough for CO₂-rich bubbles to escape the pseudotachylytes. Because
182 it is an open system, this stage is not recorded in H₂O – CO₂ concentrations, yet is
183 evidenced by comparing volatile concentrations before and after melting. 2) Loss of water-
184 rich mixtures (80 mol% H₂O, 20 mol% CO₂ for PT1; ≥ 97 mol% H₂O, ≤ 3 mol% CO₂ for
185 PT2) is consistent with melts degassing in closed system (solid lines in Fig. 4b). This
186 second stage of closed system degassing occurs because the viscosity of the cooling melts
187 becomes too large to let the bubbles escape, resulting in the entrapment of fluid inclusions.
188 To summarize, pseudotachylytes in the Nojima fault behave as open systems at the
189 beginning of flash friction melting, and then as closed systems during the last stage of melt
190 cooling.

191

192 **3. Implication for fault mechanics**

193 The first essential implication of our findings is that CO₂ degassing may increase the fluid
194 pressure (P) in the fault zone during and/or after an earthquake, depending on the rate of
195 exsolution, the permeability of the fault core, the carbonate content of the precursory fault
196 rocks and the depth considered. To estimate the fluid pressure increase solely caused by
197 frictional exsolution, we consider the effect of CO₂ emission at constant temperature (~200
198 °C at 5 km and ~400 °C at 11 km), and neglect elastohydrodynamic or thermal
199 pressurization [4, 6-8], keeping in mind that these effects may be considerable if combined
200 with exsolution. Moreover, the ~15 volume % increase caused by the transformation of

201 cataclasite into pseudotachylyte is neglected, although it may contribute to increasing the
 202 fluid pressure and reducing the shear stress on the fault plane. For the sake of simplicity, we
 203 also consider the porosity of the fault zone to be entirely filled with pure CO₂, even though
 204 other fluids such as H₂O may be dominant before an earthquake. This assumption does not
 205 yield significant error in the calculation because the compressibility factors and viscosities
 206 of H₂O and CO₂ are nearly equal in the supercritical state within the pressure and
 207 temperature ranges considered here. Accordingly, the fluid pressure increase (P_f/P_0) is
 208 computed from the equation of state (EOS) of pure CO₂:

209

$$210 \quad P = \frac{mZRT}{M^{CO_2} \phi v}, \quad (1)$$

211 which yields

$$212 \quad \frac{P_f}{P_0} = \frac{\phi_0 Z_f m_f}{\phi_f Z_0 m_0} \quad (2)$$

213 Parameter values, units and definitions are given in Table 1. The subscripts 0 and f refer to
 214 quantities before and after exsolution, respectively. R , T , ϕ and M^{CO_2} denote the gas
 215 constant, the temperature, the porosity of the fault zone and the molar mass of CO₂,
 216 respectively. Z , the compressibility factor of pure CO₂, is calculated using the Saxena and
 217 Fei EOS [31]:

$$218 \quad Z = (1 - 0.5917) \left(\frac{T^c}{T} \right)^2 + 0.09122 \frac{T^c P}{T P^c} + \left[1.4164 \times 10^{-4} \left(\frac{T^c}{T} \right)^2 - 2.8349 \times 10^{-6} \ln \frac{T}{T^c} \left(\frac{P}{P^c} \right)^2 \right] \quad (3)$$

219 where P^c and T^c represent the pressure and temperature at the critical point of CO₂. m_0 and
 220 m_f are the masses of CO₂ present before and after friction melting in a volume of fault zone

221 equal to $1 \times 1 \times w \text{ m}^3$. m_0 is calculated assuming hydrostatic pressure in equation (1). m_f is
 222 equal to $(m_0 + m_e)$, where m_e is the mass of CO_2 exsolved by a 1 mm thick
 223 pseudotachylyte. w is the maximum distance of coseismic CO_2 outflow in the direction
 224 perpendicular to the fault plane, taken as the half width of the pseudotachylyte (0.5 mm)
 225 plus twice the hydraulic diffusion length scale of CO_2 (L_f). L_f is given by $L_f = \sqrt{D_f \psi}$ [8], ψ
 226 being the characteristic timescale of frictional exsolution, set at 5 sec (the time lapse for
 227 glass melting and quenching does not exceed a few seconds [32]). D_f is the hydraulic
 228 diffusivity after exsolution, given by $D_f = k_f / \eta \beta_f$, where k_f denotes the final permeability
 229 of the fault zone, β_f its storage capacity, and η the P-T dependent viscosity of supercritical
 230 CO_2 . β_f is computed from $\beta_f = \beta^b - \beta^s + \phi_f (\beta_f^{CO_2} - \beta^s)$, β^s being the compressibility of
 231 mineral grains, β^b the bulk rock compressibility, and $\beta_f^{CO_2} = -\frac{P_f}{Z_f} \left(\frac{\partial Z/P}{\partial P} \right)_f^{T=cte}$ the
 232 compressibility of supercritical CO_2 .

233 To calculate the pressure-dependent permeability of the slipping fault (k_f), we use an
 234 empirical law (Fig. 5) derived from the available data at different effective pressures ($P_{\text{rock}} -$
 235 P):

$$236 \quad k = 3 \times 10^{-17} e^{-6.14 \times 10^{-8} (P_{\text{rock}} - P)} \quad (4)$$

237 Note that permeability in the Nojima fault is at least two orders of magnitude larger than
 238 the permeability of some other crustal faults (at similar effective pressures) investigated so
 239 far [8, 33-36]. In absence of specific laws of pressure dependence for ϕ and β^b on the
 240 Nojima fault core, we are left to adapt to our case the empirical relations determined on the
 241 Median Tectonic Line [8]:

$$242 \quad \phi = \phi e^{-2.97 \times 10^{-8} (P_{rock} - P)} \quad (5)$$

$$243 \quad \beta^b = 2.5 \times 10^{-10} e^{-1.38 \times 10^{-13} (P_{rock} - P)} \quad (6)$$

244 using $\phi = 0.03$, which is the mean porosity measured on samples from the Nojima fault
245 core at room pressure [37].

246 The fluid pressure increase (P_f/P_0) due to frictional exsolution is depicted in Figure 6. At 11
247 km depth, a flash release of 56 – 95 g CO₂ per m² of fault plane raises the pore fluid
248 pressure of 78 to 90 % above the hydrostatic pressure, or an 80 – 100 MPa increase, even
249 without considering thermal pressurization. At 5 km, the release of 1.4 – 14 g CO₂ raises
250 the fluid pressure by 5 – 15 % above the hydrostatic pressure. Note that the magnitude of
251 fluid pressure increase strongly depends on the permeability of the fault core (Fig. 6), as do
252 other mechanisms of pore pressurization. For example, at 11 km depth the fluid pressure
253 increases by 100 – 110 % if the permeability is ten times smaller than the selected
254 permeability law (Fig. 5), and is still of 50 – 60 % if the permeability is ten times larger.
255 Frictional CO₂ exsolution can therefore be a significant pressurization mechanism in fault
256 zones, even at relatively high permeability, and even at hydrostatic starting fluid pressure.
257 Slip-weakening by frictional exsolution should be taken into account when considering
258 earthquake processes at slip velocities large enough to produce friction melts. In addition,
259 the low velocity of seismic waves from the Kobe earthquake aftershocks suggests the
260 presence of high pore fluid pressures in the fault zone after the main shock [38]. Since the
261 coseismic exsolution of CO₂ may sustain such fluid pressurization, it could also enhance
262 later ruptures and trigger aftershock sequences in the Nojima fault, in a same way than
263 mantle CO₂ degassing triggers aftershock trees in thrust faults from Northern Italy [39].

264

265 4. Implication for fault degassing

266 The second major consequence of our findings is that co-seismic carbon discharge in near-
267 fault springs might result from friction melting. The relative abundance of pseudotachylytes
268 in carbonate-rich cataclasites on different cores and outcrops of the Nojima fault suggest
269 that coseismic CO₂ loss might be the rule rather than an exception. In addition, core sample
270 studies conclude that magnitude 6 – 7 earthquakes are responsible for the formation of
271 millimetre thick pseudotachylytes [22]. In the following discussion, we assume that an
272 earthquake such as the M7.2 1995 Kobe earthquake produces pseudotachylytes at least as
273 wide as those observed in cores [22] and outcrops [23] of the Nojima fault. Under this
274 assumption, the friction melts caused by a single earthquake at 11 km and 5 km along the
275 fault plane should be similar to the pseudotachylytes (PT1 and PT2) caused by two separate
276 slip events in the sample. To calculate the minimum CO₂ production of a Kobe-like
277 earthquake, we hence consider a very idealistic model in which the rupture produces PT1
278 from 11 km to 8 km and PT2 from 8 km to 5 km. The production of CO₂ beneath 11 km
279 and above 5 km is unknown and therefore not considered, even though it might be
280 significant. Accordingly, a minimum range of 170 to 330 kg CO₂ is released per meter of
281 fault trace, or a total emission of 1.8 – 3.4 10³ tons CO₂ for a 10.5 km surface rupture of the
282 Nojima fault such as in the Kobe earthquake. Note that thermal decomposition of
283 carbonates in cataclasites could also contribute to release carbon in the Nojima fault, and
284 hence increase the proposed budget. However, a large part of this CO₂ likely re-precipitates
285 as new carbonate minerals soon after the earthquake. Yet a fraction of CO₂ may be

286 evacuated through the ground waters that leach the fault. Indeed, an excess of ~20 tons
287 equivalent CO₂ was emitted by the Awaji Island springs within the ten months of the Kobe
288 earthquake [11, 14], i.e. about 1 wt% of the CO₂ possibly produced by friction melting. As
289 the carbon isotopic signature in past and present ground waters from the Nojima fault is
290 biogenic and not consistent with a deep degassing source [18, 19], the coseismic carbon
291 discharge in springs might well have come from frictional exsolution. This possibility
292 opens promising applications for soil and spring gas monitoring in active faults, such as in
293 the San Andreas fault that is also degassing biogenic carbon [40]. In the absence of a deep
294 contribution, post-seismic CO₂ discharge might be taken as an evidence of frictional
295 exsolution. The amount of CO₂ released should be proportional to the amount of heated
296 carbon-bearing fault rock, and to the heat generated by shear friction. In deep wells probing
297 those faults, measuring the CO₂ flux could therefore provide an additional tool to constrain
298 the frictional strength of the fault, and the physical processes that govern seismic slip.

299

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306

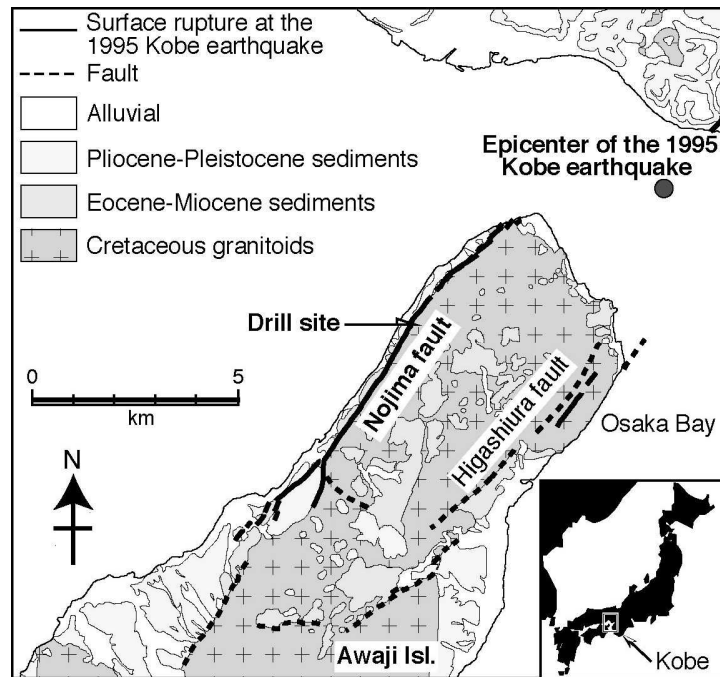
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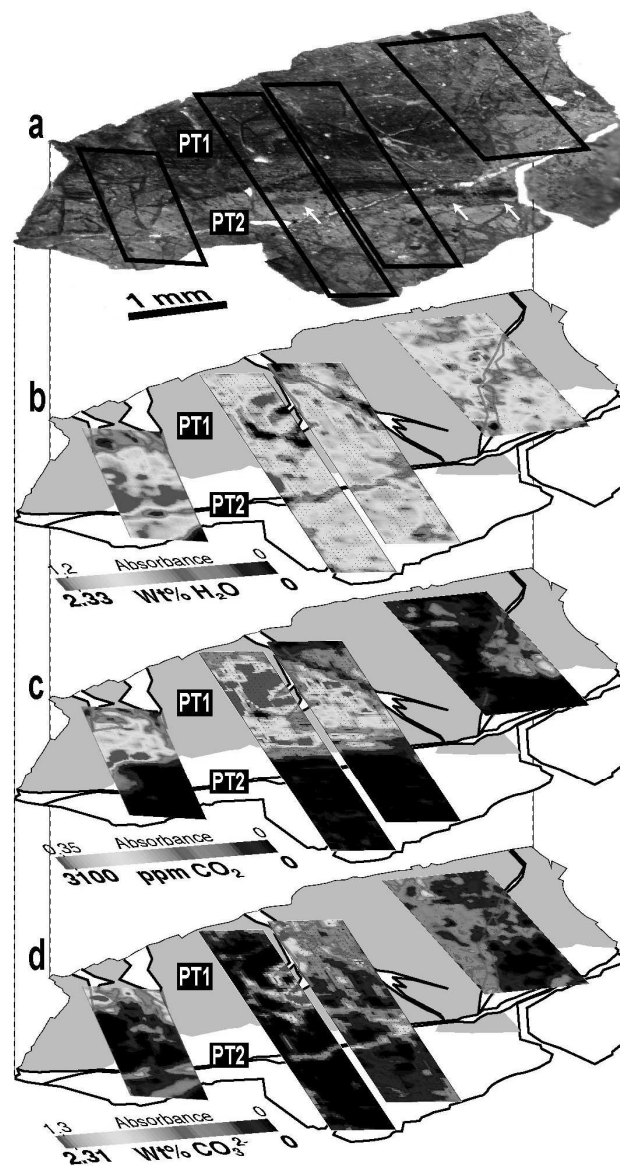
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415 **Figure caption**



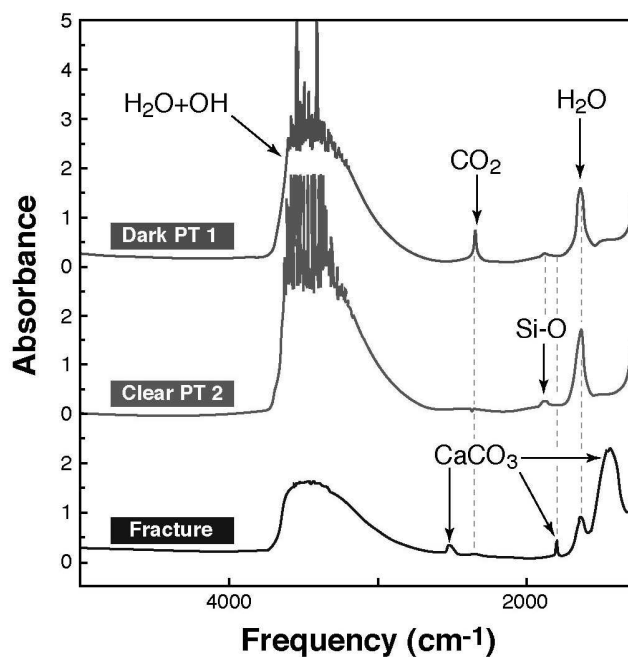
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 417 **Figure 1:** Simplified geological map of Awaji Island, modified from [16].
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420 **Figure 2:** FTIR mapping in pseudotachylytes from the Nojima fault. a) Optical
 421 microphotograph showing the older dark pseudotachylyte (PT1) re-molten into a younger
 422 clear pseudotachylyte (PT2). PT2 contains plastically deformed fragments of PT1 (white
 423 arrows) and fewer mineral remnants than PT1. Carbonate veins crosscut the two
 424 generations of friction melts. b-d) Peak height (absorbance) mapping of molecular H₂O
 425 (1630 cm⁻¹), molecular CO₂ (2340 cm⁻¹) and CO₃²⁻ (1460 cm⁻¹) converted into
 426 concentrations (wt%).

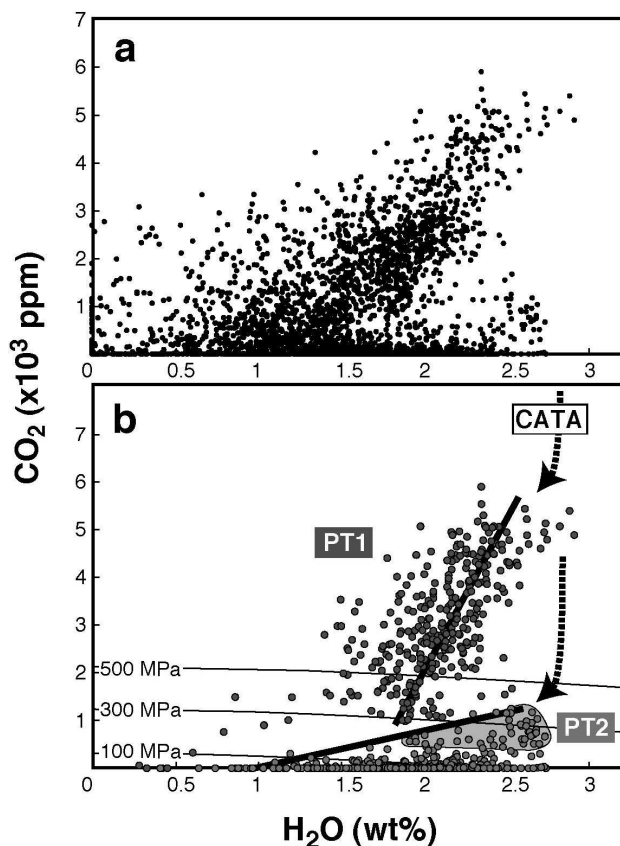
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429 **Figure 3:** Typical FTIR spectra of pseudotachylytes from the sample cored in the Nojima
 430 fault. Upper (red) spectrum: dark older pseudotachylyte (PT1). Middle (green) spectrum:
 431 clear younger pseudotachylyte (PT2). Lower (blue) spectrum: fracture. There is virtually no
 432 dissolved hydroxyl in the glass (the absorption peak of bound OH is at 4500 cm^{-1}). The
 433 absorption peak of total OH (corresponding to the O-H stretching vibration at 3450 cm^{-1} in
 434 hydroxyl and water molecules) is saturated (and useless) in the glasses due to the high
 435 water concentration, but not in the fractured areas. The absorption peak of molecular CO_2
 436 (recognized by its stretching vibration at 2340 cm^{-1}) is observed in the dark
 437 pseudotachylyte, but not in the clear one. Molecular H_2O (recognized by its bending
 438 vibration at 1630 cm^{-1}) displays a higher absorption peak and is therefore more abundant in
 439 the pure glass than in the fractures. The three absorption bands of calcite (at 2510 , 1790 and
 440 1460 cm^{-1}) are observed in fractured zones. A combination of Si-O vibrations (at 1870 cm^{-1})
 441 ¹) is detected in pure glass.

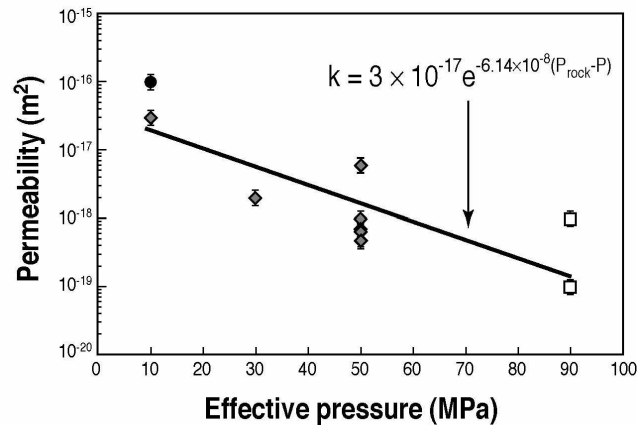
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444 **Figure 4:** H₂O versus CO₂ concentrations measured by FTIR in the pseudotachylytes. a)
 445 Complete dataset from the 3420 spectra. b) Dataset after filtering: spectra showing
 446 carbonate peaks (2510, 1790 and 1460 cm⁻¹) were removed in order to consider only pure
 447 glass without calcite. The isobars have been calculated using the VolatileCalc software
 448 [30]. Pseudotachylytes first degas as an open system (thick dashed arrows). Because of
 449 melt cooling, the pseudotachylytes eventually enter into a second step of closed-system
 450 degassing (solid lines). The degassing trend of PT1 (red dots) is consistent with an exsolved
 451 fluid phase at 80 mol% H₂O, 20 mol% CO₂ (upper solid line drawn by linear regression).
 452 PT2 (green dots) degassed a more water-rich mixture (≥ 97 mol% H₂O; ≤ 3 mol% CO₂,
 453 domain delimited by the lower solid line). The shaded area corresponds to the border of
 454 PT1, which is affected by incomplete re-melting and has a transitional CO₂ content between
 455 fresh PT1 and final PT2 (Fig. 2c).

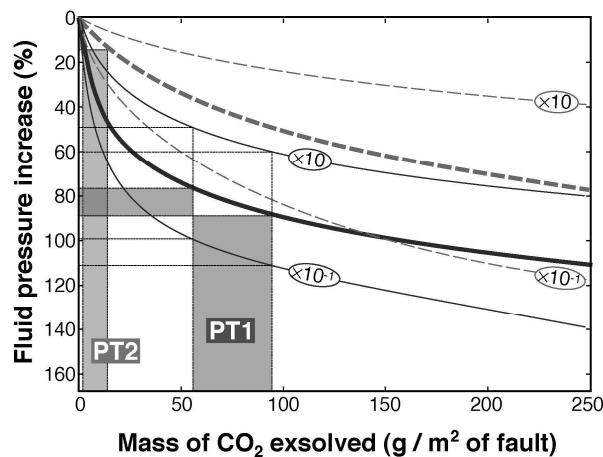
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458 **Figure 5:** Best fit log-linear equation for permeability in the Nojima fault core with
 459 increasing effective pressure. Black dots compiled from [41], grey diamonds from [42], and
 460 empty squares from [43].

461



462

463 **Figure 6:** Fluid pressure increase (P_f/P_0) caused by CO_2 exsolution at two different depths,
 464 assuming a hydrostatic initial fluid pressure, and without considering thermal
 465 pressurization. Plain (blue) curves: 11 km, 400 °C. Dashed (orange) curves: 5 km, 200 °C.
 466 Each color set includes three curves: One curve calculated using the permeability law
 467 defined by equation 4 (Fig. 5), one curve using a permeability ten times larger ($\times 10$), and
 468 one curve using a permeability ten times smaller ($\times 10^{-1}$). The red and green areas
 469 correspond to the CO_2 production caused by PT1 (56 – 95 g/m^2) and PT2 (1.4 – 14 g/m^2),
 470 respectively, on 1 m^2 of fault plane. Calculation detailed in text.

471

472 **Table caption**473 **Table 1:** Abbreviations and parameter values used in the calculation of the fluid pressure.

474

i	The subscripts $i = 0$ and $i = f$ refer to quantities before and after CO_2 exsolution, respectively
P_i	Fluid pressure (Pa)
P_{rock}	Lithostatic load (Pa)
T	Temperature (K)
R	Gas constant = $8.314472 \text{ J.mol}^{-1}.\text{K}^{-1}$
Z_i	Compressibility factor of CO_2 given by the Saxena & Fei EOS [31]
T^c	Temperature of the critical point of $\text{CO}_2 = 304.14 \text{ K}$ [44]
P^c	Pressure of the critical point of $\text{CO}_2 = 73.8 \times 10^5 \text{ Pa}$ [44]
M^{CO_2}	Molar mass of $\text{CO}_2 = 44 \text{ g.mol}^{-1}$
m_i	Mass of fluid CO_2 in contained in a fault zone of thickness w , i.e. in the porosity of $1 \times 1 \times w \text{ m}^3$ of fault rock (g)
ϕ_i	Porosity of the fault zone
w	Maximum distance of CO_2 outflow in the direction perpendicular to the fault plane, within the time span of friction melting (m)
L_f	Hydraulic diffusion length scale of CO_2 (m)
D_f	Hydraulic diffusivity after exsolution ($\text{m}^2.\text{s}^{-1}$)
ψ	Characteristic timescale of frictional exsolution set at 5 sec (the time lapse for glass melting and quenching does not exceed a few seconds [32])
k_i	Permeability of the fault zone (m^2)
η_i	Viscosity (Pa.s) of CO_2 in the supercritical state (data from [44])
β_i	Storage capacity of the fault zone (Pa^{-1})
β_i^{\square}	Compressibility of the bulk fault core (Pa^{-1})
β^s	Compressibility of the mineral grains assumed to be constant at $1.2 \times 10^{-11} \text{ Pa}^{-1}$
$\beta_i^{\text{CO}_2}$	Compressibility of CO_2 (Pa^{-1})

475