

Elsevier Editorial System(tm) for Earth and
Planetary Science Letters
Manuscript Draft

Manuscript Number: EPSL-D-17-00947R2

Title: Unraveling the dynamics of magmatic CO₂ degassing at Mammoth Mountain, California

Article Type: Letters

Keywords: CO₂ degassing; Mammoth Mountain; numerical modeling; TOUGH2; monitoring

Corresponding Author: Dr. Loic Peiffer, PhD

Corresponding Author's Institution: CICESE

First Author: Loic Peiffer, PhD

Order of Authors: Loic Peiffer, PhD; Christoph Wanner, PhD; Jennifer Lewicki, PhD

Abstract: The accumulation of magmatic CO₂ beneath low-permeability barriers may lead to the formation of CO₂-rich gas reservoirs within volcanic systems. Such accumulation is often evidenced by high surface CO₂ emissions that fluctuate over time. The temporal variability in surface degassing is believed in part to reflect a complex interplay between deep magmatic degassing and the permeability of degassing pathways. A better understanding of the dynamics of CO₂ degassing is required to improve monitoring and hazards mitigation in these systems. Owing to the availability of long-term records of CO₂ emissions rates and seismicity, Mammoth Mountain in California constitutes an ideal site towards such predictive understanding. Mammoth Mountain is characterized by intense soil CO₂ degassing (up to ~1000 t d⁻¹) and tree kill areas that resulted from leakage of CO₂ from a CO₂-rich gas reservoir located in the upper ~ 4 km. The release of CO₂-rich fluids from deeper basaltic intrusions towards the reservoir induces seismicity and potentially reactivates faults connecting the reservoir to the surface. While this conceptual model is well-accepted, there is still a debate whether temporally variable surface CO₂ fluxes directly reflect degassing of intrusions or variations in fault permeability. Here, we report the first large-scale numerical model of fluid and heat transport for Mammoth Mountain. We discuss processes (i) leading to the initial formation of the CO₂-rich gas reservoir prior to the occurrence of high surface CO₂ degassing rates and (ii) controlling current CO₂ degassing at the surface. Although the modeling settings are site-specific, the key mechanisms discussed in this study are likely at play at other volcanic systems hosting CO₂-rich gas reservoirs. In particular, our model results illustrate the role of convection in stripping a CO₂-rich gas phase from a rising hydrothermal fluid and leading to an accumulation of a large mass of CO₂ (~107-108 tons) in a shallow gas reservoir. Moreover, we show that both, short-lived (months to years) and long-lived (hundreds of years) events of magmatic fluid injection can lead to critical pressures within the reservoir and potentially trigger fault reactivation. Our sensitivity analysis suggests that observed temporal fluctuations in surface degassing are only indirectly controlled by variations in

magmatic degassing and are mainly the result of temporally variable fault permeability. Finally, we suggest that long-term CO₂ emission monitoring, seismic tomography and coupled thermal-hydraulic-mechanical modeling are important for CO₂-related hazard mitigation.

1 Unraveling the dynamics of magmatic CO₂ degassing at Mammoth Mountain, California

2

3 Loïc Peiffer^{1*}, Christoph Wanner², Jennifer L. Lewicki³

4

5 1. Departamento de Geología, CICESE, Ensenada, B.C., Mexico

6 2. Institute of Geological Sciences, University of Bern, Bern, Switzerland

7 3. U.S. Geological Survey, Menlo Park, CA, USA

8

9 *Corresponding author: Loïc Peiffer, Departamento de Geología, CICESE, Ensenada, B.C.,
10 Mexico (peiffer@cicese.mx)

11

12 Abstract

13

14 The accumulation of magmatic CO₂ beneath low-permeability barriers may lead to the
15 formation of CO₂-rich gas reservoirs within volcanic systems. Such accumulation is often
16 evidenced by high surface CO₂ emissions that fluctuate over time. The temporal variability
17 in surface degassing is believed in part to reflect a complex interplay between deep
18 magmatic degassing and the permeability of degassing pathways. A better understanding of
19 the dynamics of CO₂ degassing is required to improve monitoring and hazards mitigation in
20 these systems. Owing to the availability of long-term records of CO₂ emissions rates and
21 seismicity, Mammoth Mountain in California constitutes an ideal site towards such
22 predictive understanding. Mammoth Mountain is characterized by intense soil CO₂
23 degassing (up to ~1000 t d⁻¹) and tree kill areas that resulted from leakage of CO₂ from a
24 CO₂-rich gas reservoir located in the upper ~ 4 km. The release of CO₂-rich fluids from

25 deeper basaltic intrusions towards the reservoir induces seismicity and potentially
26 reactivates faults connecting the reservoir to the surface. While this conceptual model is
27 well-accepted, there is still a debate whether temporally variable surface CO₂ fluxes
28 directly reflect degassing of intrusions or variations in fault permeability. Here, we report
29 the first large-scale numerical model of fluid and heat transport for Mammoth Mountain.
30 We discuss processes (i) leading to the initial formation of the CO₂-rich gas reservoir prior
31 to the occurrence of high surface CO₂ degassing rates and (ii) controlling current CO₂
32 degassing at the surface. Although the modeling settings are site-specific, the key
33 mechanisms discussed in this study are likely at play at other volcanic systems hosting
34 CO₂-rich gas reservoirs. In particular, our model results illustrate the role of convection in
35 stripping a CO₂-rich gas phase from a rising hydrothermal fluid and leading to an
36 accumulation of a large mass of CO₂ (~10⁷-10⁸ tons) in a shallow gas reservoir. Moreover,
37 we show that both, short-lived (months to years) and long-lived (hundreds of years) events
38 of magmatic fluid injection can lead to critical pressures within the reservoir and potentially
39 trigger fault reactivation. Our sensitivity analysis suggests that observed temporal
40 fluctuations in surface degassing are only indirectly controlled by variations in magmatic
41 degassing and are mainly the result of temporally variable fault permeability. Finally, we
42 suggest that long-term CO₂ emission monitoring, seismic tomography and coupled thermal-
43 hydraulic-mechanical modeling are important for CO₂-related hazard mitigation.

44

45 Keywords: CO₂ degassing, Mammoth Mountain, numerical modeling, TOUGH2,
46 monitoring

47

48 1. Introduction

49

50 Globally, temporal variations in diffuse volcanic CO₂ emissions have been attributed to
51 mechanisms such as magma and/or magmatic fluid injection, change in crustal permeability
52 and meteorological forcing (e.g., Rogie et al., 2001; Hernandez et al., 2001; Granieri et al.,
53 2010; Arpa et al., 2013; Melian et al., 2014; Lewicki et al., 2014; Werner et al., 2014). In
54 the particular case where volcanic systems host large volumes of CO₂-rich gas beneath low-
55 permeability barriers (e.g. Albani Hills and Latera Caldera, Italy; Dieng Volcanic complex,
56 Indonesia; Mammoth Mountain, USA), temporal variations in CO₂ emissions may result
57 from a complex, yet poorly understood interplay between injection of magmatic CO₂ from
58 below and the permeability of faults controlling CO₂ migration from the reservoir to the
59 surface (e.g., Allard et al., 1989; Annunziatellis et al., 2008; Carapezza et al., 2012;
60 Lewicki et al., 2014; Werner et al., 2014). Accumulation of CO₂ in the near surface may
61 cause vegetation stress and the death of animals (Carapezza et al., 2012; Beaubien et al.,
62 2008). Human fatalities have also been reported, for example, at Mammoth Mountain,
63 California (Hill, 2000), Lakes Monoun and Nyos, Cameroun (Sigurdson, 1987; Tazieff,
64 1989; Giggenbach et al., 1991), and Dieng Volcanic Complex, Indonesia (Allard et al.,
65 1989). A predictive understanding of volcanic CO₂ emissions is therefore fundamental to
66 develop adequate monitoring strategies. Over the past decades, numerical modeling of fluid
67 and heat transport has evolved towards such a predictive tool and numerous applications to
68 volcanic systems are found in the literature (e.g. Hurwitz et al., 2003; Costa et al., 2008;
69 Ingebritsen et al., 2010; Todesco et al., 2010; Chiodini et al., 2016). The number of
70 modeling studies simulating episodic CO₂-dominated degassing at volcanic systems,
71 however, is still limited and the general understanding of such systems is solely based on a

72 qualitative conceptual model involving the presence of CO₂-rich gas reservoirs or pockets
73 in the subsurface (Giggenbach et al., 1991).

74

75 Here we present a numerical modeling study of the dynamics of magmatic CO₂ degassing
76 at Mammoth Mountain (California). Owing to the availability of long-term records of CO₂
77 emissions rates and seismicity (Werner et al., 2014 and references therein), Mammoth
78 Mountain constitutes an ideal site for gaining more quantitative insight into the CO₂
79 degassing dynamics of volcanic systems. In particular, we evaluate the processes that (i)
80 favor the formation of large scale CO₂-rich gas reservoirs within the shallow subsurface,
81 and (ii) subsequently control CO₂ emission rates at the surface. Moreover, we discuss the
82 implications of our results in terms of volcanic monitoring and hazard mitigation.

83

84 2. Site description

85

86 Mammoth Mountain is a dacitic volcano located on the southwestern rim of the Long
87 Valley caldera in California (Fig. 1a). In 1989, Mammoth Mountain transitioned to a state
88 of unrest marked by an 11 month-long low-magnitude ($M \leq 3$) seismic swarm and the onset
89 of intense non-thermal (i.e., cold) CO₂ soil degassing. This led to the formation of areas of
90 tree kill on the volcano flanks, amongst which the Horseshoe Lake tree kill (HSL) is the
91 largest (0.28 km²) (e.g., Hill and Prejean, 2005). Over the next two decades, further swarms
92 (e.g., 1997, 2006, 2008, 2009, 2011, 2014) occurred and surface degassing fluctuated
93 significantly. Interestingly, CO₂ degassing maxima occurred two to three years after the
94 onset of the 1989, 1997 and 2009 swarms (Fig. 1b).

95

96 The conceptual model for explaining such long-term degassing involves a laterally
97 extensive, shallow (<5 km) CO₂-rich gas reservoir, which is overlain by a low-permeability
98 caprock or zone of hydrothermal alteration (Sorey et al., 1998). Gas geothermometry
99 predicts a gas reservoir temperature of ~150 °C (Sorey et al., 1998). Furthermore, a liquid
100 dominated hydrothermal system was postulated to occur beneath the gas reservoir (Sorey et
101 al., 1998). The origin of CO₂ in the reservoir is attributed to the long-term degassing of
102 basaltic intrusions at greater depth (> 10 km), while the observed seismicity is believed to
103 reflect increases in pore pressure associated with the episodic migration of CO₂ from the
104 magmatic intrusion towards the shallow reservoir and the surface. Using a model linking
105 pore geometry and fluid compressibility to Vp/Vs ratios (Takei, 2002), Dawson et al.
106 (2016) estimated the total mass of CO₂ within the shallow gas reservoir as 4.6 x 10⁶ to 1.9 x
107 10⁸ tons (t).

108

109 Although short-term (month-to-month) variations in observed CO₂ emissions at HSL were
110 attributed in part to meteorological forcing, Werner et al. (2014) assumed that the long-term
111 (inter-annual) variations (Fig. 1b) largely reflected deep processes. However, there is still a
112 debate regarding the controls on the observed variation in CO₂ emission rates. On the one
113 hand, Werner et al. (2014) suggested that these oscillations reflect pressurization events
114 caused by changes in the intensity of the magmatic CO₂ input to the reservoir. They
115 excluded the possibility that CO₂ flux oscillations were directly related to changes in
116 permeability of the faults connecting the reservoir to the tree-kill areas. Accordingly, the
117 time lag between major seismic events and maximum surface degassing corresponds to the
118 time required for the CO₂-saturated fluid to ascend from the reservoir to the surface. On the
119 other hand, Lewicki et al. (2014) invoked a permeability control to explain why certain

120 seismic swarms (e.g., 1989, 2009) were followed by an initial increase and subsequent
121 decrease in surface CO₂ emissions, while others (e.g., 2006, 2008) were not. They proposed
122 that if a critical pressure threshold within the reservoir is exceeded, mechanical stress
123 causes the reactivation of existing and/or the opening of new fractures or faults (e.g.,
124 Rutqvist et al., 2007), thus increasing the permeability of the stressed rock. Subsequent
125 mineral precipitation and fault strengthening ('fault healing') have the potential to
126 progressively decrease the fracture/fault permeability over time (Gratier, 2011). Variations
127 in permeabilities of degassing pathways hence form an alternative explanation for the
128 observed fluctuations of the CO₂ degassing rate.

129

130 3. Numerical model

131

132 3.1. Numerical simulator and model mesh

133

134 Simulations were performed with TOUGH2 (Pruess et al., 1999), a well-established code
135 for modeling mass and heat flow in volcanic and geothermal systems (Chiodini et al., 2003;
136 Rinaldi et al., 2010; Todesco et al., 2010). Thermophysical properties are provided by the
137 equation of state module ECO2N V2.0 (Pan et al., 2016).

138

139 Given the lack of structural information at depth, our model considers an idealized 2D
140 cross-section extending laterally over 6 km from south of Horseshoe Lake to north-west of
141 Mammoth Mountain fumarole (Figs. 1a and 2). The model geometry is based on: (i) the
142 Sorey et al. (1998) schematic cross-section, and (ii) recent seismic tomography studies
143 (Lin, 2013; Dawson et al., 2016). Lin (2013) reinvestigated the 1989-1990 seismic events

144 and located the gas reservoir at a depth of 2-3.5 km. The reservoir depth was confirmed by
145 Dawson et al (2016) who analyzed recent seismic events (2011-2013) while using a
146 different velocity model, although the new study proposes a slightly larger reservoir extent
147 ranging from 0.5–4.5 km depth. Accordingly, the vertical extent of the mesh is set to 3.5
148 km (depth; z-axis). The model width (E-W direction; y-axis) is 500 m, which includes the
149 extent of the HSL area across the N-S profile. Considering that the reservoir extends ~2.5
150 km horizontally on a perpendicular cross-section (Lin, 2013), we simulate about a fifth of
151 the actual reservoir volume. Consequently, we consider a fifth of the total CO₂ mass
152 estimated by Dawson et al. (2016) (a “scaled value” of $9.2 \times 10^5 - 3.8 \times 10^7$ t) for the gas
153 reservoir in order to constrain our simulations.

154

155 The mesh is divided into 4 domains: (i) reservoir, (ii) reservoir seal, (iii) shallow aquifer,
156 and (iv) a fault domain, which connects the reservoir to the HSL area (Fig. 2). The fault
157 zone is simplified to only represent the permeable damage zone, with a width of 20 m, in
158 accordance with field observations worldwide (meters to hundreds of meters; Sibson,
159 2003). In order to identify the main parameters controlling surface CO₂ degassing at the
160 best-characterized site on Mammoth Mountain, we only model degassing at HSL. Based on
161 the altitude at which springs discharge on the lower volcano flanks and on water table
162 measurements in domestic wells (Evans et al., 2002), we assume that (i) the shallow aquifer
163 appears at the base of the volcanic edifice, roughly at the altitude of HSL, while vertically
164 extending down to the reservoir seal, and (ii) the upper part of the volcano is largely water
165 unsaturated (i.e., filled with air/CO₂). Because pressure gradients induced by an unsaturated
166 porous medium are negligible and topographic load does not affect its pore pressure, we
167 consider atmospheric pressure conditions at the base of the edifice and we do not include

168 the upper part of the volcanic edifice in our model (gray area, Fig. 2). Accordingly, we
169 simulate a flat surface topography. The fault-zone connecting the reservoir to the HSL area
170 is vertical although we do not know the actual geometry. The geometry of the reservoir seal
171 is cone-shaped with an arbitrary thickness varying between 300 and 800 m. Furthermore,
172 the low angle ($\sim 10^\circ$) of the cone-shaped reservoir boundary allows us to simulate the
173 formation of the proposed large-scale CO₂-rich gas reservoir. With these specifications, the
174 reservoir ranges from a minimum depth of 1.5-2 km down to the lower model boundary at
175 3.5 km depth, which is in accordance with Lin (2013). Dawson et al. (2016) proposed that
176 the gas reservoir could extend to shallower depths (ca. 0.5 km). While we do not negate this
177 possibility, we chose the Lin (2013) depth range because it is in agreement with the inferred
178 temperature of the CO₂-rich gas reservoir (150 °C, Sorey et al., 1998) and a more
179 conservative geothermal gradient of ~ 70 °C/km.

180

181 3.2. Initial and boundary conditions

182

183 At the upper model boundary, the temperature and pressure were fixed to 1 bar and 10 °C,
184 respectively (Fig. 2). Initially, a hydrostatic pressure distribution and a conductive
185 geothermal gradient of ~ 70 °C/km were defined throughout the whole model domain to
186 reach the proposed 150 °C at the top of the reservoir domain. The temperature and pressure
187 obtained for the lower boundary (T = 250°C; P = 320 bar) were fixed throughout all our
188 simulations. The upper boundary was open to fluid and heat flow, while lateral boundaries
189 were heat conductive but impermeable to fluid flow. The lower boundary was divided into
190 3 different sections (LB1-LB3; Fig. 2) as described below.

191

192 Owing to the lack of available data, permeability and other rock properties were defined
193 based on preliminary calibration simulations or were chosen based on related modeling
194 studies (Table 1 and references therein). In particular, a permeability of 10^{-14} m^2 was
195 defined for the reservoir domain because it allows the simulation of convective fluid flow,
196 while a value of 10^{-20} m^2 was defined for the reservoir seal to generate an impermeable
197 formation favoring the development of an overpressured reservoir ($P_{\text{reservoir}} > P_{\text{hydrostatic}}$). The
198 permeability of the shallow aquifer was set to a moderate value of $5 \times 10^{-16} \text{ m}^2$ in order to
199 focus fluid flow along the fault domain and to limit lateral gas migration as suggested by
200 the vertical alignment of shallow ($< 2.5 \text{ km}$ depth) hypocenters associated with the 1989
201 swarm (Lin, 2013). The permeability of the area around the upper section of the fault-zone
202 (Fig. 2) was set to that of the fault zone to allow gas to spread laterally in the shallow
203 subsurface and to mimic the surface CO_2 degassing pattern at HSL. The permeability of the
204 fault domain and the lower boundary were varied for different simulation scenarios. The
205 porosity was set to 0.01 for all domains. Values of additional rock properties (density, heat
206 conductivity, specific heat) are provided in Table 1.

207

208 4. Simulated scenarios

209

210 4.1. Initial gas reservoir formation (A simulations)

211

212 We first investigate the initial formation of a large CO_2 -rich gas reservoir prior to the
213 occurrence of high surface CO_2 degassing rates by modeling upflow and accumulation of a
214 CO_2 -rich fluid into an initially water-saturated reservoir (A simulations; Table 2). To do so,
215 the fault was sealed ($k = 1 \times 10^{-20} \text{ m}^2$) to impede any fluid flow to the surface. Upflow was

216 induced by injecting a CO₂-rich fluid, further referred to as the ‘injection fluid’, at a given
217 rate through the bottom of the reservoir (LB1, Fig. 2). Simulated fluid injection lasted
218 2,000 years to reach a fifth of the CO₂ mass estimated by Dawson et al. (2016) within the
219 reservoir. Under the modeled P-T conditions of the reservoir, the CO₂-rich phase
220 corresponds to supercritical CO₂ with a minor H₂O component (Pan et al., 2016). For
221 simplicity, however, we exclusively use the term ‘gas phase’.

222

223 An observation from preliminary simulations was that the permeability of the reservoir
224 boundaries is one of the key factors to allow the formation of a free gas-phase within the
225 reservoir. We therefore sealed the lateral boundaries to avoid lateral fluid migration and to
226 accumulate gas over the full reservoir height. Simulating a laterally isolated reservoir is
227 well supported by chemical and isotopic compositions of surface gas samples (e.g.
228 CO₂/³He, δ¹³C_{CO2}, N₂/Ar, δ¹⁵N_{N2}) that are distinct from fluid compositions of the adjacent
229 Long Valley hydrothermal system (Sorey et al., 1998). However, if the reservoir is fully
230 sealed and entirely liquid-saturated when injection starts, the reservoir pressure increases
231 due to the low compressibility of liquid water. Consequently, CO₂ becomes highly soluble
232 and no free gas phase can form. In order to obtain a persistent gas phase within the
233 reservoir, the pressure of the reservoir was limited by allowing fluid circulation across the
234 portion of the lower model boundary surrounding the injection area at LB1 (LB2 and LB3).

235

236 In addition to the permeability of the reservoir boundaries, the formation of a free gas phase
237 depends on the dissolved CO₂ content of the injection fluid as well as the fluid injection
238 rate. This is because the CO₂ content dictates whether the injection fluid corresponds to a
239 single-phase liquid or a two-phase liquid-gas mixture (Peiffer et al., 2015). According to

240 Giggenbach et al. (1991), CO₂ released from magmatic intrusions dissolves in overlying
241 liquid-dominated hydrothermal systems, where the dissolved CO₂ content is buffered by
242 water-rock interaction reactions. Upon migration to shallower depths, CO₂ exsolves in
243 response to the drop in pressure and temperature and may eventually accumulate if the
244 hydrothermal system is overlain by a low-permeability caprock. At Mammoth Mountain,
245 magmatic CO₂ degassing and convection rates are unknown. Hence, we have little
246 information on the dissolved CO₂ content and injection rate into the simulated reservoir
247 (Fig. 2), whether the fluid enters the modeled reservoir in a single or a two-phase state, and
248 how fluid injection into the reservoir and surface CO₂ degassing are linked. The specified
249 time-averaged CO₂ injection rate of 150 t d⁻¹ in simulations A (Table 2) should therefore be
250 regarded as a somewhat arbitrary injection rate although it is constrained by the average
251 surface CO₂ degassing rate at HSL over the last decades (Werner et al., 2014). A H₂O
252 injection rate of 1111 t d⁻¹ was additionally specified (simulations A1 and A2; Table 2) to
253 simulate a CO₂ content for the injection fluid of 5.2 mol %, which is similar to CO₂
254 concentrations proposed for buffered hydrothermal systems situated above magmatic
255 intrusions (< 10 mol %; Giggenbach et al., 1991). Moreover, a CO₂ concentration of 5.2
256 mol % is above the CO₂ solubility under the initial P-T conditions at the lower boundary
257 (4.4 mol % at 320 bar and 250°C). Hence, with the specified injection rates, we initiated the
258 simulations with a two-phase fluid injection, which means that boiling occurs at greater
259 depth than the modeled lower boundary (< 3.5 km depth). While the injected CO₂ is
260 considered to be magmatic (Farrar et al., 1995), the specified H₂O injection corresponds to
261 hydrothermal water that is driven upward together with the CO₂-rich magmatic gas phase
262 (Giggenbach et al., 1991).

263

264 Gas accumulation and pressure build-up within the reservoir were explicitly simulated for a
265 moderate (simulation A1; $k_{LB2} = k_{LB3} = 10^{-16} \text{ m}^2$) and a low permeability (simulation A2;
266 $k_{LB2} = 10^{-18} \text{ m}^2$, $k_{LB3} = 10^{-20} \text{ m}^2$) of the lower model boundary. The evolution of the gas
267 saturation (S_g) and liquid/gas velocity vectors for these simulations are shown in Figure 3,
268 while Figure 4 illustrates the corresponding evolution of the gas mass in the reservoir and
269 CO_2 outflow rate across the lower boundary, as well as the final P-T distribution. In the
270 case of a moderately permeable lower model boundary (simulation A1) the injected two-
271 phase fluid separates into a CO_2 -rich gas phase and a liquid aqueous phase below the lower
272 model boundary (Figs. 3a-b). Subsequently, the CO_2 -rich gas phase flows convectively to
273 the upper part of the reservoir where it accumulates beneath the reservoir seal. In contrast,
274 the liquid phase escapes the lower model domain, which physically corresponds to fluid
275 migration towards a lower section of the reservoir that was not modeled in this study. Such
276 phase separation and subsequent gas accumulation is observed because the permeability of
277 the lower model boundary is high enough to limit the pressure in the reservoir (Fig. 4c),
278 which keeps the CO_2 content of the injection fluid above saturation. It follows that the gas
279 phase progressively fills the entire reservoir domain as illustrated by the continuous
280 increase of the CO_2 mass over time (Fig. 4a). At the end of the simulated 2000-year period
281 a value of $1.5 \times 10^7 \text{ t CO}_2$ is reached, which is on the upper range of the Dawson et al.
282 (2016) estimate (scaled value = $3.8 \times 10^7 \text{ t}$).

283

284 For a low permeability of the lower model boundary ($k_{LB2} = 10^{-18} \text{ m}^2$, $k_{LB3} = 10^{-20} \text{ m}^2$,
285 simulation A2) total gas accumulation over 2000 years decreases by a factor of two ($7.25 \times$
286 10^6 t , Fig. 4a) when compared to the moderate permeability scenario (Fig. 4a), although it
287 is still within the Dawson et al. (2016) scaled range ($9.2 \times 10^5 - 3.8 \times 10^7 \text{ t}$). This is because

288 a decrease in permeability of the lower boundary limits fluid migration towards the lower
289 portion of the reservoir and yields an increase in reservoir pressure and thus CO₂ solubility.
290 The initial two-phase injection fluid therefore transitions to a single-phase liquid state. In
291 this case, boiling occurs within the modeled reservoir, impeding the gas phase to
292 accumulate over the full height of the reservoir. Therefore, the lower section of the modeled
293 reservoir remains liquid-dominated (Fig. 3c).

294

295 At the top of the CO₂-rich gas reservoir the pressure in the two permeability scenarios
296 differs by 105 bar (Fig. 4c). Hereafter, we refer to the reservoir pressure states in the two
297 simulation scenarios as highly (simulations A2, low permeability) and mildly (simulation
298 A1, moderate permeability) overpressured. In contrast, the temperature profiles for the two
299 scenarios are very similar (Fig. 4c). Likewise, the average CO₂ concentration within the
300 gas-dominated section of the reservoir is not sensitive to lower-boundary permeability and
301 is around 90 mol % at 2,000 years.

302

303 Figure 4b shows that most of the injected CO₂ flows downward across the lower model
304 boundary in the dissolved state (hereafter referred to as the 'LB outflow'), while only a
305 limited fraction accumulates as a gas phase in the reservoir. After an initial time period, the
306 ratio between the LB outflow and the CO₂ injection rate within the reservoir (Fig. 4b) has
307 evolved to a steady state, which is not sensitive to the permeability of the lower model
308 boundary. This is why at steady state simulations A1 and A2 are characterized by very
309 similar CO₂ accumulation rates ($\alpha' = 8.8 \text{ t d}^{-1}$, $\beta = 10.5 \text{ t d}^{-1}$; Fig .4a). In the supplementary
310 information section 1 we further show that the CO₂ accumulation rate, CO₂ mass and P-T
311 distribution at steady-state are insensitive to the CO₂ concentration of the injection fluid.

312

313 4.2. Surface CO₂ degassing

314

315 The goals of the second set of simulations were to investigate CO₂ release from the
316 reservoir towards the surface at HSL and to better understand observed variations in surface
317 CO₂ emissions. As such, we conducted two types of simulations to assess the hypotheses
318 that variations in CO₂ input into the reservoir (Werner et al., 2014) versus fault
319 permeability (Lewicki et al., 2014) exerted primary control over surface CO₂ emissions at
320 HSL.

321

322 4.2.1. Degassing through a fault with constant permeability (simulations B,

323 C)

324

325 To test the effect of reservoir pressure variations on surface CO₂ emission rates, we kept the
326 permeability of the fault constant over time. The B simulations evaluate the loss of CO₂
327 from the reservoir through the fault zone, assuming a constant magmatic CO₂ injection rate
328 into the reservoir over a period of 30 years. Initial and boundary conditions were taken
329 from the end of simulations A1 and A2 to assess the effect of different initial gas masses
330 and reservoir pressures. The effects of different fault permeabilities ($k_f = 5 \times 10^{-15} - 2 \times 10^{-14}$
331 m^2) that are held constant over time are investigated through simulations B1-B4 (Table
332 2). The specified permeability values were all within the range estimated for transient
333 permeability increase associated with fluid migration at Mammoth Mountain ($10^{-14.4} - 10^{-13.9}$
334 m^2 , Ingebritsen and Manning, 2010). Hence, by considering such elevated permeability,
335 these simulations correspond to an end-member scenario where the fault is constantly

336 permeable to fluid flow. Moreover, it should be noted that the fault connecting the reservoir
337 to the surface was initially fully water saturated, which means that the type B simulations
338 model the ‘initial’ CO₂ loss from a newly formed reservoir (Table 2). In simulations B1-
339 B4, CO₂ reaches the surface after 0.5–3 years, corresponding to the time needed to
340 advectively transport the gas phase along the initially water-saturated fault (Fig. 5a).
341 Interestingly, simulated surface CO₂ emission rates progressively increase over the
342 simulated period of time, and do not oscillate. This is because a large gas mass reservoir
343 cannot be completely depleted over a short period of time. For instance, the CO₂ mass
344 reached at the end of simulation A1 (1.5×10^7 t) would be fully depleted after 274 years
345 considering a constant surface degassing rate of 150 t d^{-1} and the absence of magmatic CO₂
346 input. The surface CO₂ emission rates are positively correlated with both the fault zone
347 permeability and initial reservoir pressure (Fig. 5a).

348

349 The only circumstances under which we observe a decrease in surface CO₂ emission rate
350 with a temporally constant fault permeability and constant magmatic CO₂ influx into the
351 reservoir is when the gas mass in the initially formed reservoir is close to the lower estimate
352 of Dawson et al. (2016) (scaled value: 9.2×10^5 t, Fig. 5a). For instance, a low initial value
353 of 1.63×10^6 t is obtained when running simulation A1 for only 120 years (Fig. 3a).
354 Simulation B5 considers such gas mass and a high permeability of 10^{-13} m^2 for the fault
355 zone as initial conditions. After degassing over 30 years, the gas phase becomes mainly
356 restricted to the upper 350 m of the reservoir (Fig. 6). Because this is shallower than the
357 intersection of the fault zone with the reservoir (Fig. 6) the surface CO₂ emission rate
358 declines sharply over time as observed at HSL after the 1997 and 2009 seismic swarms
359 (Fig. 5a). In the supplementary information section 2 we also show that varying fault

360 location (and thus where the fault intersects the CO₂-rich reservoir) influences the
361 magnitude of CO₂ emissions. The overall temporal pattern in CO₂ emissions, however, is
362 not sensitive to fault location.

363

364 Simulations C1-C4 assess the impact of varying the rate of magmatic CO₂ input into the
365 reservoir, while holding the fault permeability constant. To do so, simulations C1 and C2
366 were initiated by taking the P , T and X_{CO_2} distribution as obtained after 10 years of
367 simulation B2. This particular ‘restart’ time simulates a fault initially saturated with a
368 mixture of gas and liquid (mean $S_g = 0.33$), and that degases superficially at a rate similar
369 to measured background values at HSL (90 t d^{-1}). Both simulations are run for a period of
370 20 years. The permeabilities of the lower boundaries at LB2 and LB3 were lowered to 10^{-18}
371 and 10^{-20} m^2 , respectively, to obtain a large pressure increase within the reservoir.
372 Simulation C1 starts with a 6-month period of enhanced injection (20 times the rate used
373 for simulations A and B) and continues with the same regular injection rate as in B2 for the
374 remaining time (10.5-30 years). Simulation C2 involves an injection rate that was lowered
375 by a factor of 3 over the entire 20-year period (10-30 years) (Table 2). These two
376 simulations show that varying the rate of magmatic CO₂ input into the reservoir only affects
377 the magnitude of the surface CO₂ emission rate, whereas the temporal degassing patterns
378 remains the same as in simulation B2 (Fig. 5b).

379

380 In contrast, simulations C3 and C4 were initiated by taking the physical conditions obtained
381 after 10 years of simulation B5 to simulate the degassing of reservoir with a limited gas
382 mass. An increase in the fluid injection rate by a factor of 20 was imposed for the first 6
383 months in simulation C3, and for the first three years in simulation C4, while the same

384 injection rate as in B5 was used for the remaining time (Table 2). Under such injection
385 conditions, the pressure gradient within the reservoir increases (Fig. 4c), causing an
386 immediate increase in surface CO₂ emission rates (Fig. 5b). Once the period of enhanced
387 injection stops, the pressure gradient and surface CO₂ emission rates decrease. Maximum
388 CO₂ emission rates are reached at the end of the increased injection period and the
389 degassing evolution is similar to the trend observed at HSL between 1998-2005 and 2009-
390 2013 (Fig. 5b). In fact, setting the period of increased CO₂ injection rate to 3 years results
391 in a relatively close match with the observed pattern in surface CO₂ emissions (simulation
392 C4).

393

394 4.2.2. Surface degassing under time-dependent permeability conditions (D
395 simulations)

396

397 To investigate the effect of a temporally variable fault permeability on the surface CO₂
398 degassing rate we kept the initial gas mass within the reservoir and the rate of fluid input
399 constant (150 t d⁻¹ CO₂/ 1111 t d⁻¹ H₂O, Table 2). By doing so, we test whether a change in
400 fault permeability alone can be responsible for the observed oscillations in surface CO₂
401 emissions. While we do not explicitly simulate the cause for such permeability variations,
402 they are likely linked to increased fluid injection into the reservoir and subsequent pore
403 pressure increase.

404

405 Varying the fault permeability mimics fault zone reactivation and subsequent healing as
406 they likely occur associated with seismic events (Rutqvist et al., 2007). An important
407 consideration for this scenario is that the vertical extent of the fault whose permeability

408 changes is variable. Rinaldi et al. (2014) showed that low-magnitude ($M = 2-3.5$) seismic
409 events induced by CO_2 injection in carbon capture and storage (CCS) reservoirs do not
410 always cause the reactivation of a fault over its full vertical extent. Therefore, we ran
411 different simulations that varied the permeability of different parts of the fault to test the
412 effect on surface CO_2 degassing. Simulations D1 and D2 consider a temporally variable
413 permeability of the lower fault section (from the reservoir to the top of the reservoir seal),
414 while the permeability of the upper section (from the top of the seal to the surface) remains
415 constant ($k = 2 \times 10^{-14} \text{ m}^2$, Table 2). In contrast, simulation D3 considers a temporally
416 variable permeability along the entire vertical extent of the fault.

417

418 For each simulation (D1-D3), two cycles of temporally varying fault permeability were
419 carried out to simulate CO_2 degassing under different conditions of fluid saturation within
420 the fault (Fig. 7a). The first cycle (0-5 years) initiates with a fault fully saturated with water
421 (initial conditions inherited from simulation A1), while the second cycle (5-12 years) starts
422 when the system has already been degassing to the surface for a few years and the fault is
423 saturated with a liquid-gas mixture. Simulation D1 is run with a fault permeability that
424 decreases exponentially from 8×10^{-14} to $4 \times 10^{-15} \text{ m}^2$ during 4 years and then remains stable
425 ($4 \times 10^{-15} \text{ m}^2$) for the rest of the cycle (k_{f1} ; Fig. 7a). In simulation D2, we apply the same
426 decrease in fault permeability, but over a shorter (3-year) period of time (k_{f2} , Fig. 7a).
427 Simulation D3 is run with the temporal change in fault permeability following pattern k_{f1} .
428 The specified exponential permeability decay rate law was taken from published laboratory
429 experiments (Micklethwaite et al., 2016, Table 2). The corresponding permeability decay
430 rates in Table 1 were chosen to match observed surface CO_2 emissions rates, but are

431 consistent with laboratory experiments and field-scale observations (1 order of magnitude
432 over 1–10 years; Ingebritsen and Manning, 2010).

433

434 The three D simulations produce different temporal patterns in surface CO₂ emissions (Fig.
435 7b). As observed for the B simulations, a given time delay is needed to observe degassing
436 at the surface when the fault is initially fully saturated with water. Furthermore, if the entire
437 fault is reactivated (simulation D3) the gas reaches the surface more quickly than in the
438 partial reactivation runs (simulations D1 and D2). In response to the second cycle of
439 permeability variation, simulation D1, and to a lesser extent D2, produce surface CO₂
440 emission rates that match emission rates measured at HSL (Fig. 7b). The peak in surface
441 CO₂ emission rate is reached ~2-3 years after the instantaneous increase in permeability.
442 Conversely, simulation D3 generates a more intense peak in surface CO₂ emission rate only
443 a few months after the fault is reactivated.

444

445 5. Discussion

446

447 5.1. Initial formation of a CO₂-rich gas reservoir

448

449 Little is known about the rate and temporal pattern of migration of magmatic CO₂ fluids
450 into the shallow crustal reservoir beneath Mammoth Mountain. For an assumed CO₂
451 injection rate of 150 t d⁻¹ our A simulations suggest that the large mass of gas within the
452 reservoir beneath Mammoth Mountain has probably formed over a period of several
453 hundreds of years (Fig. 4a). However, Figure 4a illustrates that the time required for the
454 formation depends on the amount of CO₂ injected to the system and the permeability of the

455 lower boundary. The time required for gas reservoir formation could therefore be much
456 shorter if the CO₂ content of the injection fluid was higher and/or if the lower boundary was
457 more permeable. Conversely, the formation time could be longer if the injection rate is
458 sporadic and lower on average over time. Furthermore, these A simulations illustrate that
459 the accumulation of a large mass of free CO₂ beneath the reservoir seal is only possible if
460 fluid migration occurs towards a lower portion of the reservoir, a process that limits the
461 reservoir pressure over time (Fig. 3). Accordingly, a significant fraction of the CO₂ injected
462 into the reservoir flows downward through the lower model boundary in the dissolved state
463 (Fig. 4b). We propose that the outflowing CO₂-rich fluid forms an isolated, vertical
464 convection cell beneath the gas reservoir. Major lateral outflow, which would be
465 accompanied by groundwater thermal anomalies and mineralized compositions, is unlikely
466 because most springs around Mammoth Mammoth are cold and only weakly mineralized
467 (Evans et al., 2002). A final requirement for forming a large gas mass in the reservoir (as in
468 simulation A1) is that initial boiling of the upflowing CO₂-rich fluid (i.e., CO₂ exsolution)
469 occurs significantly below the reservoir seal and certainly below the lower model boundary
470 at 3.5 km depth. This is because the amount of CO₂ exsolved from a CO₂-rich fluid is
471 maximized if the difference between the P,T conditions at the reservoir top and the P,T-
472 conditions under which initial boiling occurs (i.e., equilibrium P,T for the given CO₂
473 content) is at its maximum.

474

475 5.2. Pathways for CO₂ migration

476

477 The spatio-temporal progression of seismicity beneath Mammoth Mountain has been
478 attributed to increases in pore pressure associated with the migration of CO₂-rich magmatic

479 fluids that originate from basaltic intrusions (Hill and Prejean, 2005; Shelly and Hill, 2011;
480 Lewicki et al., 2014; Shelly et al., 2015). According to our simulations, the time required to
481 pressurize the reservoir by an upflowing fluid depends on the reservoir pressure prior to
482 fluid injection into the reservoir, the permeability of the reservoir boundaries, and the rate
483 of magmatic CO₂ influx. Because the location of the tree-kill areas at Mammoth Mountain
484 are consistent with mapped faults (Sorey et al., 1998), it is likely that the maximum
485 overpressure that can be contained within the reservoir is controlled by the presence of such
486 faults (Sibson, 2003). Rutqvist et al. (2007) performed fully coupled thermal-hydraulic-
487 mechanical (THC) simulations of a hypothetical CCS reservoir. Their results showed that
488 rupture of an optimally oriented fault occurs at a critical pressure between 72-84 % of the
489 lithostatic pressure. Simulation C1 suggests that 6 months of enhanced CO₂ injection (20
490 times the background rate) into a reservoir that is initially mildly overpressured is enough
491 to increase the pressure at the top of the reservoir by 46 bars (Fig. 4c). This yields a
492 pressure that is 74 % of the local lithostatic value. Similar pressures are obtained for long-
493 term but low CO₂ injection rates such as manifested by simulation A2, where the pressure
494 approaches 90% of lithostatic at the reservoir top after 2000 years (Fig. 4c). Even though
495 this comparison with lithostatic pressure is oversimplified, it allows us to conclude that
496 either (i) short-lived events of enhanced CO₂-rich fluid injection or (ii) long-term but low
497 injection rates have the potential to significantly increase the reservoir pressure, trigger
498 fault reactivation and induce high CO₂ emission rates at the surface. The fact that some
499 seismic swarms (e.g., 2006) were not followed by an increase in CO₂ emission rates might
500 indicate that the reservoir pore pressure may not have exceeded the critical value (Fig. 1b;
501 Lewicki et al., 2014).

502

5.3. Causes of variations in surface CO₂ degassing rates

504

505 Our simulations showed that the oscillating CO₂ emission rates observed at HSL could
506 have solely resulted from (i) an increase in fluid injection rate into the reservoir at constant
507 fault permeability (simulation C4, Fig. 5b) or (ii) temporally and spatially variable fault
508 permeability associated with seismicity and subsequent fault healing (simulation D1, Fig.
509 7b). The former scenario, however, requires that the drainable portion of the CO₂-rich gas
510 reservoir is small, and that the period of enhanced injection is similar to the 2-3 year time
511 lag of the CO₂ degassing peak. Moreover, the continuous surface CO₂ degassing observed
512 at HSL since 1989 (Fig. 1b) suggests that the reservoir gas mass has remained above a
513 certain threshold value. As such, the constant permeability scenario requires a delicate mass
514 balance between magmatic input into the reservoir and surface degassing.

515

516 The variable permeability scenario requires us to define specific parameter values to match
517 the degassing pattern at HSL. Simulation results were most sensitive to the length of the
518 fault subjected to permeability variations, the magnitude of the permeability increase and
519 the timing of the subsequent permeability decay. Interestingly, very high CO₂ upflow
520 velocities were observed along the fault after it was partially saturated with gas (e.g. 13 km
521 yr⁻¹ at five years in simulations D1). It follows that the time delay of ~2-3 years (Fig. 1b)
522 observed between the occurrence of seismic swarms and the maximum rate of surface CO₂
523 degassing does not correspond to the time required for the gas to ascend from the reservoir
524 to the surface (2 km flow distance). Rather, it likely reflects the time required for the
525 permeability of the reactivated (i.e., lower) fault section to drop to its initial (pre-
526 reactivation) value (Fig. 7a).

527

528 Due to the lack of precisely constrained parameter values (Table 1) our simulations are
529 underconstrained. Accordingly, multiple parameter value combinations can yield to the
530 same degassing behavior and we cannot exclude one of the simulated scenarios.
531 Nevertheless, given the observed spatial and temporal correlations between seismic
532 swarms, fault location and degassing peaks (Fig. 1) it seems rather convincing that
533 permeability variations play a highly important role as suggested by our D simulations.

534

535 Although we did not investigate CO₂ degassing in other areas on Mammoth Mountain,
536 ⁴He/³He ratios from MMF and magmatic CO₂ concentration recorded in tree-rings at the
537 Chair 12 tree-kill area suggest similar patterns in degassing behavior (Lewicki et al., 2014;
538 Evans et al., 2011; W.C. Evans, unpublished data). Such observation might indicate that
539 other degassing areas are linked to the reservoir by faults displaying similar behavior.

540

541 6. Summary and conclusions

542

543 The accumulation of magmatic CO₂ beneath low-permeability barriers may lead to the
544 formation of CO₂-rich gas reservoirs within volcanic systems. CO₂ degassing from such
545 systems can result in human, animal and plant mortality. Owing to the availability of long-
546 term records of CO₂ emissions rates and seismicity, Mammoth Mountain is an ideal site to
547 gain quantitative insight into the dynamics of CO₂ degassing in these volcanic systems.

548

549 Here, we present the first large-scale numerical model of fluid and heat transport for
550 Mammoth Mountain. Simulations demonstrated that the occurrence of vertical convection

551 cells is crucial for the formation of a large CO₂-rich gas reservoir because it limits the
552 reservoir pressure and favors exsolution of gaseous CO₂ and accumulation within the
553 reservoir. A subsequent sensitivity analysis assessed whether temporal variations in
554 magmatic CO₂ input into the reservoir or fault permeability exert the primary control on
555 surface degassing. This analysis demonstrated that the scenario in which fault permeability
556 varied does not require a specific gas-reservoir volume or a precise fault location to induce
557 observed oscillations in surface degassing at Mammoth Mountain. Therefore, this scenario
558 offers a more generally applicable explanation. Temporal variations in fault permeability
559 are likely due to (1) increase in pore pressure associated with the migration of magmatic
560 fluids that induces fault reactivation and (2) subsequent fault healing. Although we favor
561 this explanation, variations in magmatic fluid input (with constant fault permeability) may
562 explain observed patterns in surface CO₂ emissions, but only if the drainable portion of the
563 gas reservoir is limited in volume.

564

565 Similar degassing dynamics are likely at play at other volcanic systems hosting CO₂-rich
566 gas reservoir beneath low-permeability barriers (e.g. Albani Hills and Latera Caldera,
567 Dieng Volcanic complex). Our findings generally imply that the intensity of CO₂ emissions
568 and the time delay between seismic activity and peaks in surface CO₂ emission rates should
569 not only be interpreted in terms of magmatic degassing, but also in terms of the integrity of
570 the reservoir seal and changes in fault permeability. An implication of the observation that
571 CO₂ emission peaks are not synchronous with periods of increased seismicity is that hazard
572 mitigation should include long-term CO₂ emission monitoring, especially after the
573 occurrence of increased seismicity. Moreover, the fact that CO₂ degassing is strongly
574 controlled by the presence and integrity of the reservoir seal calls for performing detailed

575 seismic tomography to locate such seals. Coupled thermal-hydraulic-mechanical modeling
576 constrained by the local stress regime and fault geometry is required to better define the
577 maximum overpressure that can be contained within the reservoir before fault rupture. Such
578 analyses will allow for improved CO₂ emission monitoring and hazard mitigation,
579 especially with respect to the time lag to be expected between increased seismicity and CO₂
580 emission peaks.

581

582 Acknowledgments

583

584 L. Peiffer was supported by the CEMIE-GEO Conacyt-SENER Laboratory project
585 ('Sistema de Laboratorios Especializados') and an internal CICESE project. The Swiss
586 Competence Center for Energy Research – Supply of Electricity (SCCER-SoE) supports
587 research in geothermal energy at the University of Bern. We thank W.C. Evans and three
588 anonymous reviewers for constructive review of the manuscript. We also thank T. Mather
589 for efficient and constructive editorial handling. Any use of trade, firm, or product names is
590 for descriptive purposes only and does not imply endorsement by the U.S. Government. All
591 the data are available upon request to the authors.

592

593 References

594

595 Allard, P., Dajlevic, D., Delarue, C., 1989. Origin of carbon dioxide emanation from the
596 1979 Dieng eruption, Indonesia: Implications for the origin of the 1986 Nyos catastrophe.
597 *J. Volcanol. Geotherm. Res.*, 39, 195-206.

598

599 Annunziatellis, A., Beaubien, S.E., Bigi, S., Ciotoli, G., Coltella, M., Lombardi, S., 2008.
600 Gas migration along fault systems and through the vadose zone in the Latera caldera
601 (central Italy): Implications for CO₂ geological storage. *Int. J. Greenh. Gas Control* 2, 353-
602 372.

603

604 Arpa, M.C., Hernández, P.A., Padrón, E., Reniva, P., Padilla, G.D., Bariso, E., Melián, G.,
605 Barrancos, J., Nolasco, D., Calvo, D., Pérez, N.M., Solidum, R.U.J., 2013. Geochemical
606 evidence of magma intrusion inferred from diffuse CO₂ emissions and fumarole plume
607 chemistry: the 2010–2011 volcanic unrest at Taal Volcano, Philippines. *Bull. Volcanol.*,
608 75:747, <https://doi.org/10.1007/s00445-013-0747-9>.

609

610 Beaubien, S. E., Ciotoli, G., Coombs, P., Dictor, M. C., Krüger, M., Lombardi, S., Pearce,
611 J.M., West, J. M., 2008. The impact of a naturally occurring CO₂ gas vent on the shallow
612 ecosystem and soil chemistry of a Mediterranean pasture (Latera, Italy). *Int.J. Greenh. Gas*
613 *Con.*, 2(3), 373-387.

614

615 Carapezza, M.L., Barberi, F., Ranaldi, M., Ricci, T., Tarchini, L., Barrancos, J., Fischer, C.,
616 Granieri, D., Lucchetti, C., Melian, G., Perez, N., Tuccimei, P., Vogel, A., Weber, K.,
617 2012. Hazardous gas emissions from the flanks of the quiescent Colli Albani volcano
618 (Rome, Italy). *Appl. Geochem.*, 27, 1767-1782.

619

620 Chiodini, G., Todesco, M., Caliro, S., Del Gaudio, C., Macedonio, G., Russo, M., 2003.
621 Magma degassing as a trigger of bradyseismic events: The case of Phlegrean Fields (Italy),
622 Geophys. Res. Lett., 30(8), 1434, doi:10.1029/2002GL016790.

623

624 Chiodini, G., Caliro, S., Cardellini, C., Granieri, D., Avino, R., Baldini, A., Donnini, M.,
625 Minopoli, C., 2010. Long-term variations of the Campi Flegrei, Italy, volcanic system as
626 revealed by the monitoring of hydrothermal activity. J. Geophys. Res. Solid Earth,
627 115(B3), doi: 10.1029/2008JB006258.

628

629 Chiodini, G., Tassi, F., Caliro, S., Chiarabba, C., Vaselli, O., Rouwet, D., 2012. Time-
630 dependent CO₂ variations in Lake Albano associated with seismic activity. Bulletin of
631 volcanology, 74(4), 861-871.

632

633 Chiodini, G., Paonita, A., Aiuppa, A., Costa, A., Caliro, S., De Martino, P., Acocella, V.,
634 Vandemeulebrouck, J., 2016. Magmas near the critical degassing pressure drive volcanic
635 unrest towards a critical state. Nat. Commun. 7, 13712, doi: 10.1038/ncomms13712.

636

637 Costa, A., Chiodini, G., Granieri, D., Folch, A., Hankin, R. K. S., Caliro, S., Avino, R.,
638 Cardellini, C., 2008. A shallow-layer model for heavy gas dispersion from natural sources:
639 Application and hazard assessment at Caldara di Manziana, Italy, Geochem. Geophys.
640 Geosyst., 9, Q03002, doi:10.1029/2007GC001762.

641

642 Dawson, P., Chouet, B., Pitt, A., 2016. Tomographic image of a seismically active volcano:
643 Mammoth Mountain, California. *J. Geophys. Res. Solid Earth*, 121, 114-133,
644 doi:10.1002/2015JB012537.

645

646 Evans, W. C., Sorey, M. L., Cook, A. C., Kennedy, B. M., Shuster, D. L., Colvard, E. M.,
647 White, L. D., Huebner, M. A., 2002. Tracing and quantifying magmatic carbon discharge in
648 cold groundwaters: lessons learned from Mammoth Mountain, USA. *J. Volcanol.*
649 *Geotherm. Res.*, 114(3), 291-312.

650

651 Evans, W.C., Mangan, M., McGeehin, J.P., King, J., Lewicki, J.L., Hilley, G., 2011.
652 Magmatic CO₂ emissions at Mammoth Mountain, California, tracked by ¹⁴C in tree core.
653 Abstract V21A-2483 presented at 2011 Fall Meeting, AGU, San Francisco, CA, 5–9Dec.

654

655 Granieri, D., Avino, R., Chiodini, G., 2010. Carbon dioxide diffuse emission from the soil:
656 ten years of observations at Vesuvio and Campi Flegrei (Pozzuoli), and linkages with
657 volcanic activity. *Bull. Volcanol.*, 72, 103–118, doi:10.1007/s00445-009-0304-8.

658

659 Gratier, J. P., 2011. Fault permeability and strength evolution related to fracturing and
660 healing episodic processes (years to millennia): the role of pressure solution. *Oil Gas Sci.*
661 *Technol.* 66 (3), 491-506.

662

663 Gruen, G., Weis, P., Driesner, T., Heinrich, C. A., de Ronde, C. E., 2014. Hydrodynamic
664 modeling of magmatic–hydrothermal activity at submarine arc volcanoes, with implications
665 for ore formation. *Earth Planet. Sci. Lett.*, 404, 307-318.

666

667 Hernández, P.A., Notsu, K., Salazar, J.M., Mori, T., Natale, G., Okada, H., Virgilli, G.,
668 Shimoike, Y., Sato, M., Perez, N.M., 2001. Carbon dioxide degassing by advective flow
669 from Usu volcano, Japan. *Science* 2001, 83–86.

670

671 Hill, P. M., 2000. Possible asphyxiation from carbon dioxide of a cross-country skier in
672 eastern California: a deadly volcanic hazard. *Wild. Environ. Med.*, 11(3), 192-195.

673

674 Hill, D.P., Prejean, S., 2005. Magmatic unrest beneath Mammoth Mountain, California. *J.*
675 *Volcanol. Geotherm. Res.* 146, 257–283.

676

677 Hurwitz, S., K. L. Kipp, S. E. Ingebritsen, Reid, M. E., 2003. Groundwater flow, heat
678 transport, and water table position within volcanic edifices: Implications for volcanic
679 processes in the Cascade Range, *J. Geophys. Res.*, 108(B12), 2557,
680 doi:10.1029/2003JB002565.

681

682 Ingebritsen, S. E., Manning, C. E., 2010. Permeability of the continental crust: dynamic
683 variations inferred from seismicity and metamorphism. *Geofluids*, 10(1-2), 193-205.

684

685 Ingebritsen, S. E., Geiger, S., Hurwitz, S., & Driesner, T., 2010. Numerical simulation of
686 magmatic hydrothermal systems. *Rev. Geophys.*, 48(1), doi: 10.1029/2009RG000287.

687

688 Lewicki, J. L., Birkholzer, J., Tsang, C. F., 2007. Natural and industrial analogues for
689 leakage of CO₂ from storage reservoirs: identification of features, events, and processes and
690 lessons learned. *Environ. Geol.*, 52(3), 457.

691

692 Lewicki, J. L., Hilley, G. E., Shelly, D. R., King, J. C., McGeehin, J. P., Mangan, M.,
693 Evans, W. C., 2014. Crustal migration of CO₂-rich magmatic fluids recorded by tree-ring
694 radiocarbon and seismicity at Mammoth Mountain, CA, USA. *Earth Planet. Sci. Lett.* 390,
695 52-58.

696

697 Lin, G., 2013. Seismic investigation of magmatic unrest beneath Mammoth Mountain,
698 California, USA. *Geology*, 41 (8), 847-850.

699

700 Manning, C. E., Ingebritsen, S. E., 1999. Permeability of the continental crust: Implications
701 of geothermal data and metamorphic systems, *Rev. Geophys.*, 37, 127–150,
702 doi:10.1029/1998RG900002.

703

704 Melián, G., Hernández, P.A., Padrón, E., Pérez, N.M., Barrancos, J., Padilla, G., Dionis,
705 S., Rodríguez, F., Calvo, D., Nolasco, D., 2014. Spatial and temporal variations of diffuse
706 CO₂ degassing at El Hierro volcanic system: Relation to the 2011–2012 submarine
707 eruption. *J. Geophys. Res.* 119, doi: 10.1002/2014JB011013.

708

709 Micklethwaite, S., Ford, A., Witt, W., Sheldon, H.A., 2016. Transient permeability in fault
710 stepovers and rapid rates of orogenic gold deposit formation. In: Gleeson, T., Ingebritsen,
711 S.E. (Eds), *Crustal permeability*. John Wiley & Sons Ltd, UK, pp. 249-259.

712

713 Pan, L., Spycher, N., Doughty, C., Pruess, K., 2016. ECO2N V2.0: A TOUGH2 fluid
714 property module for modeling CO₂-H₂O-NACL systems to elevated temperatures of up to
715 300° C. *Greenh. Gases* 7 (2), 313-327.

716

717 Peiffer, L., Wanner, C., Pan, L., 2015. Numerical modeling of cold magmatic CO₂ flux
718 measurements for the exploration of hidden geothermal systems. *J. Geophys. Res. Solid*
719 *Earth*, 120(10), 6856-6877, doi:10.1002/2015JB012258.

720

721 Pruess, K., C. Oldenburg, Moridis, G., 1999. TOUGH2: User's guide, version 2.0 Rep.
722 LBNL-43134, Lawrence Berkeley Natl. Lab., Berkeley, Calif.

723

724 Rinaldi, A., Todesco, M., Bonafede, M., 2010. Hydrothermal instability and ground
725 displacement at the Campi Flegrei caldera, *Phys. Earth Planet. Inter.*, 178, 155–161,
726 doi:10.1016/j.pepi.2009.09.005.

727

728 Rinaldi, A. P., Rutqvist, J., Cappa, F., 2014. Geomechanical effects on CO₂ leakage
729 through fault zones during large-scale underground injection. *Int. J. Greenh. Gas Con.*, 20,
730 117-131.

731

732 Rogie, J.D., Kerrick, D.M., Sorey, M.L., Chiodini, G., Galloway, D.L., 2001. Dynamics of
733 carbon dioxide emission at Mammoth Mountain, California. *Earth Planet. Sci. Lett.* 188,
734 535–541.

735

736 Rutqvist, J., Birkholzer, J., Cappa, F., Tang, C. F., 2007. Estimating maximum sustainable
737 injection pressure during geological sequestration of CO₂ using coupled fluid flow and
738 geomechanical fault-slip analysis. *Energ. Convers. Manage.* 48(6), 1798-1807.
739

740 Shelly, D. R., Hill, D. P., 2011. Migrating swarms of brittle-failure earthquakes in the lower
741 crust beneath Mammoth Mountain, California, *Geophys. Res. Lett.*, 38(20), L20307,
742 doi:10.1029/2011GL049336.
743

744 Shelly, D.R., Taira, T., Prejean, S.G., Hill, D.P., Dreger, D.S., 2015. Fluid-faulting
745 interactions: Fracture-mesh and fault-valve behavior in the February 2014 Mammoth
746 Mountain, California, earthquake swarm. *Geophys. Res. Lett.*, 42, 5803-5812,
747 doi:10.1002/2015GL064325.
748

749 Sibson, R. H., 2003. Thickness of the seismic slip zone. *B. Seismol. Soc. Am.*, 93(3), 1169-
750 1178.
751

752 Sigurdsson, H. (1987), Lethal gas bursts from Cameroon Crater Lakes, *Eos Trans. AGU*,
753 68(23), 570–573, doi:10.1029/EO068i023p00570-04.
754

755 Sorey, M. L., Evans, W. C., Kennedy, B. M., Farrar, C. D., Hainsworth, L. J., Hausback, B.,
756 1998. Carbon dioxide and helium emissions from a reservoir of magmatic gas beneath
757 Mammoth Mountain, California, *J. Geophys. Res.*, 103, 15,303–15,323,
758 doi:10.1029/98JB01389.
759

760 Takei, Y., 2002. Effect of pore geometry on VP/VS: From equilibrium geometry to crack, J.
761 Geophys. Res., 107(B2), doi:10.1029/2001JB000522.

762

763 Tazieff, H., 1989. Mechanisms of the Nyos carbon dioxide disaster and of so-called
764 phreatic steam eruptions. J. Volcanol. Geotherm. Res., 39(2-3), 109-116.

765

766 Todesco, M., Rinaldi, A. P. , Bonafede, M., 2010. Modeling of unrest signals in
767 heterogeneous hydrothermal systems, J. Geophys. Res., 115, B09213,
768 doi:10.1029/2010JB007474.

769

770 Wanner, C., Peiffer, L., Spycher, N. Sonnenthal, E., Kennedy, B. M., Iovenitti, J., 2014,
771 Reactive transport modeling of the Dixie Valley geothermal area: Insights on flow and
772 geothermometry, Geothermics, 51, 130–141.

773

774 Werner, C., D. Bergfeld, M. P. Doukas, C. D. Farrar, P. J. Kelly, Kern, C., 2014, Decadal-
775 scale variability of diffuse CO₂ emissions and seismicity revealed from long-term
776 monitoring (1995–2013) at Mammoth Mountain, California, USA, J. Volcanol. Geotherm.
777 Res., 289, 51–63.

778

779

780

781

782

783

784 **Figure captions**

785

786 Figure 1. (a) Relief map showing the location of Mammoth Mountain (white line), the
787 Horseshoe Lake tree kill area (HSL) and the Mammoth Mountain fumarole (MMF). The
788 dashed black line corresponds to the location of the Long Valley caldera rim, while the gray
789 line shows the Mammoth Mountain fault trace. The modeled cross-section is represented by
790 the dashed white line. (b) Time series of surface CO₂ emission rate (t d⁻¹) at HSL and
791 number of shallow earthquakes (< 10 km depth) per month (modified from Werner et al.,
792 2014). Arrows show time delays between major seismic events and degassing peaks. Direct
793 measurements of CO₂ emissions were not performed until 1995 (dashed line). The pre-1995
794 flux data were extrapolated from measurements of steam flux at MMF and considering
795 average steam to CO₂ emission ratio, while post-1995 data correspond to CO₂ emission
796 rates calculated based on direct CO₂ flux measurements using the accumulation chamber
797 method. Error bars associated with post-1995 data correspond to one standard deviation of
798 the mean emissions.

799

800 Figure 2. Schematic representation of the 2-D model. Different domains (reservoir, seal,
801 shallow aquifer and fault) are assigned specific permeabilities (k). Other rock properties
802 are: porosity (Φ), density (ρ), thermal conductivity (λ) and specific heat (C_r). The arrow
803 symbolizes the injection a CO₂-rich magmatic fluid through the central portion of the lower
804 boundary (dashed white area; LB1). The grey area corresponding to the volcanic summit is
805 not modeled. Mesh discretization (number of blocks (b) and their extent along x-y-z axes)
806 is also shown. Depth is relative to the topographic base of Mammoth Mountain with a
807 mean altitude of 2,500 m asl.

808

809 Figure 3. Gas saturation (S_g) distribution and corresponding liquid (grey) and gas (black)
810 velocity vectors at (a) 120 years of simulation A1, (b) 2000 years of simulation A1, (c)
811 2000 years of simulation A2.

812

813 Figure 4. (a) Temporal evolution of CO_2 gas mass within the simulated reservoir in
814 simulations A1, A2. Slopes α , α' , β correspond to the average rates of CO_2 accumulation in
815 the reservoir: $\alpha = 38 \text{ t d}^{-1}$ (computed from 0 to 800 years), $\alpha' = 8.8 \text{ t d}^{-1}$ (from 800 to 2000
816 years), $\beta = 10.5 \text{ t d}^{-1}$ (from 250 to 2000 years). (b) Corresponding temporal evolution of the
817 outflow rate in dissolved CO_2 through the lower boundaries (LB2 and LB3) as a percentage
818 of the CO_2 injection rate. (c) Pressure and temperature profiles along the mid-mesh vertical
819 axis ($x = 3000 \text{ m}$) after 2,000 years of simulation. The grey and black dotted curves show
820 the pressure distribution after 5 years of enhanced injection in simulation C1 and C3 (time
821 = 15 years). The shaded grey area symbolizes the depth of the low-permeability seal.

822

823 Figure 5. (a) Temporal evolution of simulated surface CO_2 emission rate considering the
824 effect of reservoir depletion with constant fault permeability (k_f) and magmatic fluid
825 injection rate. (b) Response in surface CO_2 emission rate to an increase or decrease in
826 magmatic fluid injection with constant k_f . Ovals indicate the particular time at which
827 simulations C were initiated, as well as the simulations from which initial conditions were
828 inherited. Dotted curves labeled '98-05' and '09-13' refer to surface CO_2 emission rates
829 observed at Horsehoe Lake over the periods 1998-2005 and 2009-2013, respectively
830 (Werner et al., 2014). Major model parameters are synthetized in boxes. Permeability
831 values refer to fault permeabilities.

832

833 Figure 6. Gas saturation (S_g) distribution for two selected simulations (B2 and B5) at 30
834 years. Triangles show the corresponding surface CO_2 emission rate at this time in Figure
835 5a.

836

837 Figure 7: (a) Simulated temporal variations in fault permeability (k_f) following patterns k_{f1}
838 and k_{f2} . Simulations D1 and D3 are run with pattern k_{f1} and simulation D2 with pattern
839 k_{f2} . (b) Times series of simulated surface CO_2 emission rate considering the effect of
840 variations in fault permeability and constant magmatic fluid injection. Sudden increase in
841 permeability occurs at 0 and 5 years to simulate fault reactivation. Emission rate of
842 simulation D3 is on right y-axis. Dotted curves labeled '98-05' and '09-13' refer to surface
843 CO_2 emission rates observed at Horsehoe Lake over the periods 1998-2005 and 2009-2013,
844 respectively (Werner et al., 2014). Maximum emission rate at the surface in simulations D1
845 and D2 is observed ~2 years after the second event of fault permeability increase.

846

847

848

849

850

851

852

853

854

855

856 **Table caption**

857

858 Table 1: Synthesis of specified model parameters and corresponding sources.

859

860 Table 2: Parameters of simulated scenarios. k_f is fault permeability. k_{LB2} and k_{LB3} are
861 permeabilities of the lower boundary at LB2 and LB3, respectively. INCON are initial
862 conditions inherited from another simulation at a certain time. L and UP are lower and
863 upper sections of the fault, respectively. The injection rates of $150 \text{ t d}^{-1} \text{ CO}_2$ and 1111 t d^{-1}
864 H_2O were specified to simulate a CO_2 content for the injection fluid of 5.2 mol %.

865

866

867

868

869

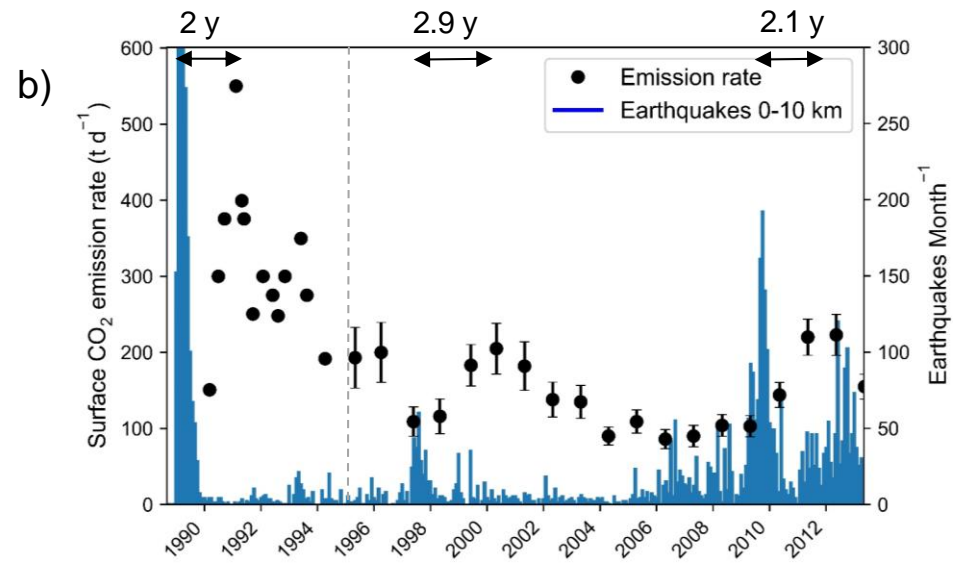
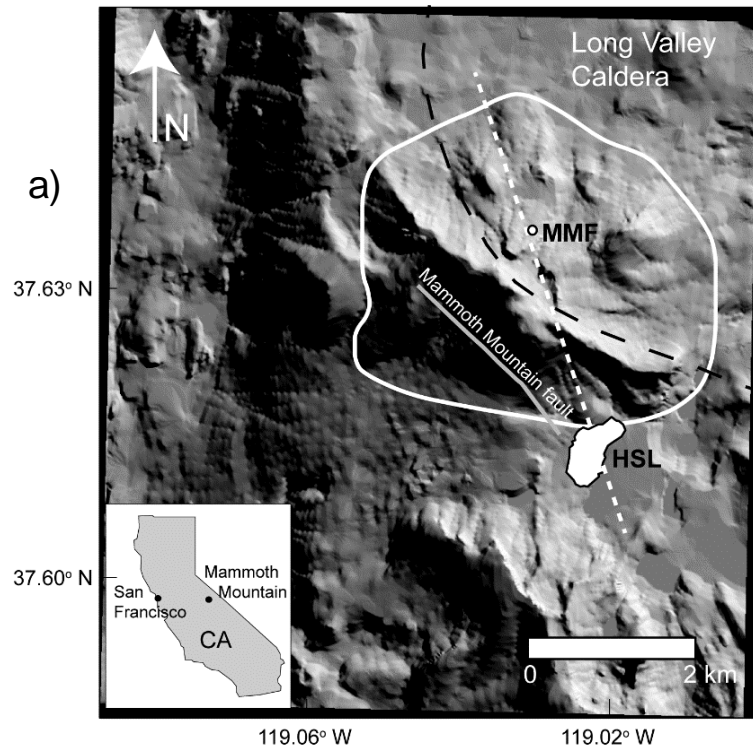
870

871

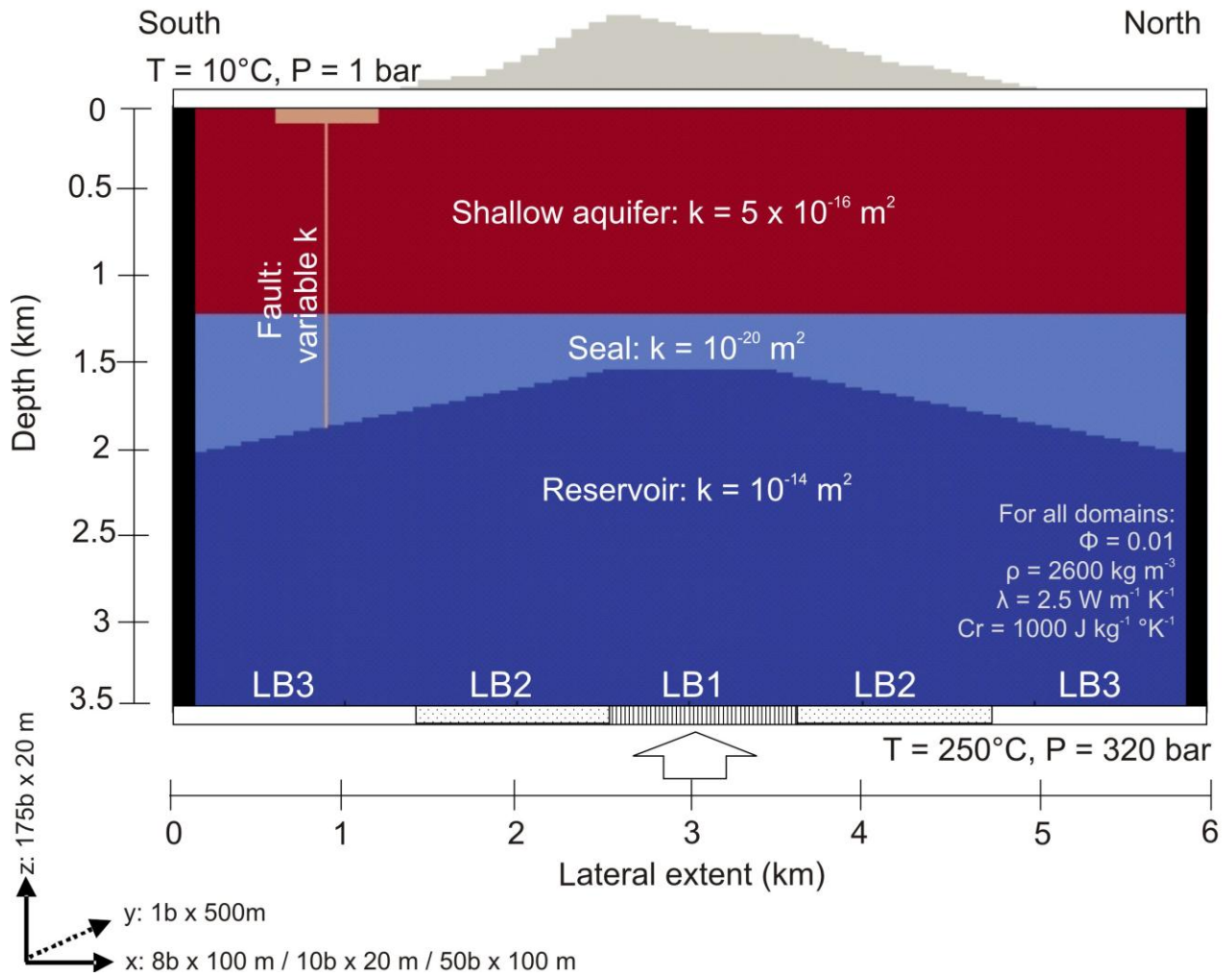
872

873

Figure 1



874 **Figure 2**
 875
 876



877
 878

879

880

881

882

883

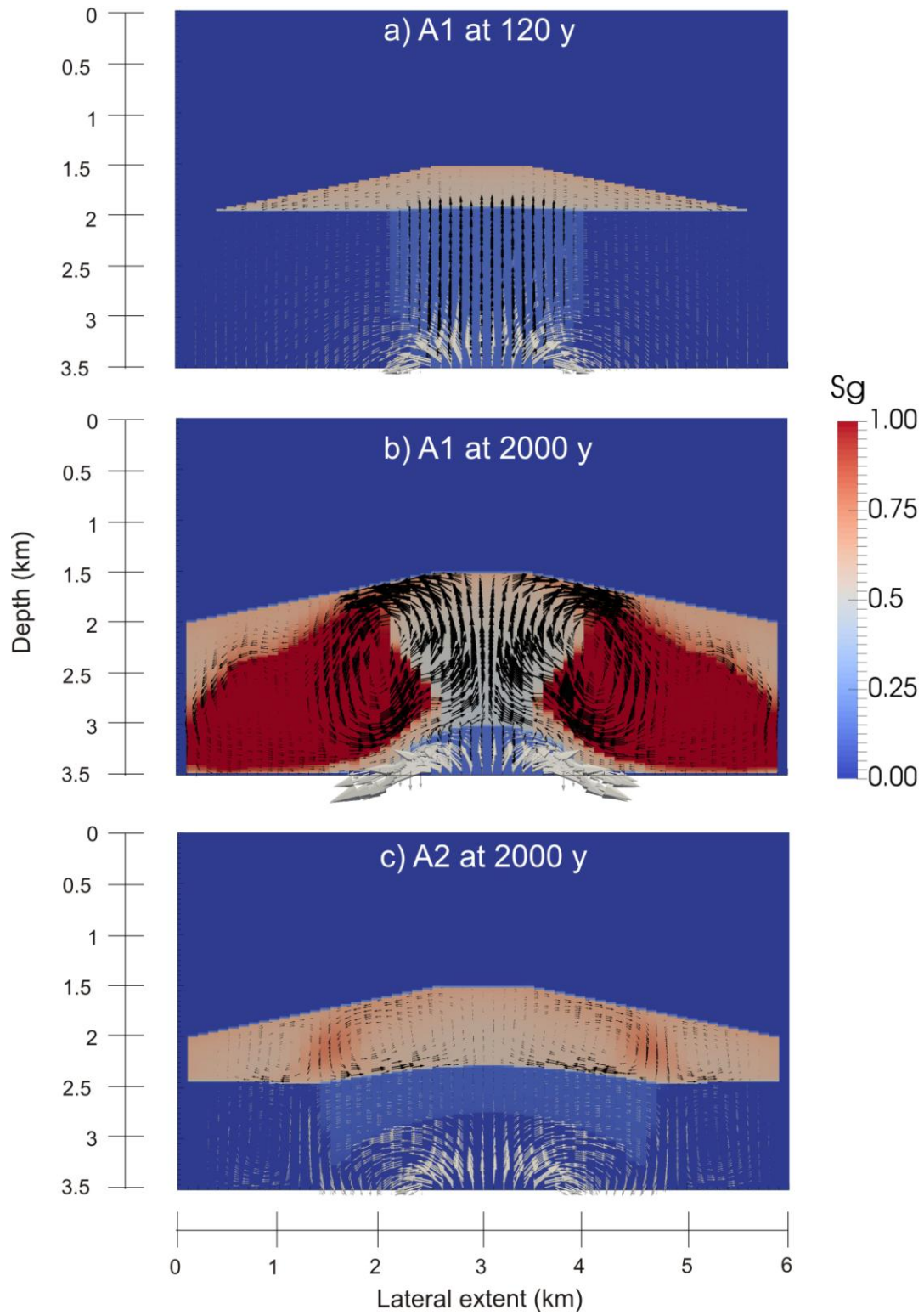
884

885

886

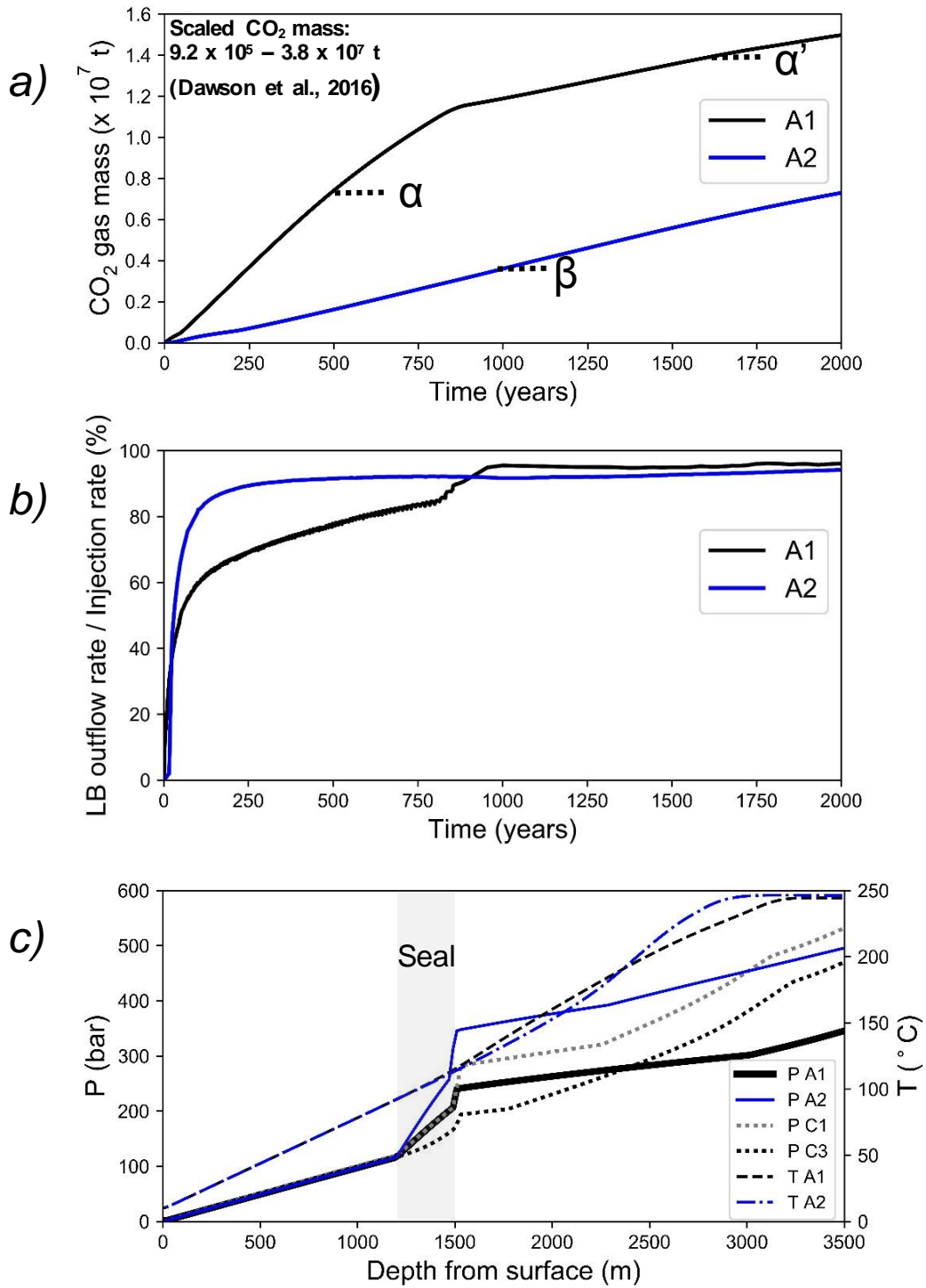
887 **Figure 3**

888



889

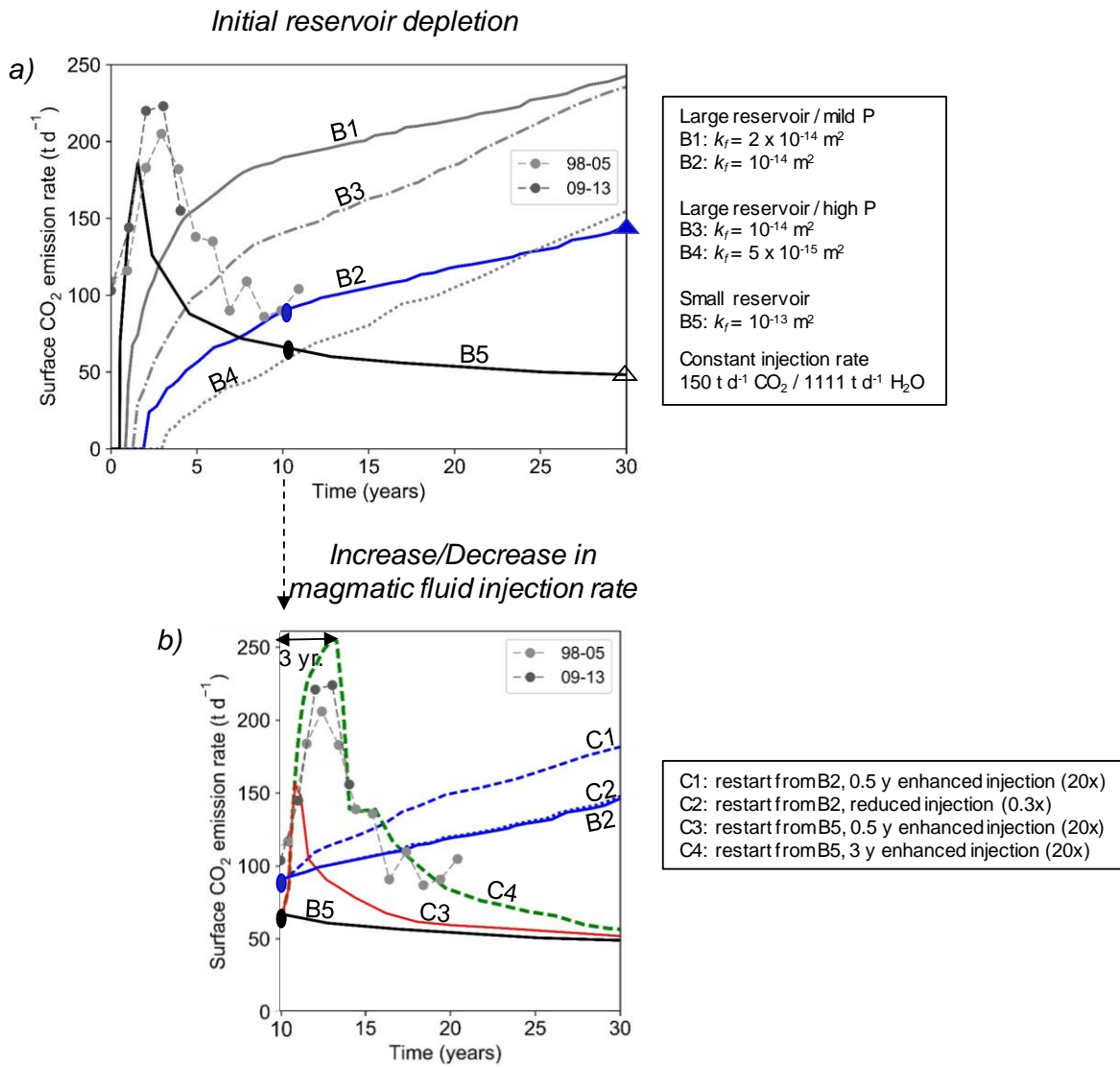
890 **Figure 4**



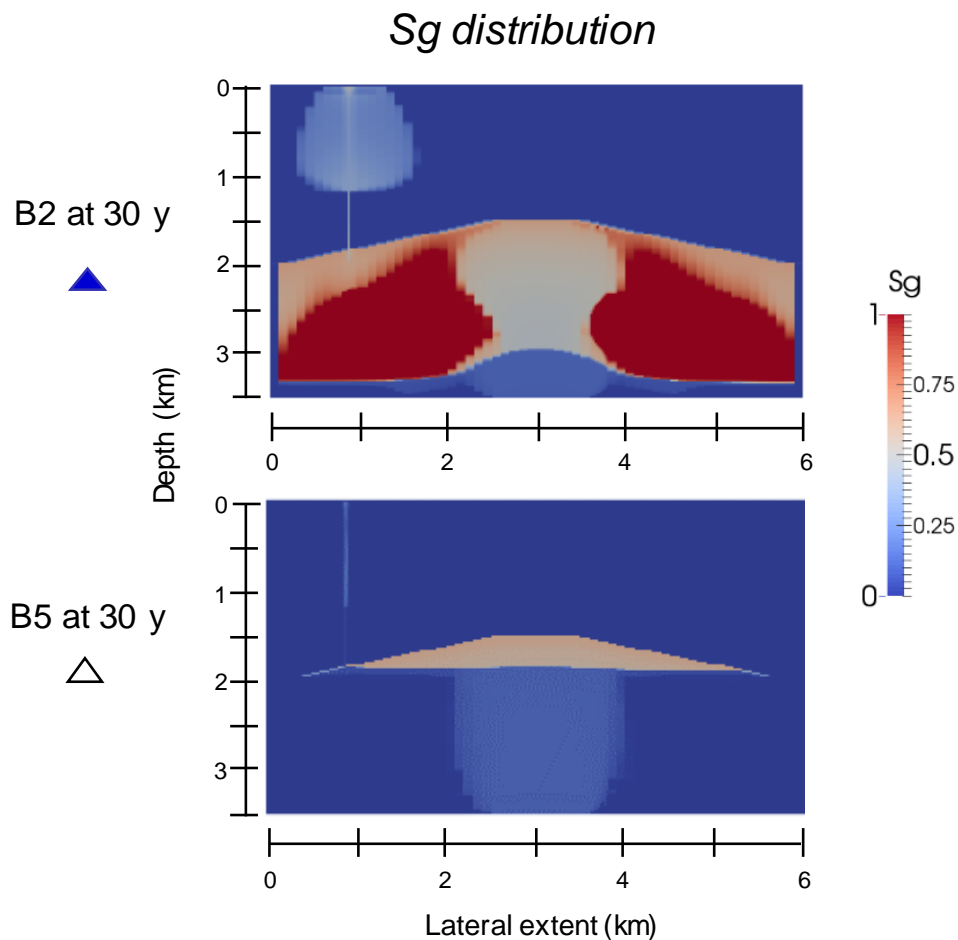
891

892

893



895
 896
 897
 898
 899
 900
 901
 902
 903



905

906

907

908

909

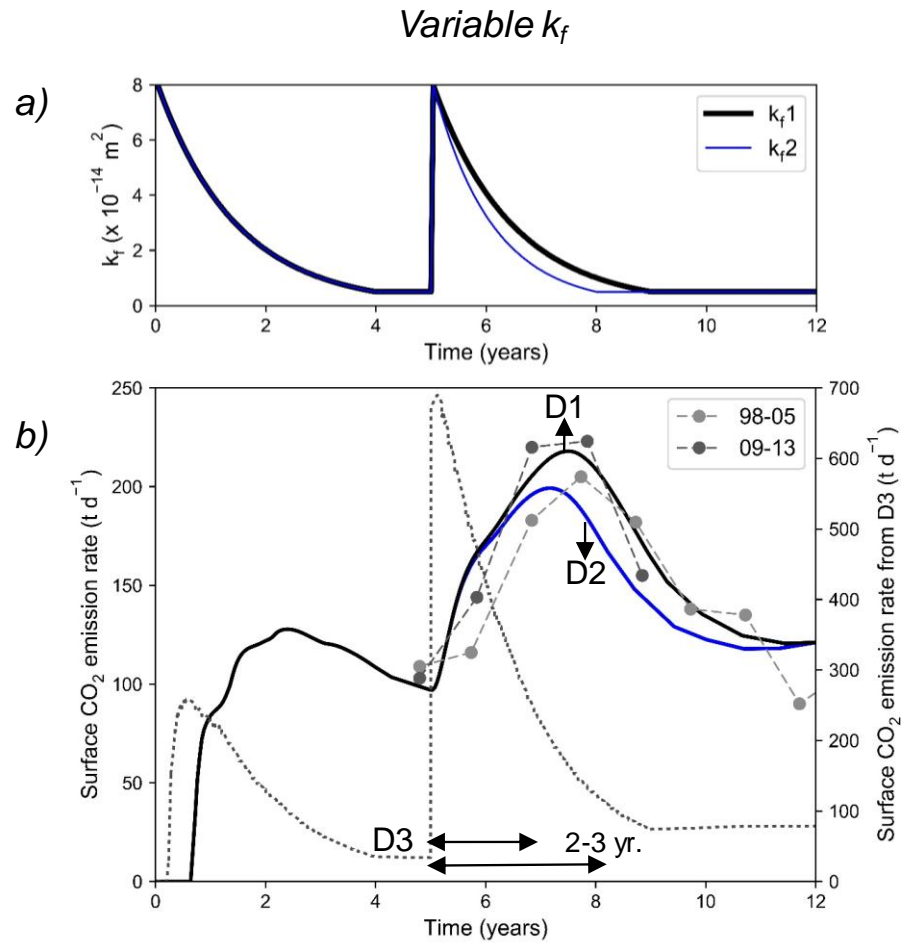
910

911

912

913

914



D1/D2: variable permeability for the lower fault section.
 Permeability of upper fault section remains stable ($2 \times 10^{-14} \text{ m}^2$).

D3: variable permeability for the whole fault section.

D1/D3: trend k_{f1}
 D2: trend k_{f2}

Restart from A1 at 2,000 y.

Constant injection rate: $150 \text{ t d}^{-1} \text{ CO}_2 / 1111 \text{ t d}^{-1} \text{ H}_2\text{O}$

Table 1

Parameter	Values	Meaning/Source
<u>Size and geometry of modeled domain</u>		
Length of modeled cross section (X)	6 km	Extent from south of HSL to north-west of Mammoth Mountain Fumarole (Fig. 1) .
Depth (Z)	3.5 km	Maximum gas reservoir depth (Lin, 2013).
Model width (Y)	0.5 km	A fifth of the gas reservoir width (2.5 km; Lin, 2013).
Fault location	See Figure 2	To simulate the degassing at Horseshoe Lake.
Reservoir seal	Thickness: 300 – 800 m Max. depth: 1.5 – 2 km Dip: ~10°	Arbitrary value. No published data available. Based on seismic tomography (Lin, 2013). To maximize reservoir domain (dischargeable CO ₂ -mass below Mammoth Mountain). ²
<u>Injection rates</u>	150 t d ⁻¹ CO ₂ /1,111 t d ⁻¹ H ₂ O	CO ₂ rate constrained by the average surface CO ₂ degassing rate at HSL (Werner et al., 2014). H ₂ O rate allows to simulate a CO ₂ content of 5.2 mol%. Higher and lower rates are investigated in simulations C.
<u>Hydraulic properties</u>		
Reservoir permeability, k_{res}	10 ⁻¹⁴ m ²	Allows convection within the reservoir (Manning and Ingebritsen, 1999). No published data available.
Seal permeability, k_{seal}	10 ⁻²⁰ m ²	Impedes advective transport (Manning and Ingebritsen, 1999). No measurement available.
Fault permeability, k_f	10 ⁻¹³ – 5 x 10 ⁻¹⁵ m ²	Tansient fault zone permeability inferred for Mammoth Mountain (Ingebritsen and Manning, 2010).
Fault permeability decay	8x10 ⁻¹⁴ to 5x10 ⁻¹⁵ m ² over 3-4 years	Exponential decay (Micklethwaite et al., 2016) ¹ . Time period and parameters ¹ allow matching CO ₂ emission rates.
Shallow aquifer permeability, k_{aq}	5 x 10 ⁻¹⁶ m ²	² Limits lateral gas spreading to the degassing area observed at Horseshoe Lake.
Lower boundary permeability (k_{LB2})	10 ⁻¹⁶ – 10 ⁻¹⁸ m ²	² Minimum permeability required for forming a gas reservoir. No published data available.
Lateral boundary permeability, k_{lb}	10 ⁻²⁰ m ²	² Inhibits lateral fluid flow consistent with the non-thermal nature of springs surrounding the volcano (Evans et al. 2002).
Porosity	0.01	Value assigned for all domains; taken from Sorey et al. (1998).
<u>Other properties</u>		
Initial geothermal gradient	~70 °C/km	Corresponds to T=150°C at the reservoir top as inferred from gas geothermometry (Sorey et al., 1998).
Upper boundary temperature	10°C	To simulate air temperature.
Thermal conductivity, λ	2.5 W m ⁻¹ K ⁻¹ /	Values assigned for all domains, taken from Todesco et al. (2010) and Wanner et al. (2014), simulating similar crystalline rocks.
Specific heat, c_p	1000 J kg ⁻¹ °K ⁻¹	
Rock density, ρ	2600 kg m ⁻³	

¹ The equation describing the permeability decay of a fault damage zone over a period of N years is:

$$k = k_0 e^{-rt}$$

Where k_0 (m²) is the enhanced permeability right after the reactivation event, k_1 is the background permeability value, k is the permeability at time t (s), and r is the decay rate computed as follows:

$$r = - \frac{1}{31,536,000 N} \ln \frac{k_1}{k_0}$$

Values of 8 x 10⁻¹⁴ m² and 5 x 10⁻¹⁵ m² were assigned to k_0 and k_1 , respectively. N was varied from 3 to 4 years.

²Determined from preliminary simulations

917 **Table 2**
918

Simulation #	Simulation period (years)	Injection rate CO ₂ /H ₂ O (t d ⁻¹)	k _f (m ²)	k _{LB2} (m ²)	k _{LB3} (m ²)	INCON
<i>Reservoir formation</i>						
A1	2,000	150/1,111	10 ⁻²⁰	10 ⁻¹⁶	10 ⁻¹⁶	-
A2	2,000	150/1,111	10 ⁻²⁰	10 ⁻¹⁸	10 ⁻²⁰	-
<i>Initial reservoir depletion</i>						
B1	30	150/1,111	2 x 10 ⁻¹⁴	10 ⁻¹⁶	10 ⁻¹⁶	A1 at 2000 y
B2	30	150/1,111	10 ⁻¹⁴	10 ⁻¹⁶	10 ⁻¹⁶	A1 at 2000 y
B3	30	150/1,111	10 ⁻¹⁴	10 ⁻¹⁸	10 ⁻²⁰	A2 at 2000 y
B4	30	150/1,111	5 x 10 ⁻¹⁵	10 ⁻¹⁸	10 ⁻²⁰	A2 at 2000 y
B5	30	150/1,111	10 ⁻¹³	10 ⁻¹⁶	10 ⁻¹⁶	A1 at 120 y
<i>Increase/Decrease in magmatic fluid injection rate</i>						
C1	10-10.5	3,000/22,220	10 ⁻¹⁴	10 ⁻¹⁸	10 ⁻²⁰	B1 at 10 y
	10.5-30	150/1,111				
C2	10-30	50/370	10 ⁻¹⁴	10 ⁻¹⁸	10 ⁻²⁰	B1 at 10 y
C3	10-10.5	3,000/22,220	10 ⁻¹³	10 ⁻¹⁶	10 ⁻¹⁶	B5 at 10 y
	10.5-30	150/1,111				
C4	10-13	3,000/22,220	10 ⁻¹³	10 ⁻¹⁶	10 ⁻¹⁶	B5 at 10 y
	15-30	150/1,111				
<i>Variable fault permeability</i>						
D1	12	150/1,111	L: trend k _{f1} / UP: 2 x 10 ⁻¹⁴	10 ⁻¹⁶	10 ⁻¹⁶	A1 at 2000 y
D2	12	150/1,111	L: trend k _{f2} / UP: 2 x 10 ⁻¹⁴	10 ⁻¹⁶	10 ⁻¹⁶	A1 at 2000 y
D3	12	150/1,111	trend k _{f1}	10 ⁻¹⁶	10 ⁻¹⁶	A1 at 2000 y

Supplementary material for online publication only

[Click here to download Supplementary material for online publication only: Supplementary Information.docx](#)