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Role of CO₂ in low to medium enthalpy geothermal systems in the Central Betic Cordillera (Spain)

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1 Role of CO₂ in low to medium enthalpy geothermal systems in the Central Betic Cordillera
2 (Spain)

3 **Abstract**

4 There is growing interest in geothermal energy, which is considered as an efficient energy
5 solution to mitigate rising atmospheric CO₂. Besides known high enthalpy geothermal systems,
6 increasing attention is paid to low temperature geothermal systems, as they are suitable for local
7 use. Although geothermal production seems to be an environmentally advantageous renewable
8 energy, it might result in significant CO₂ emissions. In this study, we investigate the relationship
9 between temperature, fugacity of CO₂ ($f\text{CO}_2$), and mineral buffers in the reservoir conditions,
10 taking the low- to medium- enthalpy thermal waters in the Central Betic Cordillera as case
11 study. Using geochemical modeling, three main groups of waters have been identified
12 depending on temperature, buffering mineral assemblage, and $f\text{CO}_2$ in their reservoir. A group
13 of waters with a reservoir temperature ranging from 70 to 90°C and located in the intramountain
14 sedimentary basins shows a $f\text{CO}_2$ in depth ranging from $\sim 6 \times 10^{-2}$ and 6×10^{-1} . The reservoir
15 chemistry of this water group seems to be mainly controlled by carbonates and evaporites
16 displaying a $f\text{CO}_2$ variation between depth and surface ($\Delta f\text{CO}_2$) of 10^{-1} . Another intermediate
17 group of waters, located in an active extension zone, displays lower temperature (50-60°C) and
18 $f\text{CO}_2$ in the reservoir (from 10^{-3} to 10^{-2}). Finally, the third group of waters, located on the
19 metamorphic complexes contacts, show the highest estimated temperatures (130 - 140°C) and
20 $f\text{CO}_2$ in the reservoir (1 to 10^2). The two latter groups suggest increasing buffering effect of
21 alumino-silicates, in addition to carbonates and quartz. Therefore, we evidenced a strong
22 relationship between temperature and $f\text{CO}_2$ in the reservoir as well as the potential mineral
23 buffers. We discussed the potential of geothermal systems as clean energy source based on the
24 estimation of the CO₂ emissions generated by the investigated thermal systems for a practical
25 case of household heating.

26 **1 Introduction**

27 Geothermal energy has been widely developed across Europe and the World for the last 50
28 years, with main focus on the conventional high-temperature geothermal reservoirs.
29 Nevertheless, low (30°C to 100°C) to medium (100 – 150°C) enthalpy geothermal systems have
30 been recently subject to increasing interest (Blasco et al., 2017; Capecchiacci et al., 2015; Fusari
31 et al., 2017) as they may be easily exploited for ground-source heat pump or greenhouses
32 (Battistel et al., 2016). In the current context of global warming and energy transition,
33 geothermal is generally considered to be an environmentally advantageous renewable source
34 of energy. However, emissions of greenhouse gases, and especially CO₂, might be generated
35 by geothermal exploitation. Although CO₂ release from geothermal electricity production has
36 been shown to be significantly lower than from fossil fuel (Ármansson, 2003; Hunt, 2001),
37 the efficiency of this energy to mitigate rising atmospheric CO₂ is a major concern for societal
38 acceptance. Scientific research programs have been recently dedicated to the development of
39 cost-effective non-carbon emitting geothermal energy (e.g., “Geothermal Emission Gas
40 Control”, Horizon 2020, European program). The studies on the CO₂ emissions in geothermal
41 systems are mainly dedicated to volcanic geothermal systems (e.g., Ármansson, 2018;
42 Chiodini et al., 1998; Harvey et al., 2017; Seward and Kerrick, 1996). However, the expansion
43 of the geothermal sector leads to consider a broader range of geothermal resources resulting in
44 possible large CO₂ emissions, even in low- and medium- enthalpy geothermal systems.

45 The CO₂ concentration in geothermal waters is strongly related to the geological setting,
46 and more specifically the lithology, of the reservoir. The role of carbonates might be
47 predominant in generation of CO₂ as carbonate dissolution or thermal decomposition of
48 carbonates might be major sources of CO₂ in fluid whereas carbonate precipitation in the
49 reservoir or in the ascent of the water might be a sink of geothermal CO₂. The equilibrium
50 relative to the carbonate minerals and the alumino-silicate minerals, often associated to the

51 chemical water-rock interactions, is an important parameter to consider as it “buffers” the fluid
52 chemical composition and the CO₂ degassing. Therefore, understanding the relationship
53 between the mineral buffer, the fugacity of CO₂ ($f\text{CO}_2$) (or its partial pressure of CO₂, $p\text{CO}_2$),
54 and the temperature in the reservoir, is crucial to estimate the CO₂ release in geothermal
55 systems. These links between $f\text{CO}_2$ and reservoir temperature have been subject to Chiodini
56 and collaborators’ investigations since the early 1990’s, although they focused mainly on
57 volcanic geothermal systems (e.g., Chiodini et al., 2007, 1998, 1995b)

58 The Central Betic Cordillera, in the South of Spain, has an interesting geothermal potential
59 with abundant low to medium geothermal resources (Arrizabalaga et al., 2015; Sánchez
60 Guzmán and García de la Noceda, 2010), major fault systems allowing a rapid ascent of the
61 deep hot water (Cerón and López-Chicano, 2002), and moderate-intensity seismic activity. This
62 region is characterized by several occurrences of thermal springs (water with temperature of
63 more than 20°C, according to the average air temperature of this area), known as baños, which
64 have been used, for some of them, as thermal bath since the Roman times. They are mainly
65 exploited for balneotherapy or spa nowadays. The thermal waters in the Central Betic Cordillera
66 are also characterized by large variability in $f\text{CO}_2$, and therefore in $p\text{CO}_2$. Low $f\text{CO}_2$ are
67 observed in the sulfated waters (e.g., Baños Alhama de Granada) whereas large amount of CO₂
68 degassing are known in few springs (e.g., Capuchina de Lanjaron) (Pérez del Villar, 2009). The
69 thermal springs of Baños Alicun de la Torres have been studied as natural analogs for CO₂
70 storage (Prado-Pérez and Pérez del Villar, 2011). Nevertheless, only old Spanish studies have
71 considered globally the thermal waters in the Central Betic Cordillera (Benavente Herrera and
72 Sanz de Galdeano, 1985; Cruz-Sanjulián et al., 1972; Cruz Sanjulián and Granda, 1979). Recent
73 studies (Campos, 2006; López-Chicano et al., 2001a; Prado-Pérez and Pérez del Villar, 2011)
74 characterized the geochemical and hydrogeological properties in specific individual thermal
75 system.

76 The aim of this study is to evaluate the suitability of the thermal waters for the geothermal
77 exploitation in the Central Betic Cordillera with regard to CO₂ emissions. Geochemical and
78 isotopic indicators and thermodynamic calculations can be applied to get insights on the fluid
79 geochemistry, temperature, and $f\text{CO}_2$ of the reservoir using the measured physical-chemical
80 characteristics at the surface. The present study attempts to assess the potential mineral
81 assemblages buffering the waters in the reservoir and the variations of $f\text{CO}_2$ at the regional
82 scale.

83

84 **2 Geological setting**

85 The sampled thermal waters (springs and wells) are located in the central region of the Betic
86 Cordillera with a greater concentration of points in the Granada Basin (

87 Figure 1). The Central Betic Cordillera is a complex structure, resulting from the
88 convergence of the Iberian and African plates, which can be subdivided into: (1) the non-
89 metamorphic External Zone, (2) the metamorphic Internal Zones, (3) the Neogene basins. The
90 External Zone is separated from the Internal Zone by a major shear zone called the Internal
91 External Boundary Zone (IEBZ) (Sanz de Galdeano, 1990). The Granada Basin is one of the
92 Neogene intramontainous basin in the Central Betic Cordillera, located at the junction between
93 the Internal and External zones.

94

95 2.1 Tectonic framework

96 The Central Betic Cordillera is a tectonically active region structured by several crustal
97 faults (Buforn et al., 2004; Sanz de Galdeano and Peláez, 2011). In the NE part of the Granada
98 Basin, the IEBZ, mentioned above, becomes nearly coincident with the so-called Cadiz-
99 Alicante faults system (CAFS,

100 Figure 1) extending along 550 km across the Betic Cordillera. This fault system forms a

101 corridor of dextral strike-slip faults generating crustal discontinuities of at least 7 km depth
102 (Sanz de Galdeano, 2008 and references therein). Besides, two main sets of normal faults affect
103 the basement and the sedimentary infilling of the Granada Basin: one set of E-W faults with
104 low angle dip ($< 30^\circ$) toward the south and the north; and a second one with NW-SE faults,
105 which dip westward, mainly located in the NE of the basin (Figure 1) (Galindo-Zaldívar et al.,
106 2015; Rodríguez-Fernández and Sanz de Galdeano, 2006). The thermal waters are strongly
107 related to the faults in the Central Betic Cordillera as the thermal systems are convective
108 fracture-controlled systems (Benavente Herrera and Sanz de Galdeano, 1985; Cruz-Sanjulián
109 et al., 1972).

110

111 2.2 Lithostratigraphy

112 The material of the Internal Zone corresponds to Paleozoic to Mesozoic metasediments
113 differentiated into three stacked metamorphic complexes, from the top to the base, by different
114 metamorphic degree and structural position: (1) Maláguide, (2) Alpujárride, and (3) Nevado-
115 Filábride. The Alpujárride Complex, well represented in our study area, consists in a series of
116 nappes of Paleozoic-Mesozoic HP/LT metasediments (Azañón et al., 1998; Azañón and
117 Crespo-Blanc, 2000). The base of the nappes consists of Paleozoic graphite mica schists, which
118 are overlain by Permo-Triassic metapelites with layers of meta-sandstones, dolomite, and
119 limestone. These meta-sediments are in turn overlain by middle-upper Triassic marbles with
120 interbedded gypsum layers and Mesozoic pelagic marls forming the top of the nappes (Martín
121 and Braga, 1987; Prado-Pérez and Pérez del Villar, 2011). The HP/LT Nevado-Filábride
122 materials, outcropping in the Sierra Nevada and Sierra Alhamilla, comprise from the base to
123 the top: Paleozoic graphitic schists, Permo-Triassic mica schists associated with metapelites,
124 Triassic dolomite and marbles, and heterogeneous rocks with Jurassic metabasite inclusions
125 (Gomez-Pugnaire et Fernandez-Soler, 1987; Gómez-Pugnaire et al., 2000).

126 The External Zone forms the northern part of the Granada Basin basement and crops out in
127 Sierra Elvira and Alicún de las Torres. It is mainly composed of Mesozoic sedimentary rocks,
128 with Triassic evaporitic-bearing marls, dolomitic limestones, and interbedded marls (Braga et
129 al., 2003; Sanz de Galdeano and Vera, 1992).

130 The sedimentary infilling of the Granada Basin ranges from the Miocene to the Quaternary
131 and is composed, from bottom to top, of clayey conglomerates, calcareous sandstones, marls
132 and silts, gypsum/anhydrite (and locally halite), lacustrine limestones, cemented breccias and
133 alluviums (Braga et al., 2003; Corbí et al., 2012).

134

135 2.3 Sample location

136 The thermal waters are mainly situated close to major tectonic and geological structures.
137 The sampling points can be gathered into three groups depending of the nature of the geological
138 features:

- 139 • The thermal waters related to the metamorphic complexes: Baño Salado de Lanjaron
140 and Capuchina de Lanjaron springs (BSL and CL) are located in the Sierra Nevada along
141 the detachment between Nevado-Filábride and Alpujárride complexes. Baños
142 Alhamilla spring (BAA) is situated further to the east in the Sierra Alhamilla along the
143 same tectonic contact, where it is also close to the trace of an important strike-slip fault
144 of near N30E direction.
- 145 • The thermal waters located in the evaporitic basins (Granada Basin and Guadix-Baza
146 Basin): Baños Santa Fe (SF), Baños de la Malahá (BM), and Sondeo Romilla de la
147 Nueva (SRN) are wells situated in the Granada Basin. Baños Alhama de Granada
148 (BAG), Baños Nuevo Alhama de Granada (BNAG), and Sierra Elvira (SE) are springs
149 located in the Granada Basin. SE is also located on the trace of an active fault, belonging
150 to the NW to NNW directed fault system. Baños de Zujar (BZ) and Baños de Alicún de

151 las Torres (AT) are springs located in the Guadix-Baza Basin, close to the above
152 mentioned IEBZ and CAFS. The springs SE, BZ, and AT are linked by faults to small
153 Subbetic carbonate outcrops.

154 • The thermal waters linked to the Baños Urquizar Chico (BUC) and Baños Urquizar
155 Grande (BUG) are located within the Valle de Lecrin tectonic graben within the
156 Alpujárride Complex along faults striking N30E, forming the western termination of the
157 Sierra Nevada Massif.

158

159 **3 Material and methods**

160 3.1 Water and dissolved gases sampling

161 Thirteen thermal water samples were collected in the Granada Basin and in the Betic
162 Cordillera, from nine springs and four wells. Two wells were artesian whereas the other water
163 samples were pumped. All water samples were filtered with 0.45 µm membrane filters and
164 samples assigned to trace elements and Al analyses were filtered with 0.2 µm membrane filters.
165 The water samples dedicated to cations, minor elements, and Al analyses were acidified using
166 suprapure nitric acid (HNO₃).

167 Waters were collected by filling 142 mL Pyrex glass bottles to analyze chemical composition
168 of dissolved gases (Capasso and Inguaggiato, 1998; Inguaggiato and Rizzo, 2004; Lix et al.,
169 2018). The glass bottles were sealed under water with silicon/rubber septa to minimize
170 atmospheric contamination (Capasso and Inguaggiato, 1998).

171

172 3.2 Water analyses

173 3.2.1 Physical-chemical properties

174 Physical-chemical parameters of the waters, including temperature, pH, electrical

175 conductivity (EC), and alkalinity were measured directly on the field. The combination pH
176 electrode was calibrated with three buffer solutions at pH 4.0, 7.0 and 10.0 (25°C) (CertiPUR®
177 Reference material) and the EC electrode with two potassium chloride standard solutions of
178 1.41 mS/cm and 12.8 mS/cm (25°C) (CertiPUR® Reference material). The uncertainties on the
179 measurements of temperature, pH, and EC were of $\pm 1^\circ\text{C}$, ± 0.1 , and ± 0.01 mS/cm respectively.
180 Alkalinity was determined by titration with an 0.01M or 0.1M hydrochloric acid solution
181 depending on the encountered alkalinity range and by following the pH evolution with the pH-
182 meter. The equivalent volume was determined with the Gran's method (Gran, 1952) and the
183 analytical error of the alkalinity measurements was of approximately $\pm 5\%$.

184

185 3.2.2 Laboratory chemical analyses

186 The major cations and anions (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , and Cl^-) were analyzed by ionic
187 chromatography. The uncertainty on Mg^{2+} , K^+ , Na^+ , SO_4^{2-} determination is $\pm 5\%$ whereas that
188 on Ca^{2+} and Cl^- is estimated to be $\pm 10\%$. Minor and trace elements (Ba, Sr, Al, Fe) were
189 analyzed by Inductively Coupled Plasma Optical Emission Spectrometry ICP-OES. The
190 uncertainty on Ba and Sr determination is $\pm 10\%$ whereas that on Al is estimated to $\pm 20\%$. The
191 silica concentrations were determined by a spectrophotometric method following the protocol
192 from Centre d'Expertise en Analyse Environnementale du Québec, (2016), suitable for natural
193 groundwater with Si concentration ranging from 0 to 20 mg/l. The total ionic balance does not
194 exceed 8% for all water samples.

195

196 3.3 Gas analyses

197 3.3.1 Extraction and analyses of dissolved gases

198 The extraction of the dissolved gases was carried out following the method described by
199 Capasso and Inguaggiato (1998) and Inguaggiato and Rizzo (2004). A known volume of host

200 gas was injected into the upside-down glass bottles while drawing out the equivalent water
201 volume through needles. After equilibration for 24 hours, a variable gas volume was extracted
202 for analyses by injecting Millipore water into the glass bottles.

203 Gas species (O₂, N₂, CH₄, CO₂ and He) were analyzed by gas chromatography (Clarus 500,
204 Perkin Elmer instrument with Carboxen 1000 columns with a hot wire detector and a flame
205 ionization detector) using argon as carrier gas. The composition of dissolved gases, expressed
206 in cc.l⁻¹ STP (Standard Temperature and Pressure), was calculated taking into account the
207 volume of gas extracted, the volume of water sample, and the solubility of each gas species
208 (Bunsen coefficient in cc gas/l water STP). The composition of bubbling gases was expressed
209 in either %vol or ppm vol. The accuracy to analyze dissolved gases following the method
210 described by Capasso and Inguaggiato (1998) is within 5.0%.

211

212 3.4 $\delta^{13}\text{C}$ of the Total Dissolved Inorganic Carbon (TDIC)

213 Analyses of $\delta^{13}\text{C}$ of Total Dissolved Inorganic Carbon (TDIC) were carried out with the
214 Analytical Precision 2003 (AP2003) mass spectrometer using the method outlined by Capasso
215 et al. (2005) based on chemical and physical stripping. The results were expressed in ‰ vs. V-
216 PDB standard and with standard deviations of ¹³C/¹²C ratios of $\pm 0.2\%$.

217

218 3.5 Geochemical calculations and modeling

219 In this study, the saturation index calculations and geothermometrical modeling were
220 performed with the (version 3-0-6) PHREEQC software (Parkhurst et al., 2013), using the
221 phreeqc thermodynamic database distributed with the code.

222

223 3.5.1 Saturation index

224 A direct thermodynamic modeling of the multi-component system equilibrium has been
225 performed from the composition of the waters and the physical-chemical parameters. The
226 saturation index of waters with respect to possible minerals (SI_m) were calculated to test the
227 equilibrium conditions or the departure from equilibrium of the system, following Equation 1:

$$SI_m = \log \Omega_m = \log \frac{\prod^i (\gamma_i [c_i])^{v_{im}}}{K_S(P, T)_m} \quad (1)$$

228 where $[c_i]$ and γ_i are the concentration and the activity coefficient of the ion i , v_{im} is the reaction
229 coefficient for the ion i and the mineral m , and $K_S(P, T)_m$ is the solubility constant of the mineral
230 m dependent on temperature and pressure.

231

232 3.5.2 Chemical geothermometers and geobarometers

233 Chemical geothermometric techniques were used to estimate the theoretical reservoir
234 temperature of the thermal waters. The application of the chemical geothermometers needs to
235 satisfy the basic assumptions that the waters circulating at depth are in chemical equilibrium
236 with the minerals of the host rocks (i.e., SI_m close to 0) and that their elemental contents have
237 not changed significantly during the water ascent to the surface (including precipitation or
238 dissolution of secondary mineral phases or degassing). Numerous chemical geothermometers
239 have been described in the literature, including silica, Na/K, Na/K/Ca, K-Mg (D'Amore et al.,
240 2000 and references therein). The silica geothermometers are the most common in geochemical
241 investigations of geothermal systems, widely used in different contexts around the world
242 (Verma, 2000a). However, the validity of the silica geothermometers, and especially SiO₂-
243 quartz geothermometers, have been questioned at low temperatures (< 100°C) (Fournier, 1977;
244 Rimstidt and Barnes, 1980; Verma, 2000a). At those temperatures, quartz precipitation rate is
245 very slow and saturation is rarely achieved (Bjorlykke and Egeberg, 1993; Rimstidt and Barnes,
246 1980). Nevertheless, these geothermometers might provide consistent results even at low to

247 medium temperatures (Blasco et al., 2018) and therefore they have been investigated in this
248 study. SiO₂-quartz geothermometers from Fournier (1977), Fournier and Potter (1982),
249 Michard (1979) and Verma (2000b) and SiO₂-chalcedony geothermometers from Arnórsson et
250 al. (1983) and Michard (1990) were applied for the studied thermal waters. Although cationic
251 (Na/K, Na/K/Ca, K-Mg) geothermometers have been proven efficient in high temperature
252 systems (> 180°C), they are usually considered as unsuitable in low temperature systems due
253 to the different mineral assemblage governing the water chemistry and equilibrium (Blasco et
254 al., 2017; Chiodini et al., 1995a). Due to these limitations, the Na/K, Na/K/Ca and K-Mg
255 geothermometers have not been applied in this study. The Ca-Mg geothermometer, developed
256 in the first place by Marini et al. (1986) and revised by Chiodini et al. (1995a), is more
257 appropriate for low temperature carbonate-evaporitic system and was therefore used here. This
258 geothermometer assumes equilibrium of the waters with calcite, dolomite and anhydrite in the
259 reservoir, which is a reasonable assumption in the investigated area where these minerals are
260 extensively present.

261 In order to get an estimation of the fugacity of CO₂ (*f*CO₂) at depth, the geobarometrical
262 relationship based on the (HCO₃⁻)²/SO₄²⁻ ratio, *f*CO₂, and temperature (Chiodini et al., 1995a)
263 was applied using the following equation:

$$\log \frac{(HCO_3^-)^2}{SO_4^{2-}} = -4.807 + 0.9871 \log pCO_2 + \frac{794.8}{T} - 0.1655 \log \Sigma_{eq} \quad (2)$$

264 where Σ_{eq} is the sum of equivalents in the waters.

265

266 3.5.3 Geothermometrical modeling

267 Another approach to estimate the reservoir temperature consists of simulating the variation
268 of the saturation states with respect to a group of selected minerals, potentially present in the
269 reservoir, to find the temperature at which the saturation indices simultaneously reach
270 equilibrium (Blasco et al., 2018). This method is based on the same assumption as the classical

271 chemical geothermometers: the thermal waters are in equilibrium with the mineral phases under
272 reservoir conditions. Hence, the most realistic reservoir temperature corresponds to the
273 temperature at which a group of minerals is at equilibrium (Asta et al., 2012; D'Amore et al.,
274 1987; Tole et al., 1993).

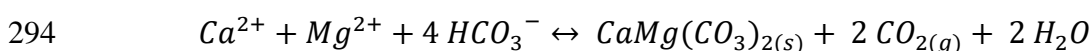
275 Saturation indices were calculated in the temperature interval between the field temperature
276 and 150°C for the following minerals: quartz, chalcedony, anhydrite, dolomite, calcite, Ca-
277 montmorillonite, laumontite, Mg-chlorite, albite, anorthite, K-feldspar, and kaolinite. Due to
278 the imprecision of the thermodynamic databases, the error on the SI at which the equilibrium is
279 reached is considered to be $SI = 0 \pm 0.25$ (D'Amore et al., 1987). This geothermometrical
280 modeling approach estimates the reservoir temperature within an uncertainty of $\pm 10^\circ\text{C}$ (Tole
281 et al., 1993).

282 An additional set of geothermometrical simulations has been performed at the end of the
283 study including addition of CO_2 to the initial solution to test the hypothesis of CO_2 degassing
284 in an open system.

285

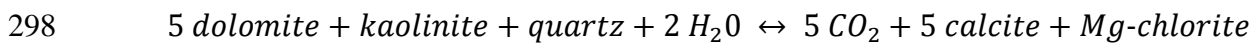
286 3.5.4 Hydrogeochemical modeling between surface and depth conditions in closed 287 system

288 In order to assess the geochemistry of the waters at reservoir conditions and the variation
289 of the $f\text{CO}_2$ between the reservoir and the surface, we carried out hydrogeochemical simulations
290 in closed systems. In sedimentary environments, the pH and $f\text{CO}_2$ of the waters are highly
291 dependent on the interaction with carbonate minerals. Dolomite is particularly important in the
292 Central Betic Cordillera where large amount are present. CO_2 generation might occurs during
293 dolomite precipitation as shown by the following reaction:



295 The $f\text{CO}_2$ in the system might also be controlled by reactions involving aluminosilicates

296 and carbonates such as the conversion of kaolinite to Mg-chlorite proposed by Coudrain-
297 Ribstein et al. (1998) and Hutcheon et al. (1993):



299

300 The modeling workflow was run with the PHREEQC code and includes the following three
301 steps:

302 (1) Saturation calculations were carried out at the outlet temperature (T_{out}) and atmospheric
303 pressure (P_{out}),

304 (2) An increase in temperature was simulated up to the temperature of the quartz
305 geothermometer (T_{qz}) and the corresponding hydrostatic pressure of the reservoir (P_{hydro}) using
306 a geothermal gradient of 30°C/km,

307 (3) Waters were equilibrated with a set of minerals at T_{qz} and P_{hydro} , to test two different
308 hypotheses:

- 309
- 310 • Equilibrium with dolomite using $\text{CO}_{2(\text{g})}$ as an alternative phase to reach the
311 equilibrium,
 - 312 • Equilibrium with carbonates and alumino-silicates using calcite, dolomite,
313 kaolinite, quartz, Mg-chlorite as mineral assemblage. These minerals are allowed
314 to dissolve or precipitate to reach equilibrium.

314 The concentrations of chemical species, pH, CO_2 fugacity, and SI of minerals were
315 computed during each step of modeling. By comparing the results of the geochemical modeling
316 (Step 3) with the initial surface geochemical characteristics (Step 1), we evaluate the possible
317 mineral assemblages in equilibrium at reservoir conditions.

318 These geochemical simulations rely on the assumption that the difference in the quartz
319 saturation index ($\text{SI}_{\text{quartz}}$) during each step of the modeling does not lead to significant change
320 in temperature. Even if $\text{SI}_{\text{quartz}}$ varies between -0.13 and 1.27, the H_4SiO_4 concentration remains

321 quite constant for all the thermal waters resulting in a change in apparent temperature (δT)
322 lower than 5°C.

323

324 **4 Results**

325 4.1 Chemical characteristics of the waters

326 The investigated thermal waters have outlet temperature ranging from 20 to 50°C,
327 corresponding to low to medium enthalpy waters, and pH values spanning between 5.8 and 7.6
328 (Table 1). The conductivity of the studied waters shows a large range of values, from 1 to 34
329 mS/cm, corresponding to total dissolved solids (TDS) values from 0.67 to 18.17 g.L⁻¹.

330 The thermal waters show a large variability in their chemical composition and a relationship
331 can be evidenced between the water-types and their location relative to the geological structures
332 in the Central Betic Cordillera (Figure 2).

333 The waters located in the graben formed in the Alpujarride Complex and close to the SE-
334 NW faults have a chemical composition of Ca²⁺-Mg²⁺-SO₄²⁻-HCO₃⁻ type, displaying interaction
335 with both carbonates and sulfates.

336 The waters in the evaporitic basins are mainly Ca²⁺-Mg²⁺-SO₄²⁻ water-type resulting from
337 clear interaction with evaporitic material and especially calcium sulfate. The samples BAG and
338 BNAG have a higher HCO₃⁻ content, with a composition close to the samples from the graben
339 in the Alpujarride Complex. The composition of the BZ water also differs from the others with
340 a Ca²⁺-Na⁺-K⁺-SO₄²⁻-Cl⁻ water-type, showing significant interaction with evaporitic and detrital
341 material.

342 The thermal waters located at contacts between metamorphic complexes display larger
343 dispersion in their chemical composition. The samples BSL and CL are Na⁺-Cl⁻ type whereas
344 BAA is Na⁺-Cl⁻-HCO₃⁻ type.

345

346 4.2 Saturation indices

347 The results of the saturation indices calculations at the outlet temperature are shown in
348 Table 2. The waters are mainly close to equilibrium or slightly oversaturated with respect to
349 calcite and dolomite whereas they are undersaturated with respect to gypsum, anhydrite, and
350 halite. However, the thermal waters of AT and BSL display slight undersaturation to
351 undersaturation with respect to the carbonate minerals (calcite and dolomite). Waters are
352 oversaturated with respect to quartz and close to equilibrium with respect to chalcedony.
353 Concerning the saturation indices with respect to alumino-silicates, the waters are oversaturated
354 with respect to kaolinite and Ca-montmorillonite whereas they display large range of saturation
355 with respect to K-feldspar and albite, spanning from undersaturated to highly oversaturated,
356 independently of the relationship with the tectonic structures. The saturation indices of the
357 waters with respect to the considered minerals are pH-dependent and therefore dependent of
358 possible CO₂ degassing of the thermal waters.

359 4.3 CO₂

360 Dissolved CO₂ concentrations range from 9.51 to 597.5 cc/L, corresponding to $f\text{CO}_2$
361 spanning from 0.02 to 0.78, i.e pCO₂ from 0.02 to 0.78 atm (Table 3). The water samples
362 characterized by higher amounts of dissolved CO₂ display lower pH values, suggesting that
363 CO₂ is the main species responsible of water acidity. The high-CO₂ springs of CL, BAA and
364 BUG are also characterized by bubbling gases with similar composition as the dissolved gases
365 (Lix et al., 2018).

366 The $f\text{CO}_2$ values obtained from the speciation-solubility calculations at the outlet
367 temperature range from 0.006 to 1.02 (Table 2). The total dissolved inorganic carbon content
368 of the thermal waters and its isotopic composition ($\delta^{13}\text{C}_{\text{TDIC}}$), listed in Table 3, range from 2.7
369 $\times 10^{-3}$ to 6.3×10^{-2} mol.L⁻¹ and from -9.04 to -1.54‰ vs. V-PDB respectively.

370 Various carbon sources and processes control the $\delta^{13}\text{C}$ of the TDIC including: (1) the

371 degradation of organic matter in the soil (of the recharge area), (2) carbonate dissolution, (3)
372 degassing of mantle-derived CO₂. Biological degradation processes in soils usually results in
373 δ¹³C values ranging from -23‰ and -9‰ (Clark and Fritz, 1997), which is not well
374 representative of the studied samples. Therefore, the δ¹³C_{TDIC} values indicate mainly inorganic
375 origin of CO₂ although possible mixing with organic carbon sources cannot be ruled out.
376 Discriminating the carbon source between carbonate dissolution and mantle-derived CO₂ might
377 be more complex as their δ¹³C values overlap, The isotopic composition of dissolved and
378 bubbling gases in these thermal waters show however a dominant crustal component (Lix et al.,
379 2018). Purely inorganic origin of CO₂ has been considered in these thermodynamical
380 calculations, given the results of δ¹³C of the TDIC.

381

382 4.4 Reservoir temperature and pressure

383 4.4.1 Chemical geothermometers and geobarometers

384 The temperatures provided by the silica and Ca-Mg geothermometers are compiled in Table
385 4. The reservoir temperatures estimated with the different SiO₂-quartz geothermometers range
386 from 42 to 146°C corresponding to a mean spanning between 51 and 143°C with a relative
387 standard deviation lower than 6°C. The SiO₂-chalcedony geothermometers yields lower
388 temperatures ranging from 20 to 115°C. The SiO₂-quartz are more reliable than the SiO₂-
389 chalcedony geothermometers since quartz might be the phase controlling the dissolved silica in
390 the thermal waters in the Betic Cordillera. Indeed, quartz occurrences and mineralizations have
391 been described in the Internal Zones of the Betic Cordillera as well as in the Neogene basins
392 whereas chalcedony have not been described in mineral assemblages. Although the kinetics of
393 quartz reaction is very slow below 100°C (Rimstidt and Barnes, 1980), the mineral equilibrium
394 approach developed in this study might support the temperatures obtained from quartz
395 geothermometers.

396 The thermal waters located in the evaporitic basins (Granada and Guadix-Baza Basins)
397 show estimated reservoir temperature from SiO₂-quartz ranging from 74 to 95°C. Assuming a
398 thermal gradient of 30°C/km, which can be expected in the studied area (Fernández et al., 1998),
399 these temperatures would correspond to depths and hydrostatic pressures varying from 2.5 to
400 3.2 km and from 250 to 320 atm respectively. The thermal waters BUC and BUG, located close
401 to the SE-NW faults, show the lowest estimated reservoir temperature, ranging from 51 to 58°C
402 and corresponding to hydrostatic pressure spanning between 170 and 200 atm respectively. The
403 thermal waters located at the contacts between metamorphic complexes (BAA, CL, and BSL)
404 show the highest estimated reservoir temperatures ranging from 126 and 142°C, corresponding
405 to depths of 4 - 4.5 km and a hydrostatic pressures of 400 to 450 atm.

406 The Ca-Mg geothermometer provides temperatures ranging mainly between 71 and 91°C
407 with little variation between the different thermal waters (Table 4). The obtained temperatures
408 are in good agreement with those of SiO₂-quartz geothermometers for the waters located in the
409 evaporitic Granada Basin. However, the Ca-Mg geothermometer give similar reservoir
410 temperatures regardless of the geological context of the studied thermal waters, due to low
411 variations in their Ca/Mg ratios, ranging mainly from 1.5 to 2.4. Therefore, it seems that this
412 geothermometer might not be suitable for all investigated thermal waters in the central Betic
413 Cordillera.

414 The results of the geobarometrical method based on the (HCO₃⁻)²/SO₄²⁻ ratio (Chiodini et
415 al., 1995a) give values of fugacity of CO₂ (*f*CO₂) in depth ranging from 0.04 to approximately
416 23. The high values (> 5) are obtained for the thermal waters located on the contact of
417 metamorphic complexes (CL, BSL, and BAA).

418

419 4.4.2 Geothermometrical modeling

420 The first results of the geothermometrical modeling including all mineral phases (quartz,

421 chalcedony, anhydrite, dolomite, calcite, Ca-montmorillonite, laumontite, Mg-chlorite, and
422 kaolinite) do not reach a common equilibrium temperature (Figures 3 and 4).

423 Although we can expect the carbonates as part of the buffering mineral assemblage in depth
424 due to their ubiquity in the sedimentary basin and in the Central Betic Cordillera, they cannot
425 reach equilibrium in the reservoir conditions. As shown in Figures 3 and 4, the waters are close
426 to equilibrium or oversaturated with respect to calcite and dolomite in the outlet conditions and
427 these minerals have retrograde solubility. The apparent oversaturation in the outlet conditions
428 might result from CO₂ outgassing process and a corresponding increase in pH during the ascent
429 of the waters to the surface.

430

431 4.4.3 Hydrogeochemical modeling

432 The results of the simulations show that, globally, $f\text{CO}_2$ in the outlet conditions varies
433 between 6×10^{-3} and 1, i.e. $p\text{CO}_2$ between $\sim 6 \times 10^{-3}$ and 1 atm. The $f\text{CO}_2$ obtained in the third
434 step of the simulation after equilibration with dolomite show values ranging from $\sim 2 \times 10^{-2}$ and
435 40 (Figure 5), whereas the values of $f\text{CO}_2$ after equilibration with alumino-silicates and
436 carbonates vary between 5.4×10^{-3} and 1.8×10^2 (Figure 6). The logarithmic relationship
437 between $f\text{CO}_2$ and temperature for the waters equilibrated with the both carbonates and
438 alumino-silicates might reflect strong control by the equilibrium mineral assemblage on the
439 chemical water composition and CO₂ content.

440

441 The geochemical modeling allows discriminating the three groups of waters, already
442 distinguished by geology, regarding the $f\text{CO}_2$ in the reservoir conditions:

- 443 • Group of waters located in the evaporitic basins

444 The results of the simulations in the evaporitic Granada Basin give a pH of the waters in
445 equilibrium with dolomite in the reservoir conditions ($74 < T < 95^\circ\text{C}$ and $250 < P_{\text{hydro}} < 320$

446 atm) ranging from 6.5 to 6.8 and an estimated $f\text{CO}_2$ spanning between 9×10^{-2} and 1.6×10^{-1}
447 (Figure 5). The simulations taking into consideration carbonates and alumino-silicates give
448 similar ranges of pH (from 6.5 to 6.7) and $f\text{CO}_2$ (from 6×10^{-2} to 2×10^{-1}) to those obtained
449 with dolomite equilibrium for the water points located in the Granada basin (Figure 6).
450 However, the two samples BNAG and BZ show slightly higher $f\text{CO}_2$ ranging from 3×10^{-1} and
451 6×10^{-1} . The thermal water of Alicun de las Torres (AT), showing a lower reservoir temperature
452 similar to BUC and BUG samples, have an estimated low $f\text{CO}_2$ at depth for both simulations
453 ranging from 1×10^{-2} to 3×10^{-2} (Figure 5 and 6). The variation in $f\text{CO}_2$ between the steps 1
454 and 3 of the simulation, $\Delta f\text{CO}_2$, estimated for this group of thermal waters ranges from 3×10^{-2}
455 to 6×10^{-1} (Figure 7). This corresponds to a difference in calculated CO_2 concentration
456 between the steps 1 and 3 of the simulations ranging from ~ 1 to 5 mmol/L.

457

- 458 • Group of waters in the graben in the Alpujarride complex

459 The results of the equilibrium simulations with dolomite in the reservoir conditions ($51 <$
460 $T < 58^\circ\text{C}$ and $170 < P_{\text{hydro}} < 200$ atm) for the waters located in the graben into the Alpujarride
461 Complex give a pH of the waters of approximately 6.8 and an estimated $f\text{CO}_2$ of 6×10^{-2}
462 (Figure 5). The simulation of these waters in equilibrium with both carbonates and alumino-
463 silicates (calcite, dolomite, quartz, kaolinite, and Mg-chlorite) give higher values of pH ranging
464 from 7.3 to 7.4 and lower values of $f\text{CO}_2$ spanning between 5×10^{-3} and 9×10^{-3} (Figure 6). The
465 estimated variation in $f\text{CO}_2$ between the depth and the surface, $\Delta f\text{CO}_2$, ranges from ~ 0 to $6 \times$
466 10^{-2} (Figure 7), corresponding to maximum 1 mmol/L of CO_2 .

467

- 468 • Group of waters located at contact with metamorphic complexes

469 Both geochemical simulations show high $f\text{CO}_2$ values ($> 7 \times 10^{-1}$) and low pH (ranging
470 from 5.1 to 6.7) at reservoir conditions ($126 < T < 142^\circ\text{C}$ and $400 < P_{\text{hydro}} < 450$ atm) for the
471 thermal waters located at the contact with the metamorphic complexes. The estimated $f\text{CO}_2$ at

472 depth is lower considering the equilibrium with dolomite only (ranging from 6×10^{-1} to 6) than
473 considering the equilibrium with the carbonate and alumino-silicate assemblage (ranging from
474 25 to 180) (Figures 5 and 6). The estimated Δf_{CO_2} for this group of thermal waters spans from
475 6×10^{-1} to 1.8×10^2 (Figure 7), corresponding to 20 mmol/L to 0.85 mol/L of CO_2 .

476

477 4.4.4 Geothermometrical modeling with CO_2 degassing (open system)

- 478 • Group of waters located in the evaporitic basins

479 The geothermometrical simulations with the lowest estimation of CO_2 addition deduced
480 from the hydrogeochemical modeling, 1 mmol/L, result in a common reservoir temperature of
481 75 to 90°C for the waters of the evaporitic basins (Figure 8). Waters are at potential equilibrium
482 with the following mineral buffer: carbonates (calcite and dolomite), anhydrite, quartz, and
483 possibly Mg-chlorite or Ca alumino-silicate (laumontite or a Ca-montmorillonite). These results
484 show that low amounts of CO_2 degassing (~ 1 mmol/L) are necessary in an open system to
485 reach the equilibrium with dolomite and alumino-silicates. Evaporites are also part of the buffer
486 mineral assemblage in this sedimentary environment.

487

- 488 • Group of waters in the graben in the Alpujarride Complex

489 The geothermometrical simulations in an open system with addition of 0.5 mmol/L CO_2
490 show estimated reservoir temperatures ranging from 50 to 60°C for the waters located in the
491 graben in the Alpujarride Complex (Figure 9) with the following mineral buffer: carbonates
492 (calcite and dolomite), quartz, and Ca alumino-silicate (Ca-montmorillonite). Higher amounts
493 of added CO_2 do not lead to a common equilibrium of mineral phases at a specific temperature.

494

- 495 • Group of waters located at contact with metamorphic complexes

496 Modeling of CO_2 degassing in an open system with geothermometrical simulations shows
497 that 7 mmol/L to 1 mol/L of added CO_2 are necessary for the waters to be at equilibrium at

498 temperature ranging from 120 and 140°C with the following mineral assemblage: quartz and
499 dolomite, and sometimes Mg-chlorite and laumontite (Figure 10).

500

501 **5 Discussion**

502 5.1 Role of the mineral buffers in CO₂ estimation

503 The thermal waters in the Central Betic Cordillera are characterized by large heterogeneity
504 in their geochemistry in the outlet conditions and in their geothermal characteristics. The three
505 groups of waters, which were defined based on water composition and geology at the thermal
506 water locations, can be also distinguished by the temperature and $f\text{CO}_2$ in the reservoir. The
507 groups of thermal waters have distinct reservoir temperatures, estimated with the SiO₂-quartz
508 geothermometer, ranging from low-enthalpy (~55°C) to medium-enthalpy (~140°C)
509 geothermal systems. Using the results of the geochemical and geothermometrical modeling we
510 discuss in this section the mineralogical buffers and chemical properties of the reservoirs and
511 the variations in $f\text{CO}_2$ between depth and the surface ($\Delta f\text{CO}_2$) in both closed and open system
512 for the three groups of waters. For all groups the assessed $\Delta f\text{CO}_2$ indicates CO₂ degassing during
513 the ascent of the water to the surface. The equilibrium with respect to mineral phases in the
514 reservoir conditions seems to have a strong control on CO₂ release (Figure 7).

515 The group of thermal waters located in the sedimentary basins (Granada and Guadix-Baza
516 Basins), whose reservoir temperatures range from 74 to 95°C, seem to be buffered at depth by
517 mainly carbonates, evaporites, quartz and a few alumino-silicates. The fact that there is a good
518 agreement in $\Delta f\text{CO}_2$ with both dolomite buffer and carbonate/alumino-silicate buffer shows that
519 carbonates are the predominant mineral buffer in this environment. The values of $f\text{CO}_2$ resulting
520 from geochemical simulations at depth are in quite good agreement with those estimated by the
521 geobarometer from Chiodini et al. (1995a), ranging from 0.04 to 0.16. This geobarometer,

522 specifically established for low- to medium- geothermal systems hosted in carbonates and
523 evaporites, is certainly an efficient tool to estimate the reservoir $f\text{CO}_2$ in this sedimentary
524 context (similar range of temperature and $f\text{CO}_2$).

525 The presence of evaporites needs to be considered for the geothermal systems in
526 sedimentary environment as it might enhance CO_2 release through a dedolomitization process.
527 Prado-Pérez and Pérez del Villar (2011) showed that the thermal water AT may result from
528 dedolomitization at depth followed by CO_2 degassing. Dedolomitization, which is a process
529 described in other natural systems (Auqué et al., 2009; López-Chicano et al., 2001b),
530 corresponds to dolomite dissolution and calcite precipitation caused by the dissolution of
531 gypsum and/or anhydrite. CO_2 loss, before or after outlet of the thermal waters, might occur as
532 evidenced by the presence of fossil and present-day massive thermogenic travertine deposits
533 (Prado-Pérez and Pérez del Villar, 2011) in the Alicun de las Torres site. This process of
534 dedolomitization is most probably occurring in other geothermal systems in the evaporitic
535 Granada and Guadix-Baza basins.

536 For the thermal waters located in the graben in the Alpujarride Complex, which show the
537 lowest estimated reservoir temperature, the buffer minerals are carbonates, quartz, and Ca
538 alumino-silicate (Ca-montmorillonite). $\Delta f\text{CO}_2$ is higher considering the dolomite buffer than
539 considering the carbonate/alumino-silicate buffer. The difference in $f\text{CO}_2$ simulated with the
540 two types of mineral buffers (dolomite only and the carbonate/alumino-silicate association) for
541 the thermal waters in the graben might be the signature of the basement, whereas the similar
542 $f\text{CO}_2$ estimated for the waters in the sedimentary basin would be the signature of the
543 sedimentary pile. Moreover, the values of $f\text{CO}_2$ for both simulations at depth are lower than
544 those estimated by the geobarometer from Chiodini et al. (1995a) of 0.54 and 0.66 for BUC and
545 BUG samples respectively.

546 On the other hand, for the group of waters located at contact with the metamorphic

547 complexes, which displays the highest estimated reservoir temperature (130 – 140°C), the
548 mineral buffer assemblage at depth is more difficult to assess due to the large CO₂ degassing.
549 Indeed, these waters show the highest measured dissolved CO₂ concentrations (> 39 cm³/L)
550 distinguishing them from the other thermal springs in the Central Betic Cordillera. They are at
551 equilibrium with quartz and dolomite, and close to equilibrium with Mg-chlorite and laumontite
552 in the reservoir conditions. The $\Delta f\text{CO}_2$ is lower with the dolomite buffer than with the carbonate
553 and alumino-silicate buffer (Figure 7).

554 The results of the simulations show that CO₂ degassing is lower in open system than in
555 closed system, highlighting the importance to evaluate the efficiency of the system to rapidly
556 ascend water from depth to the surface. Calcite precipitation might result from the CO₂
557 degassing process due to pH increase and kinetic constrains compared to dolomite precipitation.
558 The amount of precipitated calcite can be evaluated during a given time range using the amount
559 of CO₂ loss during the ascent of the water and the estimated flow rate of the springs found in
560 literature and checked in the field (ranging from 0.2 to 100 L/s). Assuming a time range
561 comprised between 1,000 and 100,000 yr, the amount of calcite precipitated is estimated to
562 range from ~ 10² to 10⁶ m³ for the waters in the basins or their borders. This estimation is in
563 good agreement with the volume of travertines that can be deduced from the study of Martín-
564 Algarra et al. (2003) in the northeastern part of the Granada Basin (from 10⁴ to 10⁵ m³ for the
565 last 200,000 yr).

566

567 5.2 Relationship between $f\text{CO}_2$ and temperature

568 Using thermodynamic calculations (hydrogeochemical and geothermometrical
569 simulations), we show the key role of the reservoir temperature and the buffer mineral
570 assemblage on the estimation of $f\text{CO}_2$ and therefore $p\text{CO}_2$. A recent study on the geochemical
571 characterization of geothermal systems pointed out that the CO₂ trapping mechanism is mainly

572 controlled by reservoir temperature (Elidemir and Güleç, 2018). In our studied area, we found
573 increasing reservoir $f\text{CO}_2$ with increasing reservoir temperature (Figure 7). The thermal waters
574 with intermediate reservoir temperature (70 to 90°C) show the lowest uncertainty on the
575 variation of $f\text{CO}_2$ between depth and the surface ($\Delta f\text{CO}_2$) with the two mineral buffers (dolomite
576 only and assemblage of carbonates and alumino-silicates). Higher uncertainty on $\Delta f\text{CO}_2$ is
577 observed for the thermal springs with the higher reservoir temperature (120-140°C): carbonates
578 and alumino-silicates buffer predicts higher $\Delta f\text{CO}_2$ than dolomite as mineral buffer. The
579 thermal waters with the lowest reservoir temperature also show a large uncertainty in $\Delta f\text{CO}_2$
580 but higher $\Delta f\text{CO}_2$ is assessed considering dolomite equilibrium in the reservoir rather than
581 equilibrium with carbonates and alumino-silicates. The results of these highly-simplified
582 mineralogical systems suggest that dolomite tends to equilibrate at low temperature whereas
583 more silicates might be involved at high temperature leading respectively to higher uncertainty
584 in $f\text{CO}_2$. The difference in $\Delta f\text{CO}_2$ between low and high temperature with respect to the
585 considered mineral buffers might also be interpreted by the large uncertainty in thermodynamic
586 data at the system temperature conditions.

587

588 5.3 Implications for sustainability of geothermal energy in the Central Betic 589 Cordillera

590 In order to estimate the environmental impact associated with the CO_2 degassing of the
591 investigated thermal waters, the CO_2 emissions generated by these thermal systems were
592 estimated for potential household heating purpose and were compared to those produced by a
593 natural gas heating system. The average household energetic consumption (Q) for heating
594 system of a 100 m² house in Western Europe is 11,600 kWh/yr, equivalent to 4.18×10^{10} J/yr
595 (Lapillonne et al., 2014).

596 Using this average household energetic consumption, we can estimate the amount of CO_2

597 (n_{CO_2}) that would be emitted from a natural gas furnace used to heat a 100 m² house (Equation
598 3).

$$(n_{CO_2})_{emitted} = (n_{CH_4})_{consumed} = \frac{Q}{HHV} \quad (3)$$

599 where HHV is the higher heating value of methane (891 kJ/mol). Hence, a natural gas furnace
600 would consume 4.69×10^4 mol of CH₄ and would hence produce the equal amount of CO₂.

601 This value can be then compared to the amount of CO₂ that would be produced by the use
602 of the geothermal energy of the thermal springs in the Betic Cordillera area. If we first consider
603 the ideal case of a thermal water with reservoir temperature (T_{depth}) equivalent to the maximum
604 temperature of the heating system ($T_{depth} = T_{max} = 60^\circ C$), the amount of water that has to be
605 pumped to heat a 100 m² house, n_{water} , expressed in mol, can be estimated according to the
606 following equation:

$$n_{water} = \frac{Q}{Cp_{water} * \Delta T} \quad (4)$$

607 where Q is the average value of household energetic consumption, Cp_{water} is the isobaric heat
608 capacity of water and ΔT is the temperature range of the internal heating cycle ($20^\circ C$ with T_{max}
609 $= 60^\circ C$ and $T_{min} = 40^\circ C$).

610 Assuming a constant Cp_{water} of 75.4 J/mol/K and an efficiency of the heat exchanger of 100 %,
611 the necessary quantity of water to heat a 100 m² house would therefore be 2.77×10^7 mol.

612 We can assess the amount of water that has to be pumped for the two other groups of
613 thermal waters considered earlier with reservoir temperature (T_{depth}) of 90 and $140^\circ C$ using to
614 the following equation:

$$(n_{water})_{pumped} = \frac{Q}{Cp_{water} * (T_{depth} - T_{max})} \quad (5)$$

615 We found that the amount of water that has to be pumped is 1.85×10^7 and 6.15×10^6 mol
616 respectively. Using the average CO₂ concentration estimated for each thermal water groups (2
617 $\times 10^{-4}$, 5×10^{-3} , 8×10^{-1} mol/L), we can estimate the amount of natural CO₂ degassed during

618 household heating ranging between 1.0×10^2 and 8.9×10^4 mol. The estimated amount of CO_2
619 released from geothermal waters used in heating is lower by 1 to 2 orders of magnitude than
620 the amount of CO_2 generated by a natural gas furnace for the two first groups of thermal waters
621 ($T_{\text{depth}} < 130^\circ\text{C}$) (Figure 11). However, similar quantity of CO_2 could be released from the
622 thermal waters with the higher T_{depth} as those produced by a natural gas furnace.

623 These estimations of CO_2 emissions in this simple practical application of heating a 100 m^2
624 house show that the geothermal energy is globally a cleaner energy than natural gas but might
625 release as much CO_2 as a natural gas furnace in certain conditions (high reservoir temperature
626 and $f\text{CO}_2$). These estimations are based on possible gas venting during the heat production,
627 which are usually neglected in life cycle assessment of carbon intensity of geothermal system
628 (McCay et al., 2019).

629 These estimations, giving us the order of magnitude of CO_2 emissions that could be generated
630 by the investigated geothermal systems, lead to explore possible exploitations of the geothermal
631 resource. Direct electricity production (e.g. enhanced geothermal systems) might be considered
632 for the thermal waters with the highest reservoir temperature ($T_{\text{depth}} = 140^\circ\text{C}$) emitting large
633 quantity of CO_2 . This use would have to be coupled to CO_2 capture and storage to make it a
634 renewable and clean energy.

635

636 **6 Conclusions**

637 Our study provides the first characterization of the reservoir conditions (T, P, and
638 geochemistry) for the thermal waters in the central part of the Betic Cordillera. The $f\text{CO}_2$ at
639 depth were tentatively assessed with both a chemical geobarometer and direct geochemical
640 simulations. The variation of $f\text{CO}_2$ ranges from approximately 6×10^{-3} to 10^2 at the scale of
641 the area. Based on the geology of the thermal water locations and the results of the
642 geothermometrical and thermodynamic geochemical simulations three groups of waters have

643 been determined.

644 The group of the thermal waters located in the sedimentary basin has estimated reservoir
645 temperatures ranging from approximately 70 to 90°C and $f\text{CO}_2$ varying between 6×10^{-2} and
646 6×10^{-1} . The estimated variations in $f\text{CO}_2$ between the depth and the surface ($\Delta f\text{CO}_2$) were quite
647 similar considering both the dolomite buffer and carbonate/alumino-silicate buffer for the
648 thermal waters in the Granada Basin. A mineral assemblage buffering at depth mainly
649 composed of carbonates, evaporites, and quartz characterizes this system.

650 The group of waters located in the graben in the Alpujarride Complex presents the lowest
651 reservoir temperature of 55-60°C and $f\text{CO}_2$ ranging from 5×10^{-3} to 7×10^{-2} , depending of the
652 considered buffering minerals. The $\Delta f\text{CO}_2$ between the depth and the surface is higher with the
653 dolomite buffer than with the carbonate and alumino-silicate buffer. The buffering mineral
654 assemblage at depth is estimated to be carbonates, quartz, and Ca alumino-silicates.

655 On the other hand, the group of waters located at contact with metamorphic complexes
656 shows the highest reservoir temperature of 130 – 140°C and $f\text{CO}_2$ ranging from approximately
657 1 to 100. The $\Delta f\text{CO}_2$ between the depth and the surface is lower with the dolomite buffer than
658 with the carbonate and alumino-silicate buffer. The buffering mineral assemblage in the
659 reservoir might be dolomite, quartz, Mg and Ca alumino-silicates.

660 This study highlights the importance of evaluating the mineral buffers in the reservoir
661 conditions of the geothermal systems. The mineral assemblage at equilibrium in the reservoir
662 conditions constrains the estimated CO_2 generation and release at depth. In the case study of
663 the Central Betic Cordillera, CO_2 degassing is more constrained in the evaporitic basins thanks
664 to a strong carbonate/evaporite/quartz buffer than in the surrounding areas of the basins where
665 the alumino-silicates play a non-negligible role. Moreover, we pointed out the key role of the
666 reservoir temperature on the estimation of the reactions between CO_2 , water, and rocks for the
667 geothermal systems in sedimentary basins.

668 The estimations of CO₂ emissions generated by the thermal systems for potential
669 household heating purpose indicate that the geothermal energy is globally a clean energy but
670 might release as much CO₂ as a natural gas furnace for the thermal waters with the highest
671 reservoir temperature. This study points out the importance to estimate properly the amount of
672 CO₂ degassing in geothermal waters depending of the reservoir conditions. Our results
673 highlight the importance of considering geochemical estimates for heat exchanger design. In
674 the case of thermal waters with the highest temperatures and high CO₂ contents, heat
675 exchangers allowing to maintain fluids under pressure might be preferred to avoid CO₂ release
676 in the atmosphere.

677

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686 **References:**

- 687 Ármannsson, H., 2018. An overview of carbon dioxide emissions from Icelandic geothermal
688 areas. *Appl. Geochemistry* 97, 11–18. <https://doi.org/10.1016/j.apgeochem.2018.07.013>
- 689 Ármannsson, H., 2003. CO2 emission from geothermal plants, in: *International Geothermal*
690 *Conference*. pp. 56–62.
- 691 Arnórsson, S., Gunnlaugsson, E., Svavarsson, H., 1983. The chemistry of geothermal waters in
692 Iceland. III. Chemical geothermometry in geothermal investigations. *Geochim.*
693 *Cosmochim. Acta* 47, 567–577. [https://doi.org/10.1016/0016-7037\(83\)90278-8](https://doi.org/10.1016/0016-7037(83)90278-8)
- 694 Arrizabalaga, I., De Gregorio, M., García del la Noceda, C., Hidalgo, R., Urchueguía, J.F.,
695 2015. Country Update for the Spanish Geothermal Sector, in: *World Geothermal Congress*
696 2015. p. 9.
- 697 Asta, M.P., Gimeno, M.J., Auqué, L.F., Gómez, J., Acero, P., Lapuente, P., 2012.
698 Hydrochemistry and geothermometrical modeling of low-temperature Panticosa
699 geothermal system (Spain). *J. Volcanol. Geotherm. Res.* 235–236, 84–95.
700 <https://doi.org/10.1016/j.jvolgeores.2012.05.007>
- 701 Auqué, L.F., Acero, P., Gimeno, M.J., Gómez, J.B., Asta, M.P., 2009. Hydrogeochemical
702 modeling of a thermal system and lessons learned for CO2 geologic storage. *Chem. Geol.*
703 268, 324–336. <https://doi.org/10.1016/j.chemgeo.2009.09.011>
- 704 Azañón, J.M., Crespo-Blanc, A., 2000. Exhumation during a continental collision inferred from
705 the tectonometamorphic evolution of the Alpujarride Complex in the central Betics
706 (Alboran Domain, SE Spain). *Tectonics* 19, 549–565.
707 <https://doi.org/10.1029/2000TC900005>
- 708 Azañón, J.M., García-Dueñas, V., Goffé, B., 1998. Exhumation of high-pressure metapelites
709 and coeval crustal extension in the Alpujarride complex (Betic Cordillera).
710 *Tectonophysics* 285, 231–252. [https://doi.org/10.1016/S0040-1951\(97\)00273-4](https://doi.org/10.1016/S0040-1951(97)00273-4)
- 711 Battistel, M., Hurwitz, S., Evans, W.C., Barbieri, M., 2016. The chemistry and isotopic
712 composition of waters in the low-enthalpy geothermal system of Cimino-Vico Volcanic
713 District, Italy. *J. Volcanol. Geotherm. Res.* 328, 222–229.
714 <https://doi.org/10.1016/j.jvolgeores.2016.11.005>
- 715 Benavente Herrera, J., Sanz de Galdeano, C., 1985. Relacion de las direcciones de karstificacion
716 y del termalismo con la fracturacion en las Cordilleras Beticas. *Estud. Geológicos* 41, 177–
717 188.
- 718 Bjorlykke, K., Egeberg, P.K., 1993. Quartz cementation in sedimentary basins. *Am. Assoc. Pet.*
719 *Geol. Bull.* 77, 1538–1548.

720 Blasco, M., Auqué, L.F., Gimeno, M.J., Acero, P., Asta, M.P., 2017. Geochemistry,
721 geothermometry and influence of the concentration of mobile elements in the chemical
722 characteristics of carbonate-evaporitic thermal systems. The case of the Tiermas
723 geothermal system (Spain). *Chem. Geol.* 466, 696–709.
724 <https://doi.org/10.1016/J.CHEMGEO.2017.07.013>

725 Blasco, M., Gimeno, M.J., Auqué, L.F., 2018. Low temperature geothermal systems in
726 carbonate-evaporitic rocks: Mineral equilibria assumptions and geothermometrical
727 calculations. Insights from the Arnedillo thermal waters (Spain). *Sci. Total Environ.* 615,
728 526–539. <https://doi.org/10.1016/J.SCITOTENV.2017.09.269>

729 Braga, J.C., Martín, J.M., Quesada, C., 2003. Patterns and average rates of late Neogene--
730 Recent uplift of the Betic Cordillera, SE Spain. *Geomorphology* 50, 3–26.
731 [https://doi.org/10.1016/S0169-555X\(02\)00205-2](https://doi.org/10.1016/S0169-555X(02)00205-2)

732 Buforn, E., Bezzeghoud, M., Udías, A., Pro, C., 2004. Seismic Sources on the Iberia-African
733 Plate Boundary and their Tectonic Implications. *Pure Appl. Geophys.* 161, 623–646.
734 <https://doi.org/10.1007/s00024-003-2466-1>

735 Campos, J.C.R., 2006. Guía de manantiales de la provincia de Granada: Una visión sobre su
736 origen y naturaleza. Publicaciones de Diputación Provincial de Granada.

737 Capasso, G., Favara, R., Grassa, F., Inguaggiato, S., Longo, M., 2005. On-line technique for
738 preparing and measuring stable carbon isotope of total dissolved inorganic carbon in water
739 samples ($\delta^{13}\text{C}_{\text{TDIC}}$). *Ann. Geophys.* 48, 159–166.

740 Capasso, G., Inguaggiato, S., 1998. A simple method for the determination of dissolved gases
741 in natural waters. An application to thermal waters from Vulcano Island. *Appl.*
742 *Geochemistry* 13, 631–642. [https://doi.org/10.1016/S0883-2927\(97\)00109-1](https://doi.org/10.1016/S0883-2927(97)00109-1)

743 Capecchiacci, F., Tassi, F., Vaselli, O., Bicocchi, G., Cabassi, J., Giannini, L., Nisi, B.,
744 Chiocciara, G., 2015. A combined geochemical and isotopic study of the fluids discharged
745 from the Montecatini thermal system (NW Tuscany, Italy). *Appl. Geochemistry* 59, 33–
746 46. <https://doi.org/10.1016/j.apgeochem.2015.03.010>

747 Centre d'Expertise en Analyse Environnementale du Québec, 2016. Détermination de la silice
748 réactive dans l'eau : méthode par spectrophotométrie UV-visible, MA. 303 – SiO₂ 1.0,
749 rév. 1. Ministère du Développement durable, de l'Environnement, de la Lutte contre les
750 changements climatiques.

751 Cerón, J.C., López-Chicano, M., 2002. Thermal waters in Andalucía. *Newsl. Int. Geotherm.*
752 *Assoc.* 48, 4–5.

753 Chiodini, G., Baldini, A., Barberi, F., Carapezza, M.L., Cardellini, C., Frondini, F., Granieri,

754 D., Ranaldi, M., 2007. Carbon dioxide degassing at Latera caldera (Italy): Evidence of
755 geothermal reservoir and evaluation of its potential energy. *J. Geophys. Res.* 112, 1–17.
756 <https://doi.org/10.1029/2006JB004896>

757 Chiodini, G., Cioni, R., Guidi, M., Raco, B., Marini, L., 1998. Soil CO₂ flux measurements in
758 volcanic and geothermal areas. *Appl. Geochemistry* 13, 543–552.

759 Chiodini, G., Frondini, F., Marini, L., 1995a. Theoretical geothermometers and PCO₂ indicators
760 for aqueous solutions coming from hydrothermal systems of medium-low temperature
761 hosted in carbonate-evaporite rocks. Application to the thermal springs of the Etruscan
762 Swell, Italy. *Appl. Geochemistry* 10, 337–346. [https://doi.org/10.1016/0883-
763 2927\(95\)00006-6](https://doi.org/10.1016/0883-2927(95)00006-6)

764 Chiodini, G., Frondini, F., Ponziani, F., 1995b. Deep structures and carbon dioxide degassing
765 in Central Italy. *Geothermics* 24, 81–94. [https://doi.org/10.1016/0375-6505\(94\)00023-6](https://doi.org/10.1016/0375-6505(94)00023-6)

766 Clark, I.D., Fritz, P., 1997. *Environmental isotopes in hydrogeology*. CRC Press/Lewis
767 Publishers, Boca Raton, FL.

768 Corbí, H., Lancis, C., García-García, F., Pina, J.-A., Soria, J.M., Tent-Manclús, J.E., Viseras,
769 C., 2012. Updating the marine biostratigraphy of the Granada Basin (central Betic
770 Cordillera). Insight for the Late Miocene palaeogeographic evolution of the Atlantic --
771 Mediterranean seaway. *Geobios* 45, 249–263.
772 <https://doi.org/10.1016/j.geobios.2011.10.006>

773 Coudrain-Ribstein, A., Gouze, P., de Marsily, G., 1998. Temperature-carbon dioxide partial
774 pressure trends in confined aquifers. *Chem. Geol.* 1, 73–89.
775 [https://doi.org/https://doi.org/10.1016/S0009-2541\(97\)00161-7](https://doi.org/https://doi.org/10.1016/S0009-2541(97)00161-7)

776 Cruz-Sanjulián, J., Rossell, L.G., Blasco, J.G., 1972. Aguas termales de la provincia de
777 Granada. *Bol. Geológico y Min. T.LXXXIII-III* 266–275.

778 Cruz Sanjulián, J., Granda, J.M., 1979. Temperatura de base de las aguas termales de la
779 provincia de Granada, in: *II Simposio Nacional de Hidrogeología*. pp. 547–568.

780 D'Amore, F., Arnórsson, S., *Geothermometry, S.A.*, 2000. *Isotopic and Chemical Techniques*
781 *in Geothermal Exploration. Dev. Use Sampl. Methods, Data Handl. Interpret. Int. At.*
782 *Energy Agency, Vienna, Austria* 152–199.

783 D'Amore, F., Fancelli, R., Caboi, R., 1987. Observations on the application of chemical
784 geothermometers to some hydrothermal systems in Sardinia. *Geothermics* 16, 271–282.

785 Elidemir, S., Güleç, N., 2018. Geochemical characterization of geothermal systems in western
786 Anatolia (Turkey): implications for CO₂trapping mechanisms in prospective CO₂-EGS
787 sites. *Greenh. Gases Sci. Technol.* 8, 63–76. <https://doi.org/10.1002/ghg.1747>

788 Fernández, M., Marzán, I., Correia, A., Ramalho, E., 1998. Heat flow, heat production, and
789 lithospheric thermal regime in the Iberian Peninsula. *Tectonophysics* 291, 29–53.
790 [https://doi.org/10.1016/s0040-1951\(98\)00029-8](https://doi.org/10.1016/s0040-1951(98)00029-8)

791 Fournier, R.O., 1977. Chemical geothermometers and mixing models for geothermal systems.
792 *Geothermics* 5, 41–50. [https://doi.org/10.1016/0375-6505\(77\)90007-4](https://doi.org/10.1016/0375-6505(77)90007-4)

793 Fournier, R.O., Potter, R.W., 1982. An equation correlating the solubility of quartz in water
794 from 25° to 900°C at pressures up to 10,000 bars. *Geochim. Cosmochim. Acta* 46, 1969–
795 1973. [https://doi.org/10.1016/0016-7037\(82\)90135-1](https://doi.org/10.1016/0016-7037(82)90135-1)

796 Fusari, A., Carroll, M.R., Ferraro, S., Giovannetti, R., Giudetti, G., Invernizzi, C., Mussi, M.,
797 Pennisi, M., 2017. Circulation path of thermal waters within the Laga foredeep basin
798 inferred from chemical and isotopic ($\delta^{18}\text{O}$, δD , 3H , $87\text{Sr}/86\text{Sr}$) data. *Appl. Geochemistry*
799 78, 23–34. <https://doi.org/10.1016/J.APGEOCHEM.2016.11.021>

800 Galindo-Zaldívar, J., Gil, A.J., Sanz de Galdeano, C., Lacy, M.C., García-Armenteros, J.A.,
801 Ruano, P., Ruiz, A.M., Martínez-Martos, M., Alfaro, P., 2015. Active shallow extension
802 in central and eastern Betic Cordillera from CGPS data. *Tectonophysics* 663, 290–301.
803 <https://doi.org/10.1016/j.tecto.2015.08.035>

804 Gran, G., 1952. Determination of the equivalence point in potentiometric titrations. Part II.
805 *Analyst* 77, 661–671. <https://doi.org/10.1039/AN9527700661>

806 Harvey, M.C., Rowland, J. V, Chiodini, G., Rissmann, C.F., Bloomberg, S., Fridriksson, T.,
807 Oladottir, A.A., 2017. CO₂ flux geothermometer for geothermal exploration. *Geochim.*
808 *Cosmochim. Acta* 213, 1–16. <https://doi.org/10.1016/j.gca.2017.06.025>

809 Hunt, T.M., 2001. Five Lectures on Environmental Effects of Geothermal Utilization,
810 Geothermal Training Programme.

811 Hutcheon, I.A.N., Shevalier, M., Abercrombie, H.J., 1993. pH buffering by metastable mineral-
812 fluid equilibria and evolution of carbon dioxide fugacity during burial diagenesis.
813 *Geochim. Cosmochim. Acta* 57, 1017–1027.

814 Inguaggiato, S., Rizzo, A., 2004. Dissolved helium isotope ratios in ground-waters: a new
815 technique based on gas--water re-equilibration and its application to Stromboli volcanic
816 system. *Appl. Geochemistry* 19, 665–673.
817 <https://doi.org/10.1016/j.apgeochem.2003.10.009>

818 Lapillonne, B., Pollier, K., Samci, N., 2014. Energy efficiency trends for households in the EU.
819 Enerdata. Retrieved June 22, 2015.

820 Lix, C., Zuddas, P., Inguaggiato, C., Guichet, X., Benavente, J., Barbier, M., 2018. New insights
821 on Betic Cordillera structure from gas geochemistry. *Geochemistry, Geophys. Geosystems*

822 1–12. <https://doi.org/10.1029/2018GC007712>

823 López-Chicano, M., Bouamama, M., Vallejos, A., Pulido-Bosch, A., 2001a. Factors which
824 determine the hydrogeochemical behaviour of karstic springs. A case study from the Betic
825 Cordilleras, Spain. *Appl. Geochemistry* 16, 1179–1192. [https://doi.org/10.1016/S0883-](https://doi.org/10.1016/S0883-2927(01)00012-9)
826 [2927\(01\)00012-9](https://doi.org/10.1016/S0883-2927(01)00012-9)

827 López-Chicano, M., Cerón, J.C., Vallejos, A., Pulido-Bosch, A., 2001b. Geochemistry of
828 thermal springs, Alhama de Granada (southern Spain). *Appl. Geochemistry* 16, 1153–
829 1163. [https://doi.org/10.1016/S0883-2927\(01\)00020-8](https://doi.org/10.1016/S0883-2927(01)00020-8)

830 Marini, L., Chiodini, G., Cioni, R., 1986. New geothermometers for carbonate-evaporite
831 geothermal reservoirs. *Geothermics* 15, 77–86. [https://doi.org/10.1016/0375-](https://doi.org/10.1016/0375-6505(86)90030-1)
832 [6505\(86\)90030-1](https://doi.org/10.1016/0375-6505(86)90030-1)

833 Martín-Algarra, A., Martín-Martín, M., Andreo, B., Julià, R., González-Gómez, C., 2003.
834 Sedimentary patterns in perched spring travertines near Granada (Spain) as indicators of
835 the paleohydrological and paleoclimatological evolution of a karst massif. *Sediment. Geol.*
836 161, 217–228. [https://doi.org/10.1016/S0037-0738\(03\)00115-5](https://doi.org/10.1016/S0037-0738(03)00115-5)

837 Martín, J.M., Braga, J.C., 1987. Alpujárride carbonate deposits (southern Spain) - Marine
838 Sedimentation in a Triassic Atlantic. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 59, 243–
839 260.

840 McCay, A.T., Feliks, M.E.J., Roberts, J.J., 2019. Life cycle assessment of the carbon intensity
841 of deep geothermal heat systems: A case study from Scotland. *Sci. Total Environ.* 685,
842 208–219. <https://doi.org/10.1016/j.scitotenv.2019.05.311>

843 Michard, G., 1990. Behaviour of major elements and some trace elements (Li, Rb, Cs, Sr, Fe,
844 Mn, W, F) in deep hot waters from granitic areas. *Chem. Geol.* 89, 117–134.
845 [https://doi.org/10.1016/0009-2541\(90\)90062-C](https://doi.org/10.1016/0009-2541(90)90062-C)

846 Michard, G., 1979. Géothermomètres chimiques. *Bull. BRGM* 2, 183–189.

847 Parkhurst, D.L., Appelo, C.A.J., others, 2013. Description of input and examples for
848 PHREEQC version 3 - a computer program for speciation, batch-reaction, one-
849 dimensional transport, and inverse geochemical calculations. *US Geol. Surv. Tech.*
850 *methods*, B. 6, 497. [https://doi.org/10.1016/0029-6554\(94\)90020-5](https://doi.org/10.1016/0029-6554(94)90020-5)

851 Pérez del Villar, L., 2009. Almacenamiento geológico de CO₂: Análogos del almacenamiento
852 y escape. Fundamentos, ejemplos y aplicaciones para la predicción de riesgos y la
853 evaluación del comportamiento a largo plazo. *Congr. Nac. del Medio Ambient.*

854 Prado-Pérez, A.J., Pérez del Villar, L., 2011. Dedolomitization as an analogue process for
855 assessing the long-term behaviour of a CO₂ deep geological storage: The Alicún de las

856 Torres thermal system (Betic Cordillera, Spain). *Chem. Geol.* 289, 98–113.
857 <https://doi.org/10.1016/j.chemgeo.2011.07.017>

858 Rimstidt, J.D., Barnes, H.L., 1980. The kinetics of silica-water reactions. *Geochim.*
859 *Cosmochim. Acta* 44.

860 Rodríguez-Fernández, J., Sanz de Galdeano, C., 2006. Late orogenic intramontane basin
861 development: the Granada basin, Betics (southern Spain). *Basin Res.* 18, 85–102.
862 <https://doi.org/10.1111/j.1365-2117.2006.00284.x>

863 Sánchez Guzmán, J., García de la Noceda, C., 2010. The Evolution of Geothermal Energy in
864 Spain - Country Update (2005-2009), in: *Proceedings World Geothermal Congress.*

865 Sanz de Galdeano, C., 2008. The Cadiz-Alicante fault: an important discontinuity in the Betic
866 Cordillera. *Rev. la Soc. Geológica España* 21.

867 Sanz de Galdeano, C., 1990. Geologic evolution of the Betic Cordilleras in the Western
868 Mediterranean, Miocene to the present. *Tectonophysics* 172, 107–119.
869 [https://doi.org/10.1016/0040-1951\(90\)90062-D](https://doi.org/10.1016/0040-1951(90)90062-D)

870 Sanz de Galdeano, C., Peláez, J.A., 2011. Fallas activas en la Cordillera Bética: una
871 aproximación a partir de la información tectónica y sísmica. Editorial Universidad de
872 Granada.

873 Sanz de Galdeano, C., Peláez, J.A., 2011. Fallas activas en la Cordillera Bética: una
874 aproximación a partir de la información tectónica y sísmica.

875 Sanz de Galdeano, C., Vera, J.A., 1992. Stratigraphic record and palaeogeographical context of
876 the Neogene basins in the Betic Cordillera, Spain. *Basin Res.* 4, 21–36.
877 <https://doi.org/10.1111/j.1365-2117.1992.tb00040.x>

878 Seward, T.M., Kerrick, D.M., 1996. Hydrothermal CO₂ emission from the Taupo volcanic
879 zone, New Zealand. *Earth Planet. Sci. Lett.* 139, 105–113.

880 Tole, M.P., Ármannsson, H., Zhong-He, P., Arnórsson, S., 1993. Fluid/mineral equilibrium
881 calculations for geothermal fluids and chemical geothermometry. *Geothermics* 22, 17–37.

882 Verma, M.P., 2000a. Chemical thermodynamics of silica: A critique on its geothermometer.
883 *Geothermics* 29, 323–346. [https://doi.org/10.1016/S0375-6505\(99\)00064-4](https://doi.org/10.1016/S0375-6505(99)00064-4)

884 Verma, M.P., 2000b. Limitations in applying silica geothermometers for geothermal reservoir
885 evaluation, in: *Proceedings, 25th Workshop on Geothermal Reservoir Engineering,*
886 *Stanford University, Stanford.* pp. 24–26.

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889 List of the figures:

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891 map of the area modified after Sanz de Galdeano and Peláez (2011).

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899 Figure 5: Relationship between $f\text{CO}_2$ and temperature ($^{\circ}\text{C}$), for the outlet (crosses) and
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901 Figure 6: Relationship between $f\text{CO}_2$ and temperature ($^{\circ}\text{C}$) for the outlet (crosses) and
902 reservoir (circles) conditions considering equilibrium with calcite, dolomite, quartz, kaolinite,
903 and Mg-chlorite in depth.

904 Figure 7: Relationship between the variations of $f\text{CO}_2$ calculated between steps 1 and 3 of the
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907 quartz, kaolinite, and Mg-chlorite, both in the reservoir conditions. The variability in $\Delta f\text{CO}_2$ is
908 expressed for the three groups of waters with average reservoir temperature of: 55°C (blue),
909 85°C (yellow), and 135°C (red).

910 Figure 8: Evolution of the mineral saturation indices with temperature for the thermal waters
911 located in the evaporitic Granada Basin by geothermometrical modeling with theoretical CO_2
912 addition (1 mmol/L) to compensate possible CO_2 outgassing during the ascent of the waters.

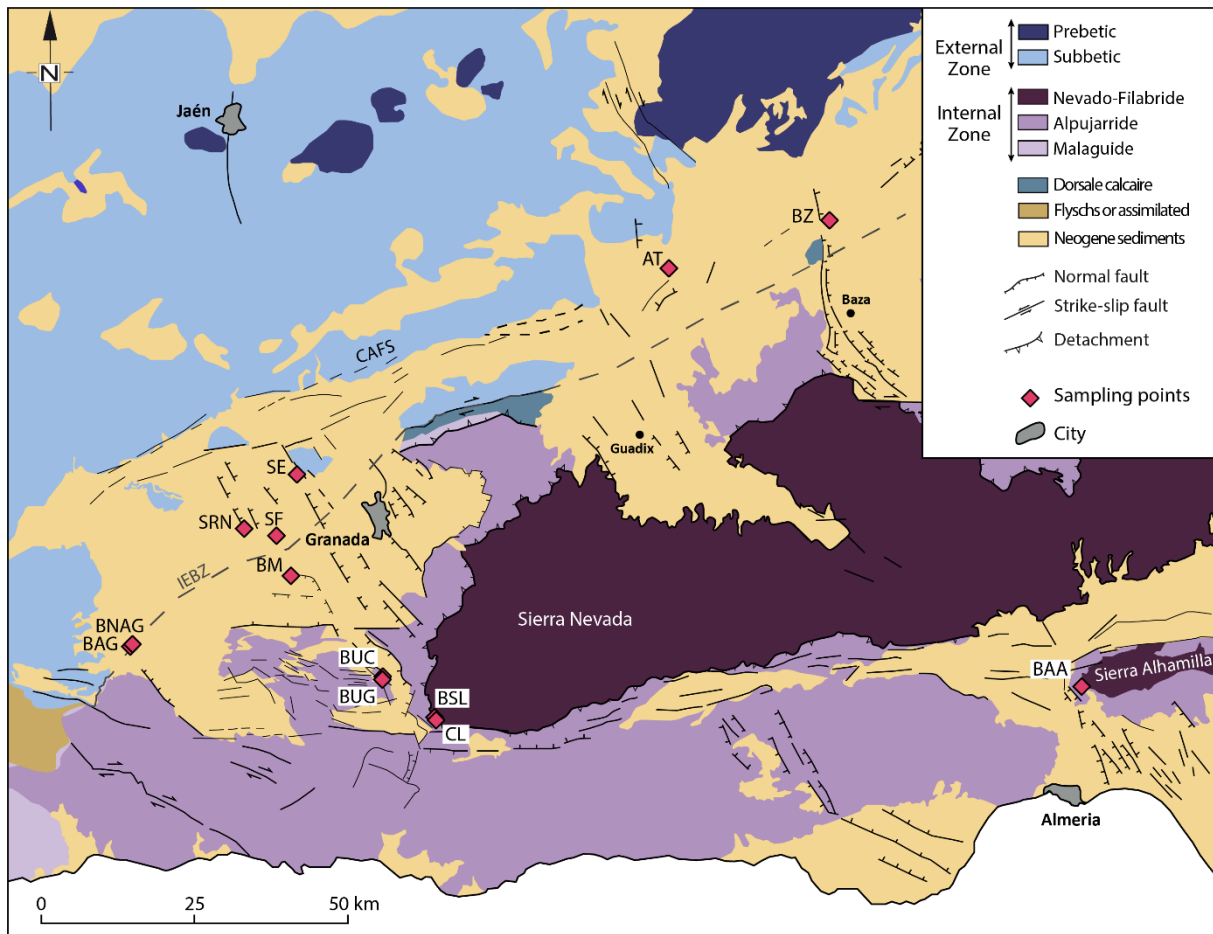
913 Figure 9: Evolution of the mineral saturation indices with temperature for the thermal waters
914 located in the Valle de Lecrin graben by geothermometrical modeling with theoretical CO_2
915 addition (0.5 mmol/L) to compensate possible CO_2 outgassing during the ascent of the waters

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917 located on the contacts of the metamorphic complexes. Geothermometrical modeling with
918 theoretical CO_2 addition to compensate possible CO_2 outgassing during the ascent of the
919 waters.

920 Figure 11: Comparison of CO_2 emissions from heating a 100 m^2 house using the investigated
921 thermal waters and a natural gas furnace.

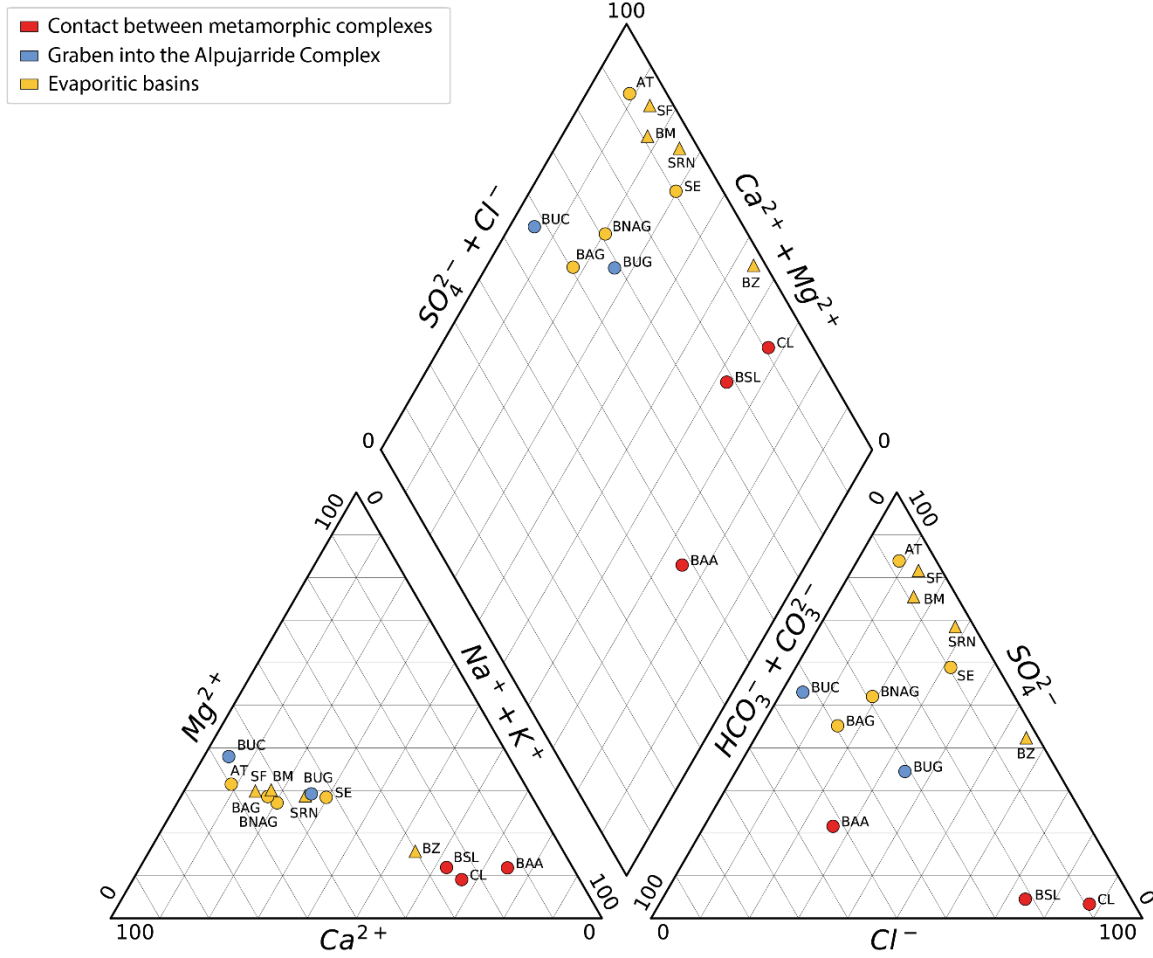
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923 Figure 1



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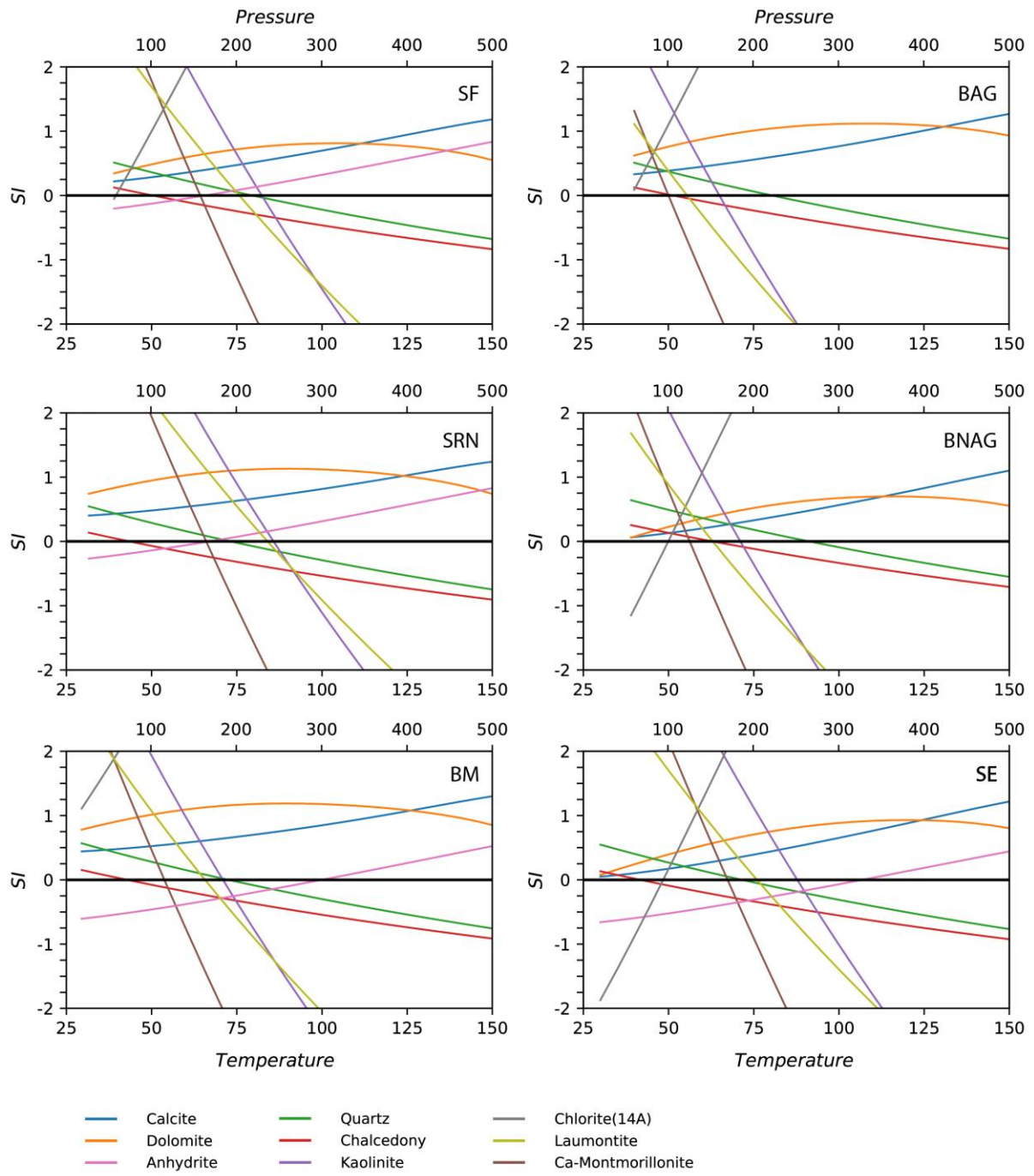
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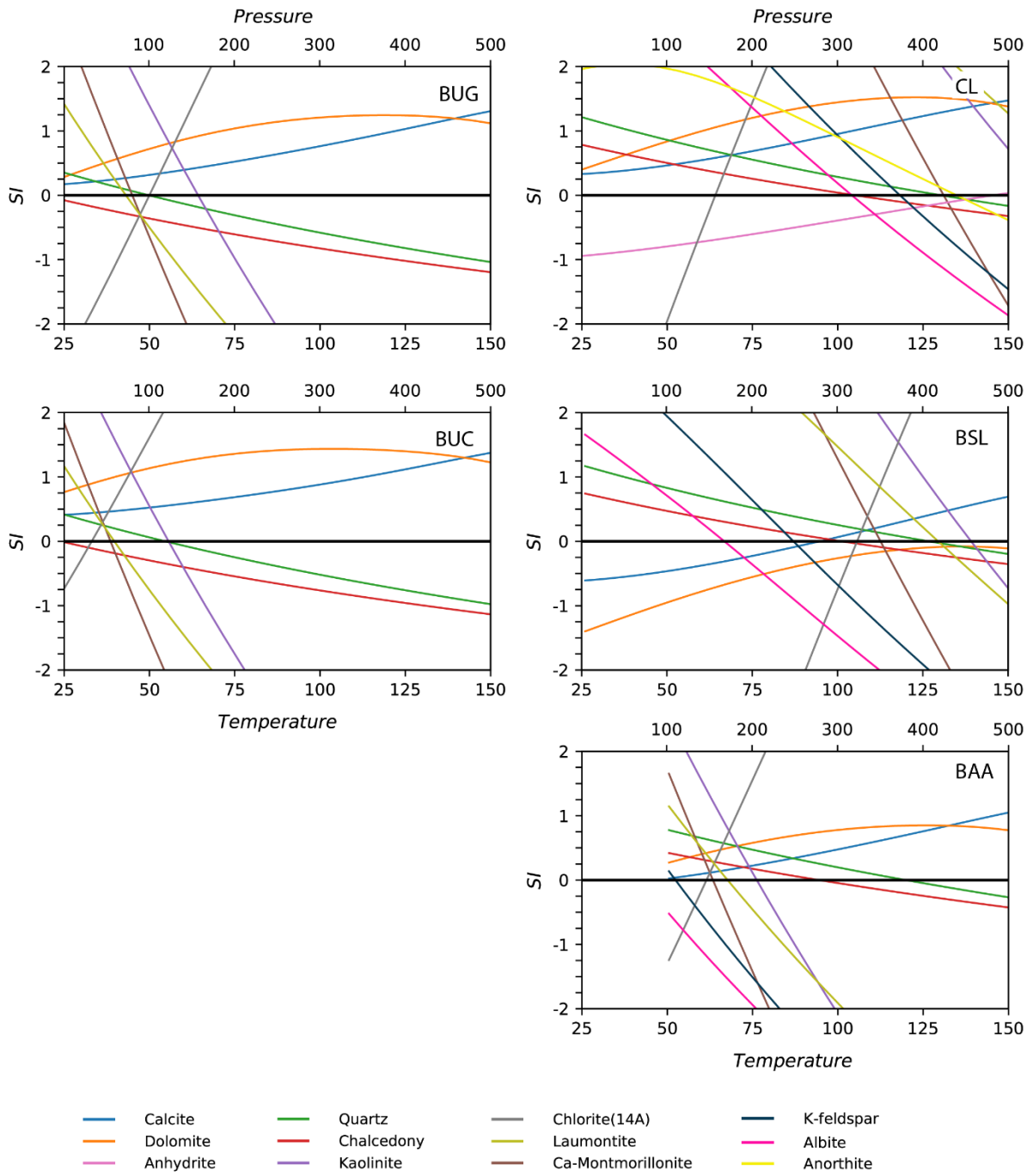
929 Figure 3



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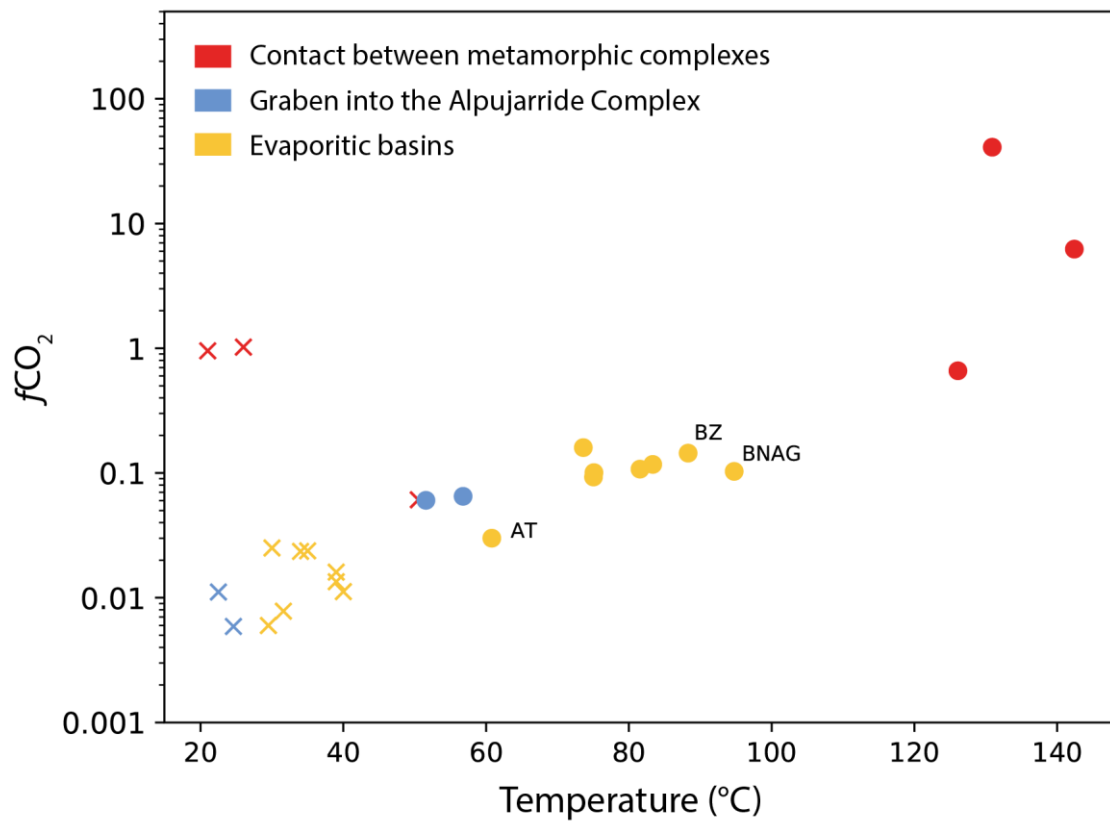
932 Figure 4



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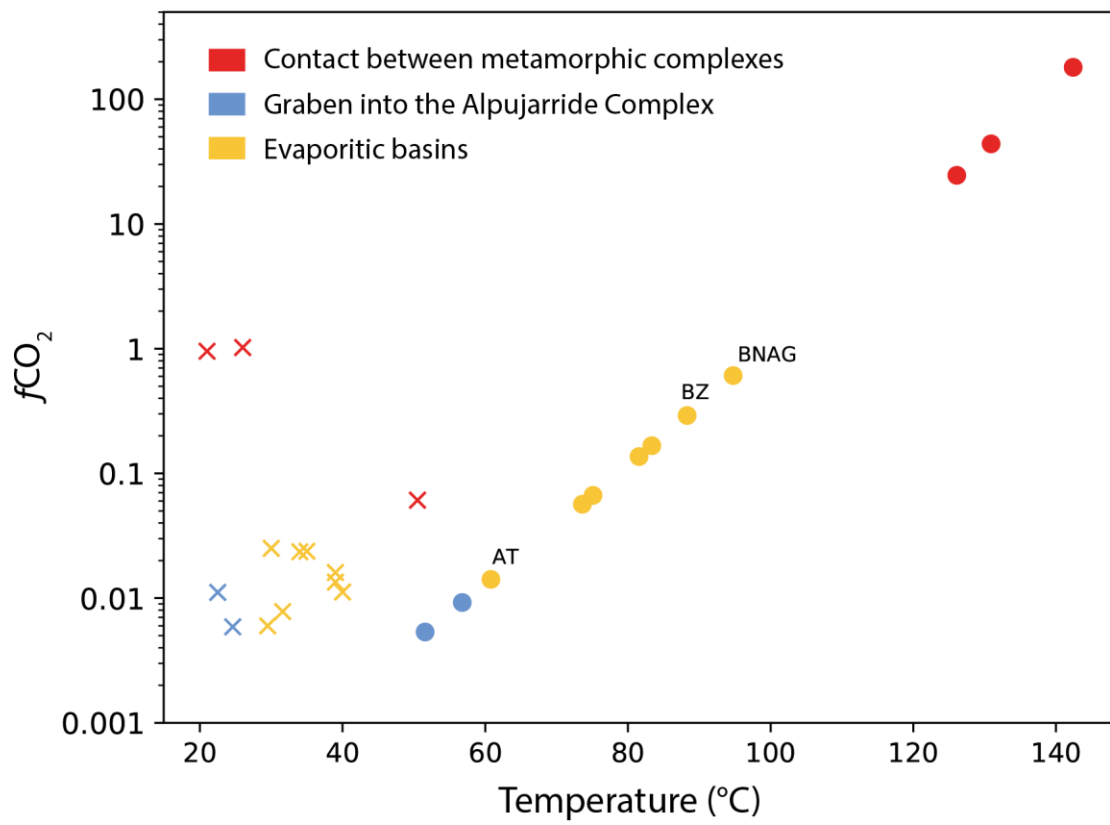
935 Figure 5



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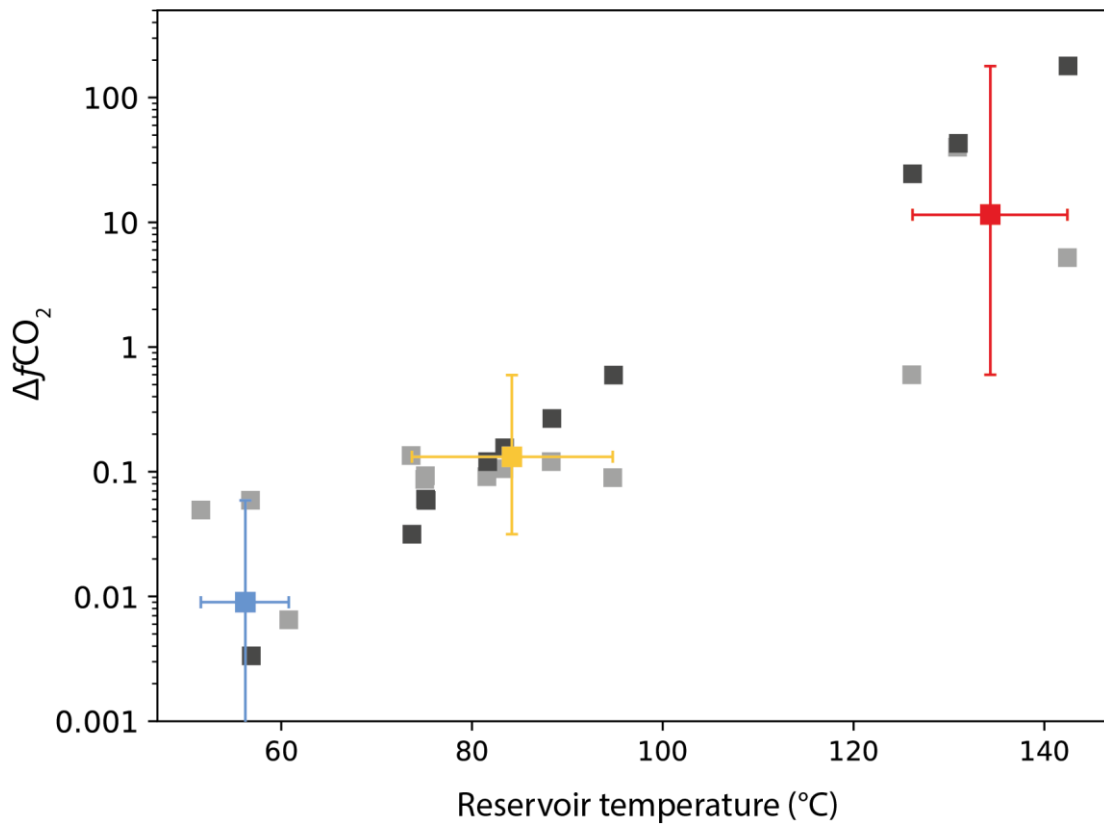
938 Figure 6



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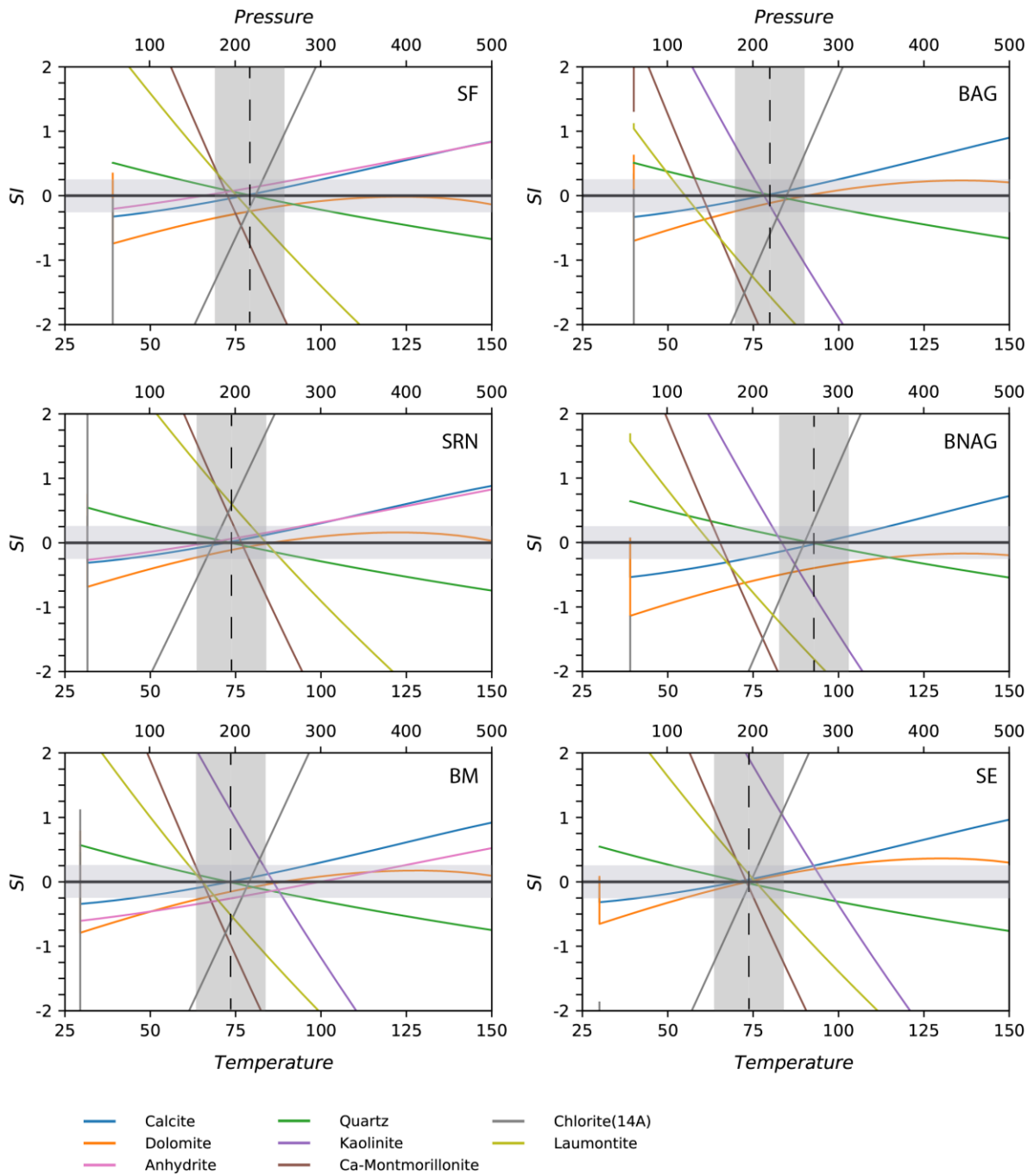
941 Figure 7



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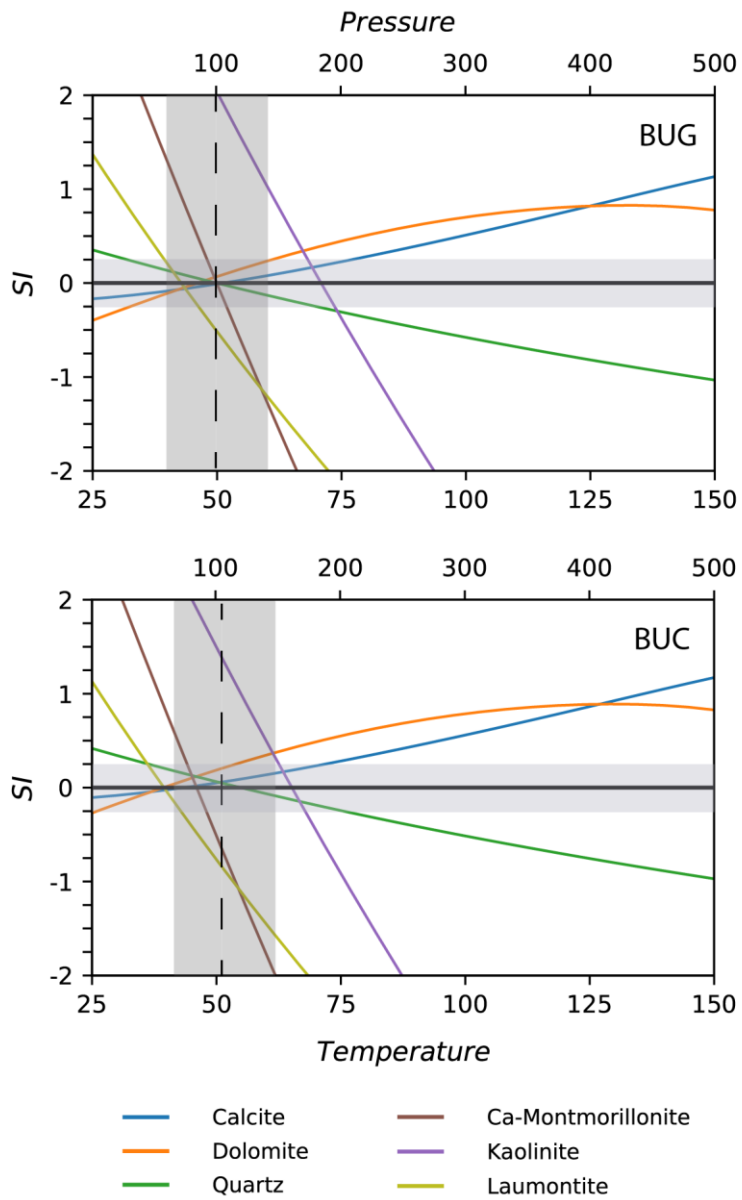
944 Figure 8



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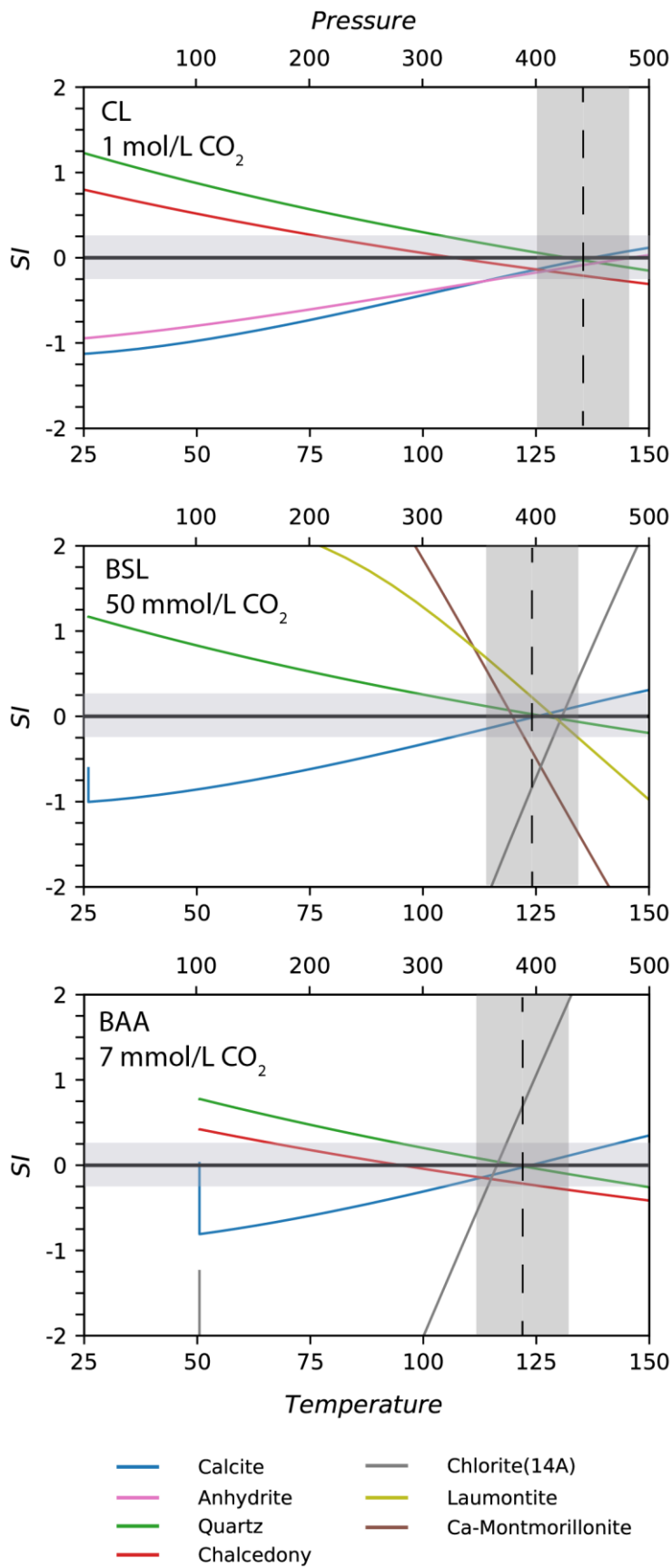
947 Figure 9



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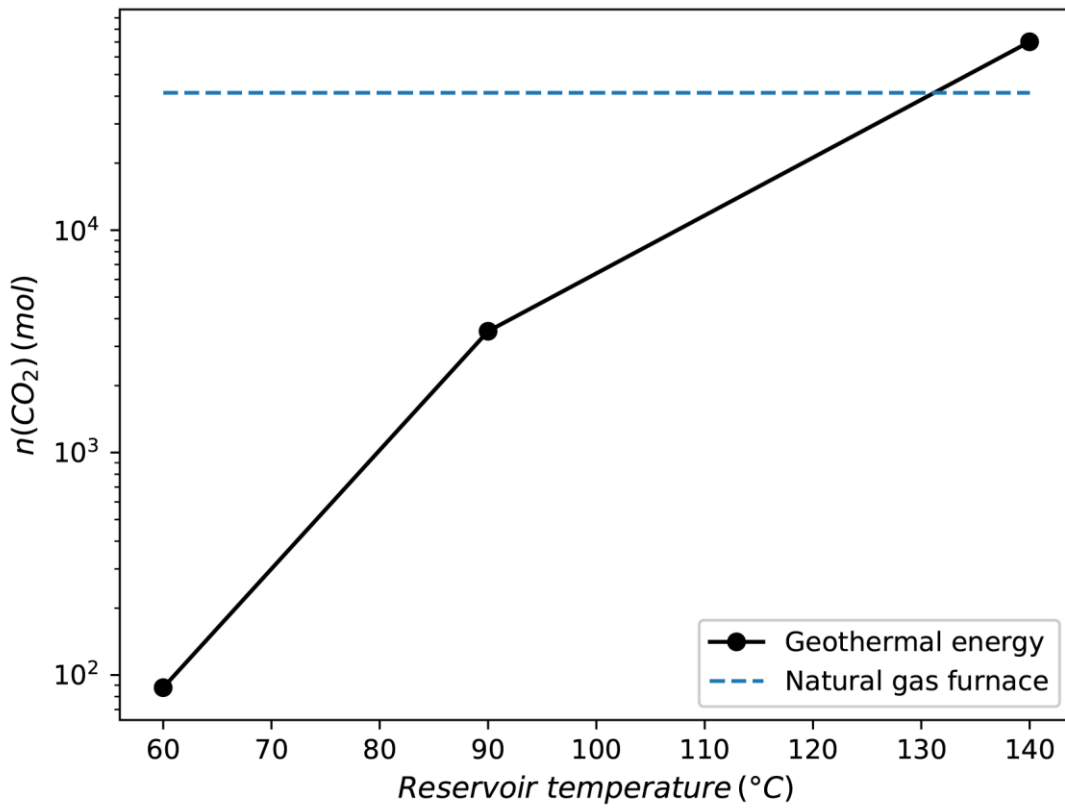
950 Figure 10



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953 Figure 11



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Sample and location	Code	Type	Depth	Temp.	pH	EC	Ca	Mg	Na	K	Alk.	Cl	SO ₄	Si	Al	Ba	Fe	Sr	TDS	CBE
			(m)	(°C)																
<i>Contacts metamorphic complexes</i>																				
Banos Salado de Lanjaron 36°55.4189'N; 3°29.5869'W	BSL	S		26	5.8	8.18	6.59	3.06	29.5	2.60	12.9	44.0	1.31	1.56	8.85E-03	1.04E-03	3.13E-01	0.19	3.72	7.29
Capuchina de Lanjaron 36°55.1523'N; 3°29.4182'W	CL	S		21	6.1	34.15	32.6	12.3	167	14.0	28.7	275	5.24	1.53	7.13E-02	7.34E-04	4.98E-01	0.62	18.17	7.40
Banos de Alhamilla 36°57.6531'N; 2°23.7875'W	BAA	S		51	7.1	1.92	0.88	0.78	9.65	0.23	7.93	3.99	1.64	1.38	4.92E-04	4.62E-04	9.66E-04	0.02	1.15	7.04
<i>Grabens into Alp. Complex</i>																				
Banos Urquizar Chico 36°58.3477'N; 3°34.5347'W	BUC	S		25	7.6	0.99	2.62	1.75	0.42	0.05	3.99	0.41	2.49	0.27	6.99E-04	2.28E-04	b.d.l	0.05	0.68	0.87
Banos Urquizar Grande 36°58.2261'N; 3°34.5854'W	BUG	S		23	7.3	1.50	2.92	1.92	3.22	0.22	4.21	4.66	2.33	0.24	1.23E-03	2.33E-04	b.d.l	0.04	0.91	1.49
<i>Evaporitic basin</i>																				
Banos de la Malaha 37°06.2946'N; 3°43.6034'W	BM	W	200	30	7.4	3.08	8.05	4.59	5.25	0.22	2.89	5.10	12.1	0.45	1.60E-03	1.18E-04	2.98E-02	0.16	2.13	2.35
Santa Fe 37°09.3813'N; 3°45.2023'W	SF	W	510	39	7.0	4.69	13.7	7.30	6.82	0.34	2.58	7.15	21.1	0.53	2.09E-03	5.10E-05	6.50E-03	0.16	3.38	2.73
Sondeo Romilla la Nueva 37°10.0216'N; 3°48.8567'W	SRN	W	740	32	7.3	6.13	14.3	8.80	15.5	0.41	2.72	18.9	23.2	0.45	5.13E-03	8.92E-05	4.25E-02	0.17	4.26	4.48
Sierra Elvira 37°13.7033'N; 3°43.3372'W	SE	S		30	6.9	3.82	7.80	5.28	10.8	0.27	3.77	12.4	11.6	0.43	3.74E-03	1.35E-04	b.d.l	0.11	2.52	2.93
Banos Alhama de Granada 37°01.1221'N; 3°58.9970'W	BAG	S		40	7.4	1.13	2.44	1.30	1.45	0.15	3.59	1.39	2.05	0.55	6.85E-04	3.49E-04	b.d.l	0.04	0.67	0.02
Banos Nuevo Alhama de Granada 37°01.3410'N; 3°58.7548'W	BNAG	S		39	7.2	1.24	2.63	1.36	1.87	0.17	2.89	1.89	2.60	0.72	6.95E-04	2.71E-04	4.42E-04	0.06	0.73	0.08
Alicun de las Torres 37°30.5418'N; 3°06.4172'W	AT	S		34	6.7	2.24	8.25	4.35	2.32	0.12	2.06	2.32	11.4	0.31	8.89E-04	1.38E-04	b.d.l	0.11	1.83	0.87
Banos de Zujar 37°34.556'N; 2°49.463'W	BZ	W	-	35	6.8	12.8	15.8	8.01	56.1	0.62	2.91	61.4	23.3	0.62	1.71E-02	1.98E-04	5.74E-03	0.23	6.80	3.03

Table 1: Sample details including sample location and water chemistry. Location of sampling points refer to WGS84 system. Type of water points: S = spring; W = well. EC is electrical conductivity in mS/cm. Concentrations of dissolved elements and TDS are expressed in mmol/kg of solution and in mg/L respectively. CBE (Charge Balance Error) is expressed in %. b.d.l = below detection limit.

Sample	Calcite	Dolomite	Gypsum	Anhydrite	Halite	Quartz	Chalcedony	K-feldspar	Kaolinite	Albite	Anorthite	Ca-Mont.	CO ₂ (g)	fCO ₂ (g)
<i>Contacts metam. complexes</i>														
BSL	-0.61	-1.39	-1.40	-1.61	-4.66	1.14	0.74	3.15	8.02	1.65	-1.03	7.96	0.01	1.03
CL	0.32	0.34	-0.63	-0.86	-3.21	1.25	0.83	5.42	10.44	3.90	1.93	11.01	-0.02	0.96
BAA	0.02	0.27	-1.83	-1.89	-6.17	0.74	0.42	0.14	2.52	-0.52	-2.79	1.65	-1.21	0.061
<i>Graben into Alp. Complex</i>														
BUC	0.41	0.75	-1.19	-1.42	-8.46	0.40	-0.01	-0.67	3.23	-2.31	-2.68	1.90	-2.23	0.006
BUG	0.16	0.23	-1.21	-1.44	-6.52	0.37	-0.05	0.18	4.36	-1.25	-2.25	3.05	-1.95	0.011
<i>Evaporitic basin</i>														
BM	0.43	0.78	-0.37	-0.57	-6.33	0.54	0.15	0.56	4.06	-0.57	-1.42	3.14	-2.22	0.006
SF	0.21	0.34	-0.07	-0.22	-6.13	0.48	0.12	0.37	4.18	-0.73	-1.20	3.23	-1.79	0.016
SRN	0.39	0.74	-0.06	-0.25	-5.35	0.52	0.14	1.15	5.12	0.25	-0.35	4.34	-2.10	0.008
SE	0.04	0.07	-0.43	-0.63	-5.65	0.52	0.13	0.91	5.65	0.00	-0.81	4.81	-1.60	0.025
BAG	0.32	0.62	-1.30	-1.44	-7.41	0.48	0.12	-0.39	2.49	-1.80	-2.54	1.31	-1.95	0.011
BNAG	0.06	0.06	-1.18	-1.33	-7.17	0.61	0.25	0.07	3.20	-1.29	-2.26	2.24	-1.87	0.013
AT	-0.32	-0.73	-0.37	-0.55	-7.03	0.31	-0.06	-0.83	4.02	-1.99	-2.45	2.63	-1.63	0.024
BZ	0.01	-0.07	-0.10	-0.27	-4.32	0.62	0.25	2.00	6.90	1.52	0.84	6.46	-1.62	0.024

Table 2: Saturation indices (SI) of the main mineral phases of interest in the investigated area. CO₂(g) corresponds to the log₁₀ of CO₂ fugacity (fCO₂). SI were calculated with the PHREEQC code at the outlet temperature (measured in the field).

Sample	O ₂ cc/L	N ₂ cc/L	CO ₂ cc/L	pCO ₂ atm	H ₂ ppm	CO ppm	CH ₄ ppm	TDIC mmol/L	δ ¹³ C _(TDIC) ‰	δ ¹³ C _(CO₂) ‰
<i>Contacts metam. complexes</i>										
BSL	0.07	1.74	576	0.78	6.82E-04	2.88E-04	5.29E-03	46.6	-5.2	-6.6
CL	0.08	1.94	597	0.71	b.d.l	1.41E-04	8.66E-05	63.0	-4.7	-7.5
BAA	1.49	12.1	39.4	0.088	9.72E-04	3.16E-04	1.53E-02	9.1	-9.0	-13.6
<i>Graben into Alp. Complex</i>										
BUG	1.57	18.6	16.2	0.020	b.d.l	2.69E-05	6.36E-04	4.6	-9.0	-16.2
<i>Evaporitic basin</i>										
SF	1.81	17.0	9.51	0.017	b.d.l	3.51E-05	1.38E-02	2.9	-1.5	-6.6
SE	0.13	18.3	22.2	0.033	b.d.l	b.d.l	2.39E-04	4.5	-8.8	-14.5
BAG	0.67	17.6	10.7	0.020	b.d.l	b.d.l	7.43E-04	3.8	-7.6	-13.3
AT	0.44	16.7	27.0	0.044	1.10E-03	7.03E-05	2.48E-05	2.7	-5.0	-9.8
BZ	0.62	13.8	16.3	0.027	1.51E-03	2.02E-04	3.37E-02	3.5	-3.4	-8.4

Table 3: Dissolved gases and carbon isotopic composition of the selected investigated thermal waters. TDIC was calculated using PHREEQC. b.d.l = below detection limit.

Sample	Outlet temp.	SiO ₂ -Quartz				SiO ₂ -chalcedony		Ca/Mg	<i>f</i> CO ₂
		Michard (1979)	Verma (2000b)	Fournier and Potter (1982)	Fournier (1977)	Arnorsson (1983)	Michard (1990)	Chiodini (1995a)	Chiodini (1995a)
<i>Contacts metam. complexes</i>									
BSL	26	145	143	146	139	115	102	86	16.34
CL	21	133	130	134	129	103	92	88	23.82
BAA	51	128	124	128	127	97	87	60	5.63
<i>Graben into Alp. Complex</i>									
BUC	25	57	47	57	62	26	24	75	0.54
BUG	23	52	42	51	58	21	20	74	0.66
<i>Evaporitic basin</i>									
BM	30	76	67	76	79	45	41	81	0.08
SF	39	83	74	83	85	52	47	87	0.05
SRN	32	76	67	76	79	45	41	75	0.04
SE	30	74	66	75	78	43	40	71	0.16
BAG	40	84	76	85	86	53	48	89	0.74
BNAG	39	96	89	97	97	65	59	91	0.38
AT	34	61	52	61	66	30	28	88	0.05
BZ	35	90	82	90	91	58	53	84	0.06

Table 4: Temperature (°C) obtained with selected geothermometers and fugacity of CO₂ (*f*CO₂) obtained with Chiodini et al. (1995a)'s geobarometer.

