

1 **Mineral equilibria and thermodynamic uncertainties in the geothermometrical**
2 **characterisation of carbonate geothermal systems of low temperature. The case of the**
3 **Alhama-Jaraba system (Spain)**

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17 **Abstract**

18 Geothermometrical characterisation of low-temperature, carbonate-evaporitic geothermal systems is
19 usually hampered by the lack of appropriate mineral equilibria to successfully use most of the classical
20 geothermometers and/or by the thermodynamic uncertainties affecting some of the most probable
21 mineral equilibria in low temperature conditions. This situation is further hindered if the thermal
22 waters are additionally affected by secondary processes (e.g., CO₂ loss) during their ascent to surface.

23 All these problems cluster together in the low-temperature Alhama-Jaraba thermal system, hosted in
24 carbonate rocks, with spring temperatures about 30 °C and waters of Ca-Mg-HCO₃/SO₄ type. This
25 system, one of the largest naturally flowing (600 L/s) low temperature thermal systems in Europe, is
26 used in this paper as a suitable frame to assess the problems in the application of chemical
27 geothermometrical techniques (classical geothermometers and geothermometrical modelling) and to
28 provide a methodology that could be used in this type of geothermal system or in potential CO₂
29 storage sites in similar aquifers.

30 The results obtained have shown that the effects of the secondary processes can be avoided by
31 selecting the samples unaffected by such processes and, therefore, representative of the conditions at
32 depth, or by applying existing methodologies to reconstruct the original composition, as is usually
33 done for medium to high temperature systems.

34 The effective mineral equilibria at depth depend on the temperature, the residence time and the
35 specific lithological/mineralogical characteristics of the system studied. In the present case, the
36 mineral equilibria on which classical cation geothermometers are based have not been attained. The
37 low proportion of evaporitic minerals in the hosting aquifer prevents the system from reaching
38 anhydrite equilibrium, otherwise common in carbonate-evaporitic systems and necessary for the
39 specific SO₄-F geothermometer or the specially reliable quartz (or chalcedony) – anhydrite
40 equilibrium in the geothermometrical modelling of these geothermal systems.

41 Under these circumstances, the temperature estimation must rely on quartz (or chalcedony), clay
42 minerals and, especially, calcite and dolomite phases. However, clay minerals and dolomite present
43 important thermodynamic uncertainties related to possible variations in composition or crystallinity
44 degree for clays and order/disorder degree for dolomite.. To deal with these problems, a sensitivity
45 analysis to the thermodynamic data for clay minerals has been carried out, comparing the results
46 obtained when considering different solubility data. The uncertainties associated with dolomite have
47 been addressed by reviewing the solubility data available for dolomites with different order degrees

48 and performing specific calculations for the order degree of the dolomite in the aquifer. This approach
49 can be used to find the most adequate dolomite thermodynamic data for the system under
50 consideration, including medium-high temperature geothermal systems.

51 Finally, the temperature estimation of the Alhama-Jaraba waters in the deep reservoir has been
52 obtained from simultaneous equilibria of quartz, calcite, partially disordered dolomite and some
53 aluminosilicate phases. The obtained value of 51 ± 14 °C is within the uncertainty range normally
54 affecting this type of estimations and is coherent with independent estimations from geophysical data.

55 **Keywords:** Low temperature geothermal system; Geothermometry; Geothermometrical modelling;
56 Calcite-dolomite equilibrium; Carbonate aquifer

57

58 1. INTRODUCTION

59 A wide variety of geothermometrical techniques are available to evaluate the reservoir temperature of
60 thermal waters: various chemical and isotopic solute geothermometers and the geothermometrical
61 modelling (or multicomponent solute geothermometry; e.g. Spycher et al., 2014). However, not all of
62 them are always applicable to all thermal systems and they should be carefully selected according to
63 the different equilibria expected at depth.

64 In the case of low temperature thermal systems hosted in carbonate rocks, a series of problems arise
65 when applying the geothermometrical techniques due to three main reasons: 1) the low temperatures
66 usually make difficult the attainment of the mineral and/or isotopic equilibria; 2) the mineral set
67 present in the reservoir is usually more limited (mainly calcite and dolomite) than in other type of
68 geothermal systems; and 3) the thermodynamic properties of dolomite and clays are uncertain.

69 An additional complication in the evaluation of the reservoir temperature in any thermal system is the
70 presence of secondary processes during the rising of the thermal waters to the surface (e.g. mixing

71 with colder and shallower waters, re-equilibrium processes through mineral-water reactions and/or
72 CO₂ outgassing).

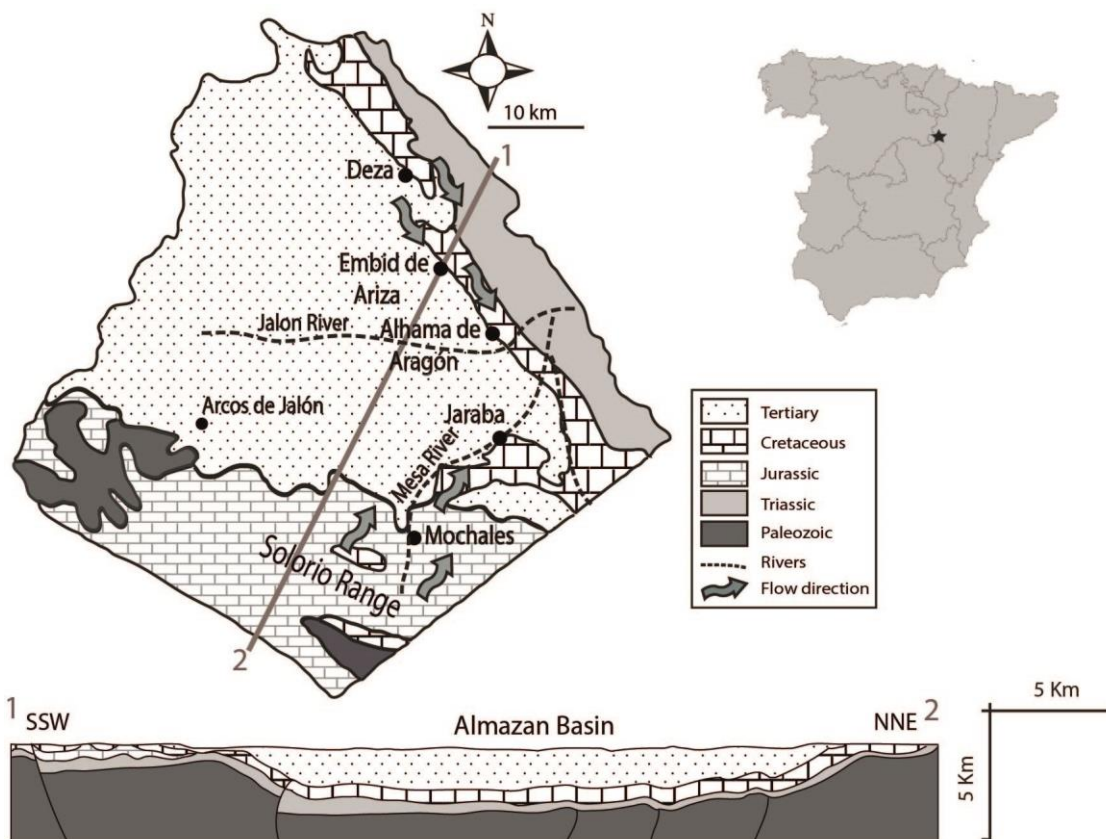
73 The work presented in this paper is focused on the use and evaluation of several geothermometrical
74 tools in order to calculate the reservoir temperature of the geothermal system of Alhama de Aragón –
75 Jaraba (from now on, Alhama–Jaraba). The characteristics of this thermal system provide the
76 opportunity to deal with almost all the aforementioned complexities (Tena et al., 1995; Auqué et al.,
77 2009; Blasco et al. 2016): 1) the reservoir is hosted mainly in carbonate rocks (limestones and
78 dolostones), 2) the temperature is, a priori, low and 3) there are different secondary processes (mixing,
79 CO₂ outgassing) affecting the chemistry of some of the waters. There are other reasons why the study
80 of this system presents a special interest. One is the importance of the system as a natural resource
81 with very high flow rates (550 L/s in Alhama and 600 L/s in Jaraba; IGME, 1980; De Toledo and
82 Arqued, 1990; Sánchez et al., 2004) comparable to those found in the area considered the Europe's
83 largest naturally flowing thermal system in Budapest (discharge of ca. 580 L/s; Goldscheider et al.,
84 2010 and references therein). The other reason is related to its special geological and
85 hydrogeochemical features which have given it the consideration of a natural analogue for the CO₂
86 geological storage (Auqué et al. 2009).

87 In summary, this study gives a suitable natural frame to test different geothermometrical techniques
88 and the associated uncertainties in low temperature systems hosted in carbonate rocks. From this, a
89 general methodology can be established to be applied in this type of geothermal systems and even in
90 the characterisation of some potential CO₂ storage sites in similar aquifers.

91 **2. GEOLOGICAL, HYDROGEOLOGICAL AND HYDROGEOCHEMICAL** 92 **SETTING**

93 The Alhama de Aragón and Jaraba springs (NE Spain, Figure 1) belong to one of the main thermal
94 systems in Spain. There are several thermal resorts and water bottling plants in the area at present. The

95 Jaraba thermal complex, close to the Mesa River, consists of 14 catalogued springs flowing at an
 96 elevation of 737 m.a.s.l. and the Alhama thermal complex, located close to the Jalón River bank, is
 97 formed by a dozen of catalogued springs flowing at an elevation of 660 m. Apart from these well-
 98 known spring complexes, there are another two minor hot springs in the nearby area, Embid and Deza
 99 springs (Tena et al., 1995; Sanz and Yélamos, 1998; Sánchez et al., 2004; Auqué et al., 2009; Figure
 100 1), which have not been included in this study.



101
 102 **Figure 1.** Location of the Alhama de Aragón and Jaraba geothermal systems in the geological map
 103 (modified from Sánchez et al., 2004) and a cross section showing the main structural and lithological
 104 characteristics of the area studied (modified from the ALGECO2 project; IGME, 2010).

105 Geologically, the Alhama-Jaraba thermal system is located on the border of the Western Iberian Range
 106 and the tertiary Almazán Basin (Figure 1). There are two main aquifers in this area: 1) the Solorio
 107 aquifer, hosted in the Jurassic carbonate formations; and 2) the Alhama aquifer, hosted in the Upper

108 Cretaceous carbonate rocks. The hydrological model of the region is not completely clear, but the
109 most accepted hypothesis states that there are two possible recharge areas located 1) in the Solorio
110 Range with a flow direction SW-NE towards Jaraba and Alhama (Figure 1) and 2) in the vicinity of
111 Deza, with a NW-SE flow direction towards Embid and Alhama (Figure 1; IGME, 1980; 1987; De
112 Toledo and Arqued, 1990; Sanz and Yelamos, 1998; Sánchez et al., 2000; Sanchez et al., 2004). The
113 fact that the rocks in the Solorio recharge area are mainly Jurassic and that all the thermal springs are
114 associated with the Upper Cretaceous formations (Sánchez et al., 2000) suggests that both aquifers
115 could be connected and that their emergence would be related to the presence of vertical or near
116 vertical layers that allow a rapid ascent of the water from depth (Sánchez et al., 2004).

117 The mineralogy of the Jurassic and Cretaceous carbonate rocks is quite similar. The rocks are mainly
118 dolostones and limestones with dispersed anhydrite/gypsum intercalations (Meléndez et al., 1985;
119 Alonso et al., 1993; Aurell, et al., 2002). The Cretaceous formations are locally affected by a
120 silicification processes with development of authigenic quartz crystals (Meléndez et al., 1985) and
121 there are also intercalations of terrigenous rocks, mainly at the base of the Utrillas Formation,
122 consisting of sandstones, claystones, siltstones, dolomitic siltstones, dolomitic marls, limestones and
123 dolomitic limestones, with a mineralogy comprising calcite, dolomite, quartz, K-feldspar, lithic
124 fragments and clay minerals (IGME, 1991).

125 The isotope $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data available (IGME, 1982; 1994; Sanz and Yélamos, 1998; Pinuaga et al.,
126 2004) indicate a clear meteoric origin. The tritium data available are also from the aforementioned
127 works and they show the absence of tritium or levels close to the detection limit (≈ 1 TU) in the hottest
128 springs. The most common interpretation for these results is that the thermal groundwaters have
129 residence times longer than 50 years and that some of them are affected by minor mixing with shallow
130 modern waters (Clark and Fritz, 1997).

131

132 **3. METHODOLOGY**

133 **3.1. *Field sampling and analysis***

134 Six and nine springs were sampled in the Alhama and Jaraba thermal sites, respectively. Field
135 sampling procedures and analytical methodology were mostly as described by Auqué et al. (2009).
136 Briefly, at each sampling point, temperature, pH and conductivity were determined *in situ* and
137 separated samples for anion and cation analysis were taken in 1N HCl pre-washed polyethylene
138 bottles. Samples for cation analysis were filtered through 0.1 µm and acidified to pH less than 1 with
139 ultrapure HNO₃. Anions were determined within 24 hours after collection. Total alkalinity was
140 determined by titration with a Mettler titrator with an end-point electrode. Chloride and fluoride
141 concentrations were determined by a selective ion analyser equipment, using the selective electrodes
142 for chloride ORION 94-17B and fluoride ORION 94-09. Sulphate was determined by colorimetry
143 using a modification of the Nemeth method (Nemeth, 1963). Potassium concentrations were analysed
144 by Flame Photometry and aluminium concentrations were determined by Electrothermal Atomisation
145 Atomic Absorption Spectrometry with Zeeman-effect background correction. Inductively Coupled
146 Plasma-Atomic Emission Spectrometry was used for the analysis of the rest of the elements (Ca, Mg,
147 Na, Li, and Si). The average analytical error was estimated <5% for alkalinity, chloride, fluoride,
148 sulphate, potassium and aluminium, < 4% for Ca, Mg, Na and Si, and < 9% for Li.
149 The calculated charge balance error for the analyses reported, as calculated with the PHREEQC code
150 (Parkhurst and Appelo, 2013), is below 5%.

151 **3.2. *Methodology for geothermometrical calculations***

152 Various geothermometrical techniques are used in this work to ascertain the reservoir temperature in
153 the Alhama-Jaraba system: classical and specific chemical geothermometers and geothermometrical
154 modelling calculations. The integration of the results has helped to propose a temperature range in the

155 reservoir. The general features of these methodologies in their application to the system studied are
156 detailed below.

157 3.2.1. Chemical geothermometers

158 Two main types of chemical geothermometers have been used (Table 1):

159 - Classical geothermometers, which include the dissolved silica geothermometer and several
160 cationic geothermometers (Na-K, Na-K-Ca, Ca-K, K-Mg, Na-Li, Li and Mg-Li, some of them
161 with several calibrations; Table 1). Most of these geothermometers have been proved to be
162 very useful for estimating subsurface temperature in high temperature systems (>180 °C)
163 where equilibria between aqueous solutions and minerals in the geothermal reservoirs are
164 easily attained (e.g. Fournier, 1977, 1981; Fouillac and Michard, 1981; Arnórsson et al., 1983;
165 Giggenbach et al., 1983; D'Amore et al., 1987; Nieva and Nieva, 1987; Giggenbach, 1988;
166 Kharaka and Mariner, 1988; Chiodini et al., 1995; Mutlu and Gülec, 1998; Stefánsson and
167 Arnórsson, 2000; Mariner et al., 2006; Sonney and Vuataz, 2010; Nicholson, 2012). However,
168 in low to medium temperature hydrothermal systems (40-180 °C) hosted in carbonate-
169 evaporitic rocks, these geothermometrical techniques encounter problems frequently related to
170 the mineral assemblage expected to govern the water chemistry and to the attainment of
171 equilibrium in the reservoir (Chiodini et al., 1995; Levet et al, 2002; Sonney and Vuataz,
172 2010). Nevertheless, some of these geothermometers have occasionally given good results in
173 this type of system (e.g. Michard and Bastide, 1988; Minissale and Duchi, 1988; Pastorelli et
174 al., 1999; Gökgöz and Tarcan, 2006; Mohammadi et al., 2010; Apollaro et al., 2012; Wang et
175 al., 2015; Blasco et al., 2017; 2018) and, therefore, their performance will be assessed at the
176 studied sites.

177 - Specific geothermometers, which were developed to be used in low-temperature carbonate-
178 evaporitic systems, like the SO₄-F and the Ca-Mg geothermometers (Marini et al., 1986;
179 Chiodini et al., 1995). The application of these geothermometers requires the existence of

180 anhydrite/gypsum – fluorite equilibrium, and calcite – dolomite equilibrium, respectively.
181 Equilibrium with anhydrite or gypsum is easily attained in systems with evaporitic rocks in the
182 host formations since these are the most common phases; however, the presence of fluorite is
183 not so common in these environments (Chiodini et al., 1995).

184 The calcite–dolomite equilibrium can be represented by the following overall reaction and equilibrium
185 equation (e.g. Appelo and Postma, 2005):



$$187 \quad K = \frac{aCa^{2+}}{aMg^{2+}} = \frac{(K_{calcite})^2}{K_{dolomite}} \quad (2)$$

188 where aCa^{2+}/aMg^{2+} represents the activity ratio of dissolved calcium and magnesium in the target
189 solution and $K_{calcite}$ and $K_{dolomite}$ represent the equilibrium constants for calcite and dolomite,
190 respectively. As can be deduced from equation (2), one of its advantages is that the aCa^{2+}/aMg^{2+} ratio
191 mainly depends on temperature and it is not significantly influenced by variations in the CO_2 partial
192 pressure or pH during the ascent of thermal waters towards spring conditions (Hyeong and Capuano,
193 2001). However, this geothermometer can also be problematic due to the uncertainties in the solubility
194 of dolomite which make its use in geothermometry very difficult (e.g. Hyeong and Capuano, 2001;
195 Palandri and Reed, 2001; Blasco et al., 2018). These uncertainties will be further evaluated.

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202 **Table 1.** Calibrations used in this work for the different classical geothermometers.
 203 Geothermometrical functions provide the temperature values in degrees Celsius. The concentration
 204 units corresponding to the different expressions are also indicated (usually mg/L or mol/L).

Geothermometer	Authors of calibration	Expression	Units
SiO ₂ -quartz	Michard (1979)	$T = \frac{1322}{0.435 - \log(SiO_2)} - 273.15$	mol/L
	Fournier and Potter (1982)	$T = \frac{1309}{5.19 - \log(SiO_2)} - 273.15$	mg/L
Na-K	Giggenbach (1988)	$T = \frac{1390}{1.75 + \log(Na/K)} - 273.15$	mg/L
	Fournier (1979)	$T = \frac{1217}{1.483 + \log(Na/K)} - 273.15$	mg/L
Na-K-Ca ¹	Fournier and Truesdell (1973)	$T = \frac{1647}{\log(Na/K) + \beta \left[\log\left(\frac{\sqrt{Ca}}{Na}\right) + 2.06 \right] + 2.47} - 273.15$	mg/L
Ca-K	Fournier and Truesdell (1973) ²	$T = \frac{2920}{3.02 + \log(Ca/K^2)} - 273.15$	mol/L
	Michard (1990)	$T = \frac{3030}{3.94 + \log(Ca/K^2)} - 273.15$	mol/L
K-Mg	Giggenbach et al. (1983)	$T = \frac{4410}{13.95 - \log(K^2/Mg)} - 273.15$	mg/L
Na-Li	Fouillac and Michard, 1981	$T = \frac{1000}{0.33 + \log(Na/Li)} - 273.15$	mol/L
Li	Fouillac and Michard, 1981	$T = \frac{2258}{1.44 + \log(Li)} - 273.15$	mol/L
Mg-Li	Kharaka and Mariner, 1988	$T = \frac{2200}{5.47 + \log(\sqrt{Mg}/Li)} - 273.15$	mg/L
Ca-Mg ³	Chiodini et al. (1995)	$T = \frac{979.8}{3.1170 - \log(Ca/Mg) + 0.07003 \log \Sigma eq} - 273.15$	mol/L

205 ¹ $\beta=4/3$ should be used if the temperature obtained is lower than 100 °C; if the temperature
 206 obtained, using that value of β , is higher than 100 °C, it should be recalculated considering $\beta = 1/3$.
 207 Mg-correction proposed by Fournier and Potter (1979) for the Na-K-Ca geothermometer cannot
 208 be applied to the studied springs, according to the criteria indicated by those authors.

209 ²Derived from Fournier and Truesdell (1973) in Michard (1990).

210 ³ Σeq is the summation (in eq/L) of the major dissolved species.

211 3.2.2. Geothermometrical modelling

212 Geochemical modelling calculations provide a more generalised approach than the classical chemical
 213 geothermometry. This technique consists of simulating a process of a progressive water temperature
 214 increase to obtain a temperature range in which the saturation state of the waters with respect to a

215 selected mineral set (assumed to be present in the reservoir) simultaneously reaches equilibrium.

216 When most of the minerals selected indicate about the same equilibrium temperature, the average
217 temperature can be considered as the best estimate (e.g. Michard and Roekens, 1983; Reed and
218 Spycher, 1984; D'Amore et al., 1987; Pang and Reed, 1998).

219 The geochemical modelling approach shows different advantages over the classical geothermometers.

220 It helps to evaluate the secondary processes during the ascent of the thermal waters, such as 1) the
221 extension of mineral reequilibrium reactions (Michard and Fouillac, 1980; Michard and Roekens,
222 1983; Michard et al., 1986), 2) the amount of lost gas and/or 3) the proportion of cold waters in
223 mixtures (Pang and Reed, 1998; Palandri and Reed, 2001). It can also be advantageous to distinguish
224 between equilibrated and non-equilibrated waters, as non-equilibrated waters result in a large range of
225 calculated mineral equilibrium temperatures (e.g. Tole et al., 1993). However, this approach also has
226 some uncertainties with respect to 1) the attainment of water-mineral equilibrium, 2) the mineral
227 solubility data input in calculations, and 3) the aluminium concentrations, which are low and can be
228 easily affected by cooling during the ascent of thermal waters (Pang and Reed, 1998; Peiffer et al.,
229 2014).

230 For the Alhama-Jaraba system, these geothermometrical modelling calculations have been carried out
231 with the assistance of the PHREEQC geochemical code (version 3.4.0; Parkhurst and Appelo, 2013)
232 and using two of the thermodynamic databases distributed with this version, WATEQ4F and LLNL, in
233 order to perform a sensitivity analysis to the thermodynamic data.

234 Based on the mineralogy identified in the aquifer, the mineral phases selected for these calculations
235 include: calcite, dolomite, quartz, gypsum/anhydrite and some aluminosilicates. Whereas the solubility
236 constants for calcite, quartz, gypsum and anhydrite are fairly well known, there are some uncertainties
237 related to the solubility dependence on temperature ($K(T)$) for the rest of the mineral phases. To
238 evaluate their effects on the results obtained, the following procedures have been adopted:

- 239
- The solubility data for illite and smectites (beidellite, montmorillonite) are affected by
240 potential problems such as their wide compositional variability, the variable degree of
241 crystallinity, particle size effect, and some order/disorder phenomena (e.g. Merino and
242 Ransom, 1982; Nordstrom et al., 1990; Palandri and Reed, 2001). However, illite has
243 been used in geothermometrical calculations with some success (e.g. Pang and Reed,
244 1998 and Palandri and Reed, 2001), and, therefore, it is also used in this study to verify its
245 performance and uncertainties. Also, the approach recommended by Helgeson et al.
246 (1978) and Palandri and Reed (2001) has been followed and pyrophyllite and paragonite
247 have been used as proxies for the whole set of clay minerals.
 - The thermodynamic data for K-feldspar, kaolinite (two types with different crystallinity
248 degrees: poorly crystalline and crystalline) and pyrophyllite from Michard et al. (1979)
249 and Michard (1983) have been added to the WATEQ4F database for comparison with the
250 data included in the LLNL.
251
 - The solubility of dolomite is strongly affected by non-stoichiometry and order/disorder in
252 Ca and Mg site occupancies (Helgeson et al., 1978; Carpenter, 1980; Reeder, 1990, 2000;
253 Hyeong and Capuano, 2001) but experimental data on these effects do not exist.
254 Therefore, in order to consider this uncertainty, we have tested the influence of several
255 solubility values on the geothermometrical calculation results. For this purpose, the values
256 included in the LLNL database, corresponding to fully-disordered and to fully-ordered
257 dolomite were considered in the calculations together with the solubility value proposed
258 for “dolomite” in the WATEQ4F database (Nordstrom et al., 1990; Dolomite_ W from
259 now on), which represents a partially-ordered dolomite (Helgeson et al., 1978; Carpenter,
260 1980). Additionally, some natural dolomites with different degree of order/disorder have
261 been included in the comparison: 1) the dolomite reported by Hyeong and Capuano
262 (2001), from the Oligocene Frio Formation (Texas Gulf Coast) with an order of 11%
263

264 (Dolomite_H&C); 2) the dolomite considered by Busby et al. (1991) from the
265 Carboniferous Madison Aquifer and an order of 23.5 % (Dolomite_B); 3) the dolomite
266 used by Vespasiano et al. (2014) from the Triassic of Calabria (Italy) and an order of 22%
267 (Dolomite_V); and 4) the dolomite reported by Blasco et al. (2018) from the Jurassic of
268 the Cameros Basin (Spain) with an order of 18.4% (Dolomite_BL).

269 For comparative purposes, the solubility values at 25 °C and the K(T) function for the different
270 mineral phases considered in the geothermometrical simulations are summarised in Table S1
271 (Supplementary Material).

272 **4. RESULTS**

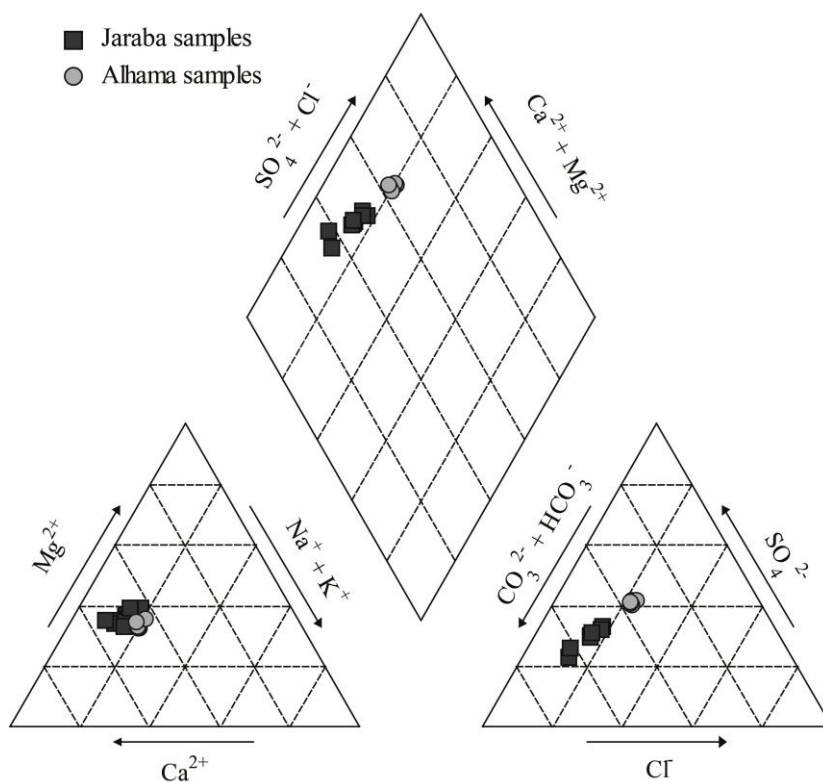
273 **4.1. *Hydrochemical characteristics of the thermal waters***

274 There are remarkable compositional differences among the springs studied. The thermal waters from
275 Jaraba are mainly of Ca-Mg-HCO₃-type whilst in Alhama, the waters show a more distinct SO₄-Cl
276 character with higher conductivity values and higher concentrations of Ca, Mg, Na, SO₄ and Cl (Table
277 2 and Figure 2). The alkalinity values are lower in Alhama than those determined in the Jaraba waters
278 and the dissolved silica concentrations are similar in all waters although slightly lower in Jaraba
279 waters.

280 The measured temperatures in the Alhama springs are always higher than 30 °C and their values are
281 rather homogeneous (temperature variability smaller than 2.3 °C; Table 2) as it is also the case with
282 the hydrochemical variability which is generally within the analytical error. The Jaraba springs,
283 however, exhibit a larger compositional variability and temperature range (between 21 and 32 °C;
284 Table 2) although the highest temperature is similar to those in Alhama. The combined variability of
285 temperature and compositional characteristics in the Jaraba thermal waters has been attributed to
286 mixing between deep thermal groundwaters and superficial and colder waters along the shallower

287 parts of the upflow towards the Jaraba springs (Tena et al., 1995; Auqué et al., 2009; Blasco et al.,
288 2016).

289 Results of speciation-solubility calculations (Table 3) indicate that most of the springs studied in the
290 Alhama and Jaraba sites are close to equilibrium or slightly oversaturated with respect to calcite and
291 partially disordered dolomite (Dolomite_W or Dolomite_H&C; see above). The differences obtained
292 in the saturation state of the waters with respect to calcite and dolomite are mainly related to the
293 different extent of CO₂ outgassing along the shallowest parts of the flow paths (see Auqué et al., 2009
294 for further explanation and calculations on this issue). The highest values are found in sample ZA-45,
295 from Alhama, which is the sample with the highest pH and a relative low log pCO₂ and, therefore, the
296 one with the most intense outgassing.



297

298 **Figure 2.** Representation of the composition of the water samples included in this study in a Piper–
299 Hill diagram.

300 **Table 2.** General hydrochemistry of the Alhama-Jaraba thermal waters included in this study.

Sample Number	Jaraba									Alhama de Aragón						
	ZA-22	ZA-23	ZA-24	ZA-25	ZA-26	ZA-27	ZA-28	ZA-29	ZA-30	ZA-39	ZA-40	ZA-41	ZA-43	ZA-44	ZA-45	
T (°C)	26.6	27.3	27.2	21.0	29.4	32.0	31.8	26.1	21.8	30.1	31.9	32.4	30.2	31.6	30.7	
pH (field)	7.40	7.40	7.30	7.40	6.80	7.05	7.25	7.30	7.30	7.15	6.90	7.05	7.15	7.45	7.85	
Cond. (μS/cm)	865	864	850	755	890	910	905	859	745	1181	1154	1161	1152	1122	1122	
mmol/L	HCO ₃ ⁻	4.73	4.72	4.72	4.92	4.65	4.62	4.68	4.68	4.81	4.38	4.47	4.39	4.49	4.47	4.58
	Cl ⁻	1.41	1.41	1.37	1.05	1.72	1.67	1.69	1.37	0.94	2.85	2.75	2.88	2.74	2.69	2.69
	SO ₄ ²⁻	1.32	1.37	1.28	0.88	1.58	1.54	1.5	1.36	1	2.6	2.56	2.6	2.44	2.44	2.52
	Ca ²⁺	2.31	2.31	2.30	2.09	2.10	2.41	2.39	2.10	2.27	3.05	2.97	3.08	3.06	2.73	2.98
	Mg ²⁺	1.74	1.67	1.61	1.35	1.92	1.68	1.55	1.76	1.44	2.08	2.07	2.13	2.17	2.21	2.22
	Na ⁺	1.4	1.4	1.3	1	1.7	1.5	1.5	1.3	0.8	2.6	2.6	2.6	2.6	2.6	2.3
	SiO ₂	0.1512	0.1509	0.1492	0.1052	0.1501	0.1511	0.1389	0.1407	0.1257	0.1709	0.1674	0.1693	0.1286	0.1636	0.1663
	K ⁺	30	30	25	25	30	30	30	30	15	40	40	40	40	40	70
μmol/L	Li ⁺	5.0	5.0	5.0	5.0	5.0	6.1	6.1	6.1	1.0	12.0	9.9	9.9	9.9	6.1	7.9
	Sr ²⁺	1.5	3.0	1.9		4.0	4.5	4.5	1.9		10	9.5	10	9.5	9.5	9.5
	B	0.19						0.28			1.00	0.83	0.74	0.74	0.56	0.46
	Al						0.64		0.36		0.41	0.74	0.82			
	F ⁻	9.2	9.5	8.5	4.8	9.7	12.0	12.0	8.7	7.7	17.0	16.0	17.0	15.0	16.0	16.0

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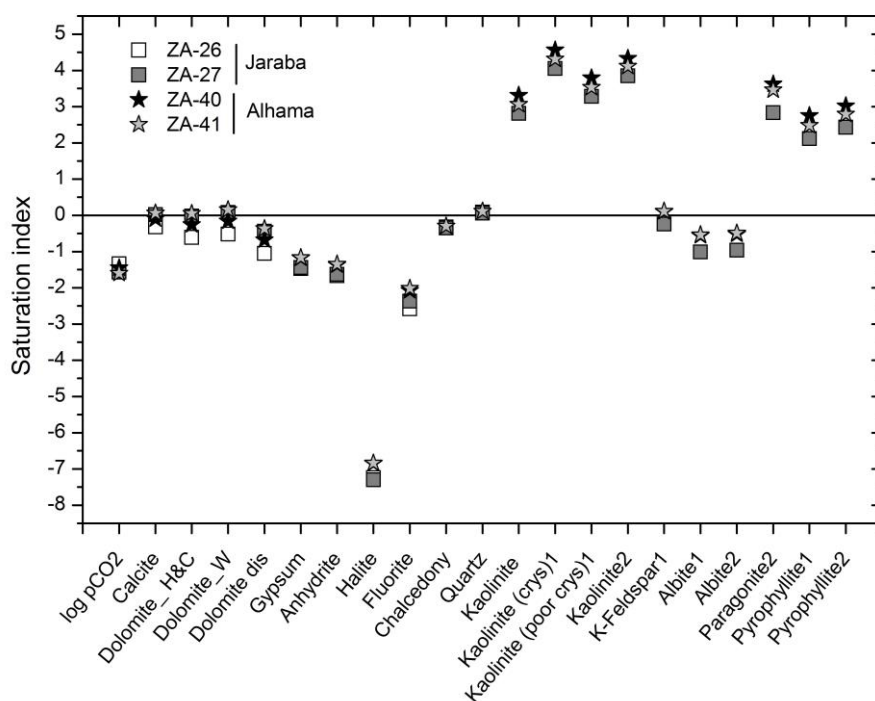
306 **Table 3.** Summary of results from speciation-solubility calculations in the Alhama-Jaraba thermal system. The calculations have been performed with the
 307 PHREEQC code (Parkhurst and Appelo, 2013) and the thermodynamic database WATEQ4F with some additional thermodynamic data included. Other
 308 results for aluminosilicate phases obtained using the LLNL thermodynamic database have been included for comparison.

Sample Number	Jaraba									Alhama de Aragón					
	ZA-22	ZA-23	ZA-24	ZA-25	ZA-26	ZA-27	ZA-28	ZA-29	ZA-30	ZA-39	ZA-40	ZA-41	ZA-43	ZA-44	ZA-45
Temperature (°C)	26.6	27.3	27.2	21.	29.4	32.0	31.8	26.1	21.8	30.1	31.9	32.4	30.2	31.6	30.7
pH (field)	7.4	7.4	7.3	7.4	6.80	7.05	7.23	7.31	7.29	7.13	6.89	7.04	7.15	7.47	7.87
TIC (mmol/L)	5.06	5.05	5.15	5.30	6.04	5.36	5.16	5.10	5.30	4.94	5.47	5.07	5.04	4.70	4.60
log pCO ₂	-1.96	-1.96	-1.86	-1.97	-1.34	-1.57	-1.76	-1.88	-1.87	-1.71	-1.45	-1.6	-1.72	-2.03	-2.44
Calcite	0.3	0.31	0.21	0.22	-0.32	0.02	0.21	0.16	0.15	0.11	-0.1	0.06	0.16	0.43	0.86
Dolomite_H&C	0.54	0.55	0.33	0.30	-0.61	-0.02	0.31	0.31	0.12	0.14	-0.26	0.05	0.25	0.87	1.67
Dolomite_W	0.62	0.63	0.42	0.35	-0.52	0.08	0.41	0.39	0.18	0.24	-0.16	0.15	0.34	0.97	1.77
Dolomite dis	0.07	0.09	-0.12	-0.21	-1.05	-0.44	-0.11	-0.15	-0.39	-0.29	-0.68	-0.37	-0.19	0.44	1.24
Gypsum	-1.51	-1.48	-1.5	-1.67	-1.47	-1.44	-1.44	-1.51	-1.58	-1.18	-1.18	-1.17	-1.2	-1.25	-1.2
Anhydrite	-1.72	-1.69	-1.71	-1.9	-1.67	-1.63	-1.62	-1.73	-1.81	-1.37	-1.37	-1.35	-1.39	-1.44	-1.39
Halite	-7.4	-7.4	-7.43	-7.67	-7.24	-7.3	-7.3	-7.43	-7.82	-6.85	-6.85	-6.84	-6.87	-6.87	-6.92
Fluorite	-2.54	-2.52	-2.61	-3.04	-2.58	-2.37	-2.35	-2.62	-2.6	-2.	-2.08	-2.02	-2.1	-2.11	-2.07
Chalcedony	-0.29	-0.3	-0.3	-0.36	-0.32	-0.35	-0.38	-0.32	-0.3	-0.28	-0.3	-0.3	-0.39	-0.32	-0.29
Quartz	0.13	0.12	0.12	0.08	0.09	0.06	0.03	0.11	0.14	0.14	0.11	0.11	0.02	0.09	0.12
Kaolinite	---	---	---	---	---	2.81	---	2.42	---	2.57	3.31	3.06	---	---	---
Kaolinite (crys) ¹	---	---	---	---	---	4.05	---	3.68	---	3.81	4.56	4.31	---	---	---
Kaolinite (poor crys) ¹	---	---	---	---	---	3.28	---	2.96	---	3.06	3.79	3.53	---	---	---
Kaolinite ²	---	---	---	---	---	3.85	---	3.50	---	3.62	4.33	4.11	---	---	---
K-Feldspar ¹	---	---	---	---	---	-0.24	---	-0.11	---	-0.01	0.10	0.11	---	---	---
Albite ¹	---	---	---	---	---	-1.01	---	-0.97	---	-0.67	-0.56	-0.54	---	---	---
Albite ²	---	---	---	---	---	-0.96	---	-0.90	---	-0.62	-0.52	-0.49	---	---	---
Paragonite ²	---	---	---	---	---	2.83	---	2.35	---	2.75	3.62	3.46	---	---	---
Pyrophyllite ¹	---	---	---	---	---	2.12	---	1.83	---	2.04	2.75	2.48	---	---	---
Pyrophyllite ²	---	---	---	---	---	2.43	---	2.19	---	2.36	3.02	2.79	---	---	---

309 ¹Thermodynamic data from Michard et al. (1979) and Michard (1983).

310 ²LLNL thermodynamic database distributed with PHREEQC.

311 The studied waters are undersaturated with respect to all silica minerals, except quartz, and also with
 312 respect to gypsum, anhydrite, fluorite, halite and albite and slightly undersaturated or near equilibrium
 313 with respect to K-feldspar (Table 3 and Figure 3). They are, however, clearly oversaturated with
 314 respect to the rest of the aluminosilicates potentially present in the deep reservoir, kaolinite, illite,
 315 paragonite and pyrophyllite. As mentioned above, knowing the uncertainties associated to the
 316 thermodynamic data for the aluminosilicates, these results have been checked using different
 317 thermodynamic data (Table 3 and Figure 3) and the variations found do not change the over- or
 318 undersaturation results commented above significantly.



319
 320 **Figure 3.** Computed saturation indices for the mineral phases considered. Results shown are for two
 321 samples from each site, those with lower pH and higher temperature and, therefore, considered most
 322 suitable for geothermometrical calculations. The calculations have been performed with the
 323 PHREEQC code (Parkhurst and Appelo, 2013) and the thermodynamic database WATEQ4F with
 324 some additional thermodynamic data included. Other results for aluminosilicate phases obtained using
 325 the LLNL thermodynamic database have been included for comparison. The thermodynamic data for
 326 mineral phases marked with the number 1 are from Michard et al. (1979) and Michard (1983), and
 327 those with the number 2 from the LLNL database.

328 Based on the combination of ion-ion plots, speciation-solubility calculations, mass-balance and
329 reaction-path modelling, Auqué et al. (2009) suggested that the most important geochemical processes
330 determining the geochemical evolution, along one of the possible flow directions from the Solorio
331 recharge zone through Mochales, Jaraba and Alhama groundwaters (see Figure 1), are: 1) halite
332 dissolution (note the 1:1 relation for Cl and Na contents both in the Jaraba and Alhama thermal waters;
333 Table 2) and 2) dedolomitisation (dolomite dissolution and concomitant calcite precipitation triggered
334 by gypsum/anhydrite dissolution).

335 The extent of the halite and gypsum/anhydrite dissolution processes seems to be constrained only by
336 the water-rock interaction time and/or by the availability of these minerals in the system. However, the
337 dolomite dissolution and calcite precipitation (dedolomitisation) appear to evolve through partial
338 equilibrium or near partial equilibrium between calcite and dolomite along the entire flow path and all
339 over the system. This situation is consistent with the very similar Mg/Ca ratio, around 0.7, found in the
340 Jaraba and Alhama thermal waters (considering the ZA-27 sample from Jaraba as it is not affected by
341 the mixing process) which is indicative of the existence of a calcite-dolomite equilibrium (or near
342 equilibrium) at similar temperatures in the aquifer. A more detailed description of the
343 hydrogeochemistry and evolution of the Alhama-Jaraba thermal system can be found in Auqué et al.
344 (2009).

345 **4.2. *Geothermometrical calculations***

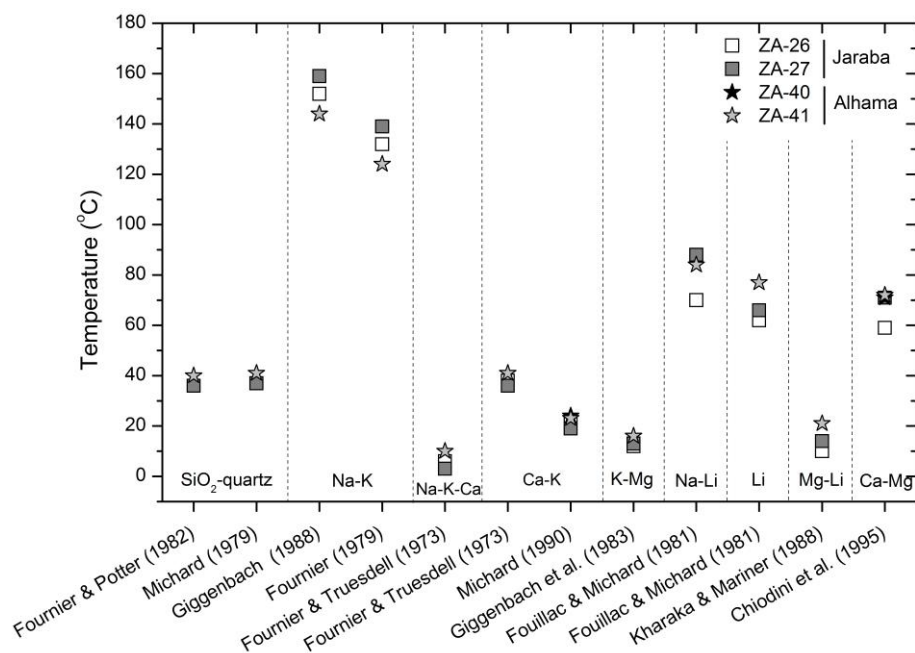
346 **4.2.1. Chemical geothermometers**

347 Table 4 and Figure 4 summarise the results obtained with the various chemical geothermometers. Prior
348 to the application of the classical cation geothermometers, the main cation concentrations of the water
349 samples were plotted in the classical Giggenbach ternary Na-K-Mg diagram (Giggenbach, 1988) in
350 order to check their applicability in this system. All the samples fall in the field of immature waters
351 (almost in the Mg vertex; see Figure S1 in the Supplementary material) indicating that they have not

352 attained equilibrium with respect to the phases on which the classical cation geothermometers are
353 based and, therefore, making their use unsuitable for this system. The spring waters from this system
354 are undersaturated with respect to all silica phases except quartz and therefore, this geothermometer is
355 the only silica geothermometer that provides temperatures higher than spring temperatures, with
356 maximum values around 40 °C for the Alhama waters and 37 °C for the Jaraba ones. The rest of the
357 cation geothermometers indicate excessively high or low temperatures, as expected from the
358 application of the Giggenbach diagram: high in the case of the Na-K geothermometer and lower than
359 the temperatures measured under spring conditions, in the case of the K-Mg geothermometer (Table 4
360 and Figure 4). The Na-K-Ca geothermometer also provides too low temperatures. The temperatures
361 obtained with the Ca-K geothermometer depend on the calibration considered (Table 4 and Figure 4):
362 the calibration proposed by Fournier and Truesdell (1973) provides reasonable temperatures about 40
363 °C, whilst the calibration from Michard (1990) estimates a temperature lower than the spring
364 temperature, about 20 °C. This situation, along with the fact that this Ca-K geothermometer is deduced
365 from the Na-K-Ca geothermometer, whose results are also inconsistent, suggests that the Ca-K
366 geothermometer's results are affected by important uncertainties and therefore, they will not be
367 considered in this study. Finally, the Mg-Li geothermometer provides temperatures below the spring
368 temperature and, although the other two lithium geothermometers (Na-Li and Li) provide higher
369 temperatures (62 - 108 °C), their results are uncertain (e.g. D'Amore et al., 1987) as they were not
370 specifically calibrated for waters with Li concentrations below 1 ppm (which is the case of the
371 Alhama-Jaraba waters).

372 It is not surprising that the application of most of these cation geothermometers leads to erroneous
373 results, but what is interesting is that in other similar carbonate-evaporitic systems, where some
374 detrital components are also present, these classical cation geothermometers have provided reliable
375 results (e.g. Fernández et al., 1988; Michard and Bastide, 1988; Pastorelli et al., 1999; Gökgöz and
376 Tarcan, 2006; Mohammadi et al., 2010; Apollaro et al., 2012; Wang et al., 2015; Blasco et al., 2017;
377 2018). This different performance will be discussed later.

378 The Ca-Mg geothermometer proposed by Chiodini et al. (1995), based on a disordered dolomite,
 379 provides temperatures ranging from 61 to 75 °C, slightly higher than the temperatures obtained with
 380 the SiO₂-quartz geothermometer. However, one has to take into account that this geothermometer is
 381 based on the simultaneous equilibrium calcite-dolomite and therefore, the results are strongly affected
 382 by the solubilities of both minerals, and as the solubility of calcite is fairly well-constrained, the main
 383 effects come from the uncertainties in the dolomite solubility. There is a wide range of proposed
 384 solubilities for dolomite depending mainly on the degree of crystallographic order assumed for this
 385 phase and as a result this can lead to different temperature results depending on the order degree of the
 386 dolomite considered. This issue will be addressed further in this study.



387
 388 **Figure 4.** Results obtained with some classical chemical geothermometers. Two samples from each
 389 site have been chosen. These samples are the ones with lower pH and higher temperature and,
 390 therefore, considered less affected by degassing and/or mixing and thus most suitable for
 391 geothermometrical calculations (see text).

392 With respect to the use of the geothermometers developed for this type of system (SO₄-F and Ca-Mg;
 393 Marini et al., 1986; Chiodini et al., 1995) some problems have also been found. The SO₄-F

394 geothermometer cannot be used in the studied system as it is only applicable in the cases where
395 equilibria anhydrite-fluorite or gypsum-fluorite are fulfilled, which is not the case for the
396 Alhama-Jaraba system neither under spring conditions nor in the deep aquifer (see below).

397

398 **Table 4.** Temperature results (in °C) obtained with some classical chemical geothermometers for the Alhama-Jaraba thermal waters. Shadowed rows
399 correspond to the most suitable samples from Alhama and Jaraba sites (highest temperatures and lowest pH values) for the geothermometrical
400 calculations (ZA-26 and ZA-27 for Jaraba; ZA-40 and ZA-41 for Alhama).

		Jaraba									Alhama					
		ZA-22	ZA-23	ZA-24	ZA-25	ZA-26	ZA-27	ZA-28	ZA-29	ZA-30	ZA-39	ZA-40	ZA-41	ZA-43	ZA-44	ZA-45
Spring Temp. (°C)		27	27	27	21	29	32	32	26	22	30	32	32	30	32	31
SiO₂-quartz	Fournier & Potter (1982)	36	36	36	26	36	36	34	34	31	40	40	40	31	38	40
	Michard (1979)	37	37	37	28	37	37	35	35	33	41	41	41	33	39	41
Na-K	Giggenbach (1988)	163	163	156	172	152	159	159	167	159	144	144	144	144	144	185
	Fournier (1979)	143	143	137	153	132	139	139	148	139	124	124	124	124	124	166
Na-K-Ca	Fournier & Truesdell (1973)	3	3	-1	-1	6	3	3	4	-14	10	10	10	10	11	21
Ca-K	Fournier and Truesdell (1973)	37	37	31	33	38	36	36	38	18	41	41	41	41	43	58
	Michard (1990)	20	20	15	16	21	19	19	21	4	24	24	23	23	25	38
K-Mg	Giggenbach et al. (1983)	13	13	10	11	12	13	14	12	3	16	16	16	15	15	25
Na-Li	Fouillac & Michard (1981)	81	81	85	100	70	88	88	96	34	95	84	84	84	59	78
Li	Fouillac & Michard (1981)	62	62	62	62	62	66	66	66	30	82	77	77	77	66	72
Mg-Li	Kharaka & Mariner (1988)	11	11	12	13	10	14	15	14	-11	24	21	21	20	12	17
Ca-Mg	Chiodini et al. (1995)	69	69	72	75	59	71	78	61	80	71	71	72	70	63	68

401 4.2.2. Geothermometrical modelling results

402 As mentioned above, this type of modelling consists of simulating a process of progressive water
403 temperature increase to obtain the temperature range at which a set of minerals (assumed to be present
404 in the reservoir in equilibrium with the waters) simultaneously reaches equilibrium. One of the main
405 difficulties when reconstructing the equilibrium situation at depth through heating simulations is
406 related to the possible hydrogeochemical modifications by secondary processes that may have affected
407 the chemistry of the waters during their ascent to the surface (Pang and Reed, 1998; Peiffer et al.,
408 2014). That is why the selection of the spring water with which the simulations are going to be
409 performed is crucial.

410 In previous works, mixing with cooler and shallower waters and CO₂ outgassing have been reported as
411 the main secondary processes affecting the hydrogeochemistry of the system studied (see Tena et al.,
412 1995, Auqué et al., 2009 and Blasco et al., 2016 for details). In order to minimise their effects in the
413 modelling, the water samples selected for the geothermometrical simulations are those with the highest
414 temperatures (less probability of have been affected by mixing) and with the lowest pH values (less
415 probability of havingbeen affected by CO₂ outgassing). The two samples are:

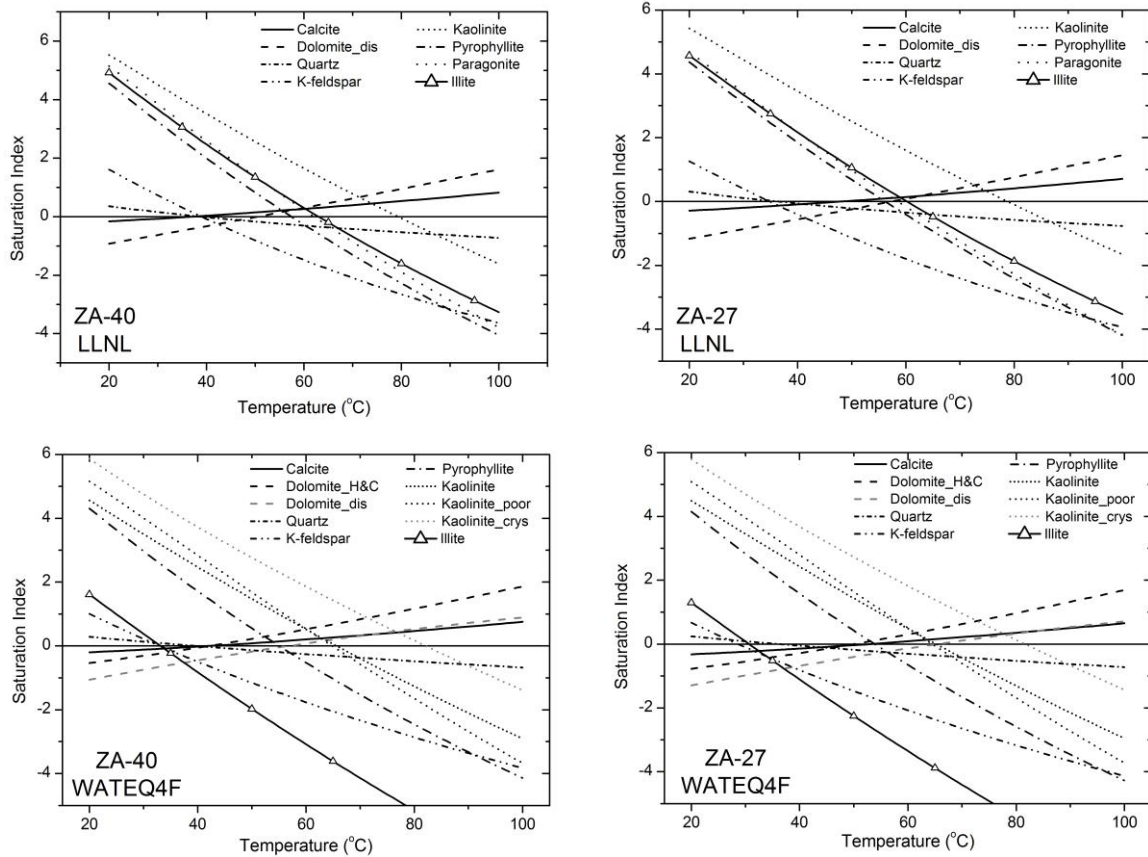
- 416 • sample ZA-40 (Alhama) which almost fulfils both conditions, the lowest pH of the site and a
417 spring temperature only 0.5 °C lower than the maximum measured temperature spring, ZA-41
418 (Table 2); and
- 419 • sample ZA-27 (Jaraba) with the highest measured spring temperature and not affected by
420 mixing (evident process in the Jaraba set; Tena et al., 1995; Pinuaga et al., 2004; Auqué et al.,
421 2009, Blasco et al., 2016) as the chemical composition is very constant with time and it
422 belongs to the group of waters without tritium in the Jaraba group (Tena et al., 1995; Blasco et
423 al., 2016). The problem with this sample is that the pH value (pH=7.05; Table 2) is not the
424 lowest among the Jaraba waters probably due to CO₂ outgassing. Therefore, in order to correct
425 the possible effects of this, a theoretical addition of CO₂ (as recommended by Pang and Reed,

426 1998 and Palandri and Reed, 2001) has been simulated with PHREEQC up to the point at
427 which the lowest pH value measured in the area is obtained (pH = 6.80 in sample ZA-26,
428 adding 0.6 mmol/L of CO₂).

429 The results of the geothermometrical simulations with the PHREEQC geochemical code, using the
430 LLNL and WATEQ4F thermodynamic databases are shown in Figure 5 and Table 5. The general
431 results indicate that these thermal waters are highly undersaturated with respect to albite, gypsum,
432 anhydrite and fluorite not only under spring conditions (as seen above) but within the whole
433 temperature range considered in the simulations.

434 Quartz equilibrium is reached at rather similar temperatures (37-40 °C) in both waters (Figure 5 and
435 Table 5) and coincides with the equilibrium for calcite and dolomite in Alhama, especially when
436 considering the partially-ordered dolomite from Hyeong and Capuano (2001; Dolomite _H&C).
437 Average equilibrium temperatures between the two databases with respect to calcite and dolomite are
438 41.5 ± 1.5 °C in Alhama and 50.5 ± 2.5 °C in Jaraba when considering the partially-ordered
439 Dolomite_H&C only. The range in the equilibrium temperatures is increased if fully-disordered
440 dolomite is considered (48 ± 8 °C for Alhama and 56 ± 8 °C for the Jaraba thermal waters) although
441 the temperature provided by this phase, which is more soluble than the others, should be considered as
442 a maximum temperature (Blasco et al., 2018). As a conclusion, it can be said that the good
443 convergence among the temperatures estimated using quartz, calcite and dolomite equilibria
444 (unaffected by possible CO₂ outgassing problems in the case of quartz, but affected for the carbonates)
445 confirm that the samples selected for the geothermometrical simulations are not significantly affected
446 by CO₂ outgassing during the rise of these thermal waters to the surface (e.g. Pang and Reed, 1998).

447



448

449 **Figure 5.** Evolution with temperature of the saturation indices of the minerals presumed to be in
 450 equilibrium with the waters in the reservoir. The waters shown here correspond to sample ZA-27 from
 451 Jaraba and ZA-40 from Alhama. The calculations have been performed with two different
 452 thermodynamic databases, LLNL (upper two plots) with the original data and WATEQ4F (lower
 453 plots) with additional data for many of the minerals of interest: the thermodynamic data for the
 454 partially ordered dolomite were taken from Hyeong and Capuano (2001; Dolomite_H&C) and the data
 455 for crystalline kaolinite (Kaolinite_crys), poorly crystalline kaolinite (Kaolinite_poor), K-feldspar and
 456 pyrophyllite were taken from Michard (1983). Dolomite_dis represents in both cases the disordered
 457 dolomite included in each database.

458

459 **Table 5.** Equilibrium temperatures (in °C) for the minerals considered in the geothermometrical
 460 simulations for the selected samples from Alhama and Jaraba thermal waters. Results with the
 461 WATEQ4F and LLNL thermodynamics databases are shown.

	ZA-27 (Jaraba)		ZA-40 (Alhama)	
	WATEQ4F	LLNL	WATEQ4F	LLNL
Calcite	53	48	43	40
Dolomite (dis)	64	57	56	51
Dolomite_H&C	51	----	42	----
Quartz	37	37	40	40
K-Feldspar	29 ¹	35	33 ¹	39
Kaolinite	65	79	63	79
Kaolinite (poor crys)	64 ¹	----	65 ¹	----
Kaolinite (crys)	81 ¹	----	82 ¹	----
Illite	31	60	44	63
Pyrophyllite	54 ¹	56	56 ¹	57
Paragonite	----	59	----	62

462 ¹ Using the thermodynamic data from Michard et al. (1979) and Michard (1983).

463 To verify the previous determinations, the modelling has been repeated for another sample presumably
 464 only affected by CO₂ outgassing, sample ZA-39 but reconstructing the characteristics of the waters at
 465 depth before the CO₂ loss (Palandri and Reed, 2001; Pang and Reed, 1998). For this purpose, about
 466 0.45 mmol/L of CO₂ have been added to the ZA-39 sample, giving a pH value identical to that in
 467 sample ZA-40 (6.90). The equilibrium temperatures obtained for the mineral phases are almost the
 468 same as those presented above for sample ZA-40, without CO₂ outgassing, which suggests that the
 469 CO₂ outgassing is the main process affecting the waters at this site and that the effects of other
 470 secondary processes such as dissolution/precipitation are negligible, if any.

471 With regard to the results obtained with the aluminosilicate minerals included in the calculations (K-
 472 feldspar, pyrophyllite, paragonite, illite and kaolinite), the temperature values depend strongly on the
 473 thermodynamic data used.

474 1. For K-feldspar, the temperature ranges between 13 and 39 °C depending on the
 475 thermodynamic data and the sample considered (Table 5 and Figure 5). K-feldspar solubility
 476 depends on the range of composition of the alkali-feldspar solid solutions and on the degree of

477 Al-Si order/disorder (Stefánsson and Arnórsson, 2000). These uncertainties make it very
478 difficult to figure out the possible participation of this phase at equilibrium at depth and,
479 therefore, these results will be disregarded.

- 480 2. The reservoir temperature values indicated by the equilibrium of illite, pyrophyllite and
481 paragonite are in all cases between 40 and 62 °C (except in the case of the temperature
482 obtained with illite and WATEQ4F in the Jaraba sample which is only 31°C), in good
483 agreement with the results obtained for calcite, dolomite and quartz.
- 484 3. Finally, the equilibrium temperature for kaolinite depends on the assumed degree of
485 crystallinity for this mineral (Michard et al., 1979; Sanjuan et al., 1988; Nordstrom et al.,
486 1990), ranging from 49 to 82 °C. The lowest values correspond to a poorly crystalline
487 kaolinite and the highest temperatures to more crystalline varieties (Table 5). This implies
488 that, if kaolinite participates in the equilibrium assemblage of the Alhama-Jaraba thermal
489 waters, which suggests temperatures mostly lower than 60 °C, it will be a poorly-crystalline
490 phase (as also found in other low-temperature carbonate aquifers; Michard and Bastide, 1988).

491 These results are also affected by the problems, associated with the analytical determination of low
492 aluminium concentrations and/or the formation of colloids and the possible precipitation of Al-bearing
493 phases during the ascent of the thermal waters (Pang and Reed, 1998; Peiffer et al., 2014). To evaluate
494 the potential effects of these uncertainties the FixAl method proposed by Pang and Reed (1998) has
495 been applied and K-feldspar equilibrium was imposed in the geothermometrical modelling (Figure S2
496 in Supplementary Material). The results indicate that in doing so, Al concentrations in the waters
497 would be higher than the measured ones and that there is a lack of convergence of the SI values for the
498 rest of the aluminosilicate phases, which is worse than the previous results (compare the results in
499 Figure 5 and Figure S2). Similar situations have been obtained when imposing equilibria with other
500 aluminosilicate phases (e.g. kaolinite, muscovite; Pang and Reed, 1998) in the calculations (not
501 shown), suggesting that dissolved aluminium in the waters studied is not meaningfully affected by

502 secondary processes (e.g. reequilibria with respect to Al-bearing phases) during the ascent of the
503 thermal waters.

504 Overall, a value of 51 ± 14 °C is indicated from the equilibria with respect to quartz, calcite, dolomite
505 (Dolomite_H&C, partially disordered; Hyeong and Capuano, 2001), pyrophyllite, paragonite and low
506 crystalline kaolinite, as the most probable temperature range at depth in the Alhama-Jaraba thermal
507 system. This range takes into account the thermodynamic uncertainties for the key minerals and
508 encloses the temperature values deduced by the quartz geothermometer.

509 **5. DISCUSSION**

510 The combination of different geothermometrical approaches and sensitivity analysis to thermodynamic
511 data has allowed defining a probable temperature range for the Alhama-Jaraba thermal waters in the
512 aquifer at depth.

513 The results presented here support the expected unsuitability of most cationic geothermometers for the
514 estimation of the reservoir temperatures in low temperature environments and/or in carbonate-
515 evaporitic reservoirs (Henley et al., 1984; D'Amore et al., 1987; Minissale and Duchi, 1988; Mutlu
516 and Gülec, 1998; López-Chicano, 2001; Levet et al., 2002; Karimi and Moore, 2008; Sonney and
517 Vuataz, 2010). The application of these classical geothermometers to the Alhama-Jaraba thermal
518 waters leads to temperatures either too high (compared with the combined results of other
519 methodologies) or too low (below spring temperature). The question that arises here is why these
520 geothermometers have provided coherent results in other similar low temperature systems hosted in
521 carbonate–evaporitic rocks and not in this particular one. Blasco et al. (2017, 2018) have studied some
522 examples of this situation and they indicate that the good results found in those systems are
523 conditioned by the existence of detrital rocks in the carbonate–evaporitic reservoir, allowing the
524 waters to reach equilibrium with respect to the phases on which these geothermometers are based. In
525 this case, their unsuitability, despite the presence of some detrital formations in the aquifer, seems to

526 be related to the shorter residence time of the waters or the less homogeneous distribution of this
527 specific mineralogy.

528 The SO₄-F chemical geothermometer, based on the anhydrite–fluorite equilibria, was developed
529 specifically for carbonate–evaporitic systems; however, it is not always applicable in them as fluorite
530 is not a common mineral in these aquifers (e.g. Blasco et al. 2017; 2018). This is also the situation in
531 the Alhama–Jaraba system and therefore this geothermometer cannot be applied here. Additionally,
532 dispersed anhydrite has been identified in the aquifer studied although in a clear undersaturation state
533 that produces its dissolution and the associated dedolomitisation process that controls the geochemical
534 evolution of these thermal waters (Auqué et al., 2009). The disequilibrium of the waters with respect
535 to anhydrite prevents the use of one of the most reliable equilibria in the geothermometrical modelling
536 of this type of system, which is the equilibrium quartz/chalcedony–anhydrite (see below).

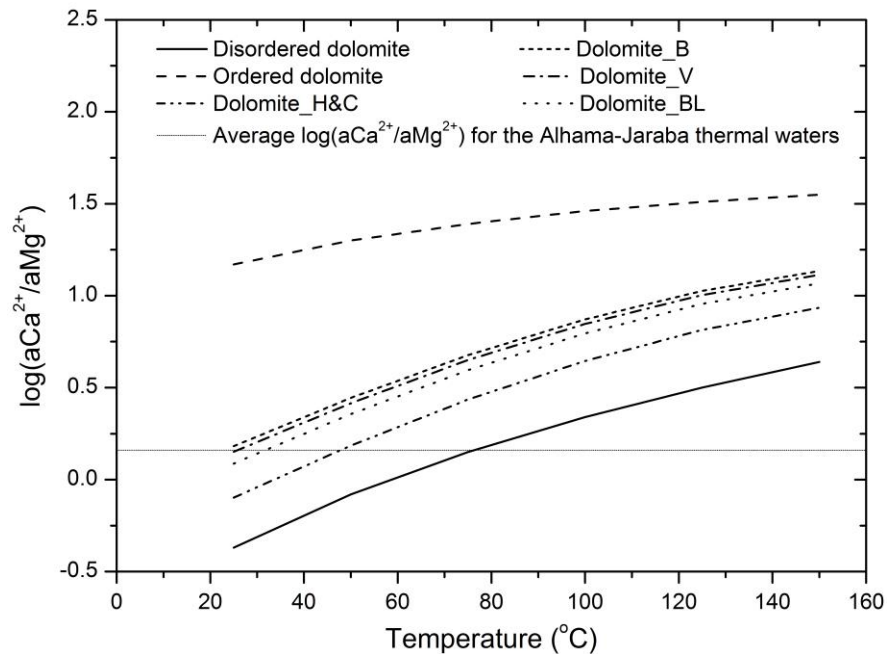
537 The results obtained with the Ca-Mg geothermometer (Marini et al., 1986; Chiodini et al., 1995), also
538 developed for carbonate–evaporitic rocks, range between 63 and 78 °C, but the uncertainties related to
539 the crystallinity and solubility of dolomite prevent it from obtaining a unequivocal estimation of the
540 reservoir temperature. As already explained, this is one of the main difficulties in the
541 geothermometrical calculations developed for this type of carbonate system and it constitutes a major
542 limitation for their application to natural systems. In order to avoid these uncertainties, various
543 dolomites have been used here in the geothermometrical modelling and the most consistent result (i.e.
544 the best convergence between calcite and dolomite towards SI=0) has been obtained considering the
545 dolomite provided by Hyeong and Capuano (2001), which indicates that the dolomite present in the
546 reservoir of the Alhama-Jaraba thermal waters should be of a similar order as Dolomite (H&C), which
547 is 11%.

548 To explore the importance of the order of dolomite on the classical geothermometrical results, log
549 ($a_{Ca^{2+}}/a_{Mg^{2+}}$) values have been calculated from equation (2) for the different dolomites included in
550 the WATEQ4F and LLNL databases, and also for other dolomites present in natural systems, at

551 different temperatures. As shown in Figure 6, there is a wide variability field of $\log (aCa^{2+}/aMg^{2+})$
552 values (and, therefore, of possible estimated temperatures) depending on the type of dolomite assumed
553 in the calculations. The average $\log (aCa^{2+}/aMg^{2+})$ values calculated with PHREEQC are very similar
554 for Alhama and Jaraba thermal waters (around 0.16; when considering the sample without mixing in
555 Jaraba) and this value corresponds to reservoir temperatures about 77 °C when considering the fully-
556 disordered dolomite (Figure 6). The presence of this type of dolomite is quite improbable in old rocks
557 from the Jurassic-Cretaceous, but, in any case, this temperature can be considered as a maximum
558 estimate (Blasco et al., 2018). On the other hand, the calculations indicate the impossibility of
559 occurrence of a fully-ordered dolomite in equilibrium with the waters studied (which would imply
560 values of $\log (aCa^{2+}/aMg^{2+})$ above 1.2; see Figure 6). In agreement with the results of the
561 geothermometrical modelling, the most consistent result is the one obtained when this calculation is
562 carried out considering the partially ordered dolomite with an order degree of 11% (dolomite_H&C).
563 Finally, following the methodology suggested by Blasco et al. (2018) to deal with these uncertainties,
564 the approximate order degree of the dolomite present in this system was calculated considering
565 samples ZA-27, from Jaraba, and ZA-40, from Alhama. The order degree obtained for the dolomite in
566 the reservoir of this thermal system is similar for both samples: 11.3% in the case of Jaraba and 14.7
567 % in the case of Alhama, as expected close to the value for the dolomite studied by Hyeong and
568 Capuano (2001).

569 Quartz equilibrium in the geothermometrical simulations (and quartz geothermometer results)
570 provides reasonable values, in the lower range of the estimated temperature (51 ± 14 °C).

571 Quartz (or chalcedony) – anhydrite equilibrium has been shown to be a reliable indication of the
572 reservoir temperature (e.g. Pastorelli et al. 1999; Levet et al., 2002; Alçiçek et al., 2016; 2017; Blasco
573 et al., 2017; 2018). Unfortunately, as mentioned above, this equilibrium is not applicable to this
574 system because anhydrite equilibrium is not reached.



575

576 **Figure 6.** Log (aCa^{2+}/aMg^{2+}) vs. temperature plot for the calcite–dolomite equilibrium using different
 577 dolomites, from 25 to 150 °C. The equilibria with respect to calcite and fully-disordered dolomite and
 578 with respect to calcite and fully-ordered dolomite, have been calculated with the thermodynamic data
 579 in the LLNL database. The equilibria with respect to calcite and some partially ordered dolomites
 580 present in natural systems are also shown (see text) The log (aCa^{2+}/aMg^{2+}) average value (0.146)
 581 calculated with PHREEQC for the Jaraba and Alhama thermal waters is also represented as a
 582 horizontal grey line.

583 For other key minerals (K-feldspar and aluminosilicate phases), the estimated reservoir temperature
 584 range in geothermometrical simulations depends strongly on the thermodynamic data selected and Al
 585 concentration. However, using reasonable solubility “end-members” for these minerals (covering
 586 differences due to the degree of crystallinity, particle size effects or the order/disorder phenomena), a
 587 relatively narrow temperature range of ± 20 °C can be obtained, in agreement with one of the scarce
 588 earlier uncertainty estimations for geothermometrical modelling, carried out by Tole et al. (1993).

589 Taking into account all the geothermometrical techniques applied in this study and the usual
 590 uncertainties considered in the temperatures obtained with classical geothermometers (± 5 to ± 10 °C

591 and may be greater than 20°C; Fournier, 1982), or geochemical modelling (± 20 °C; Tole et al., 1993),
592 the temperature estimate of 51 ± 14 °C for the Alhama-Jaraba thermal waters can be considered quite
593 probable. This common temperature range at depth for the Alhama and Jaraba thermal waters would
594 be in agreement with the idea that their origin is from the same aquifer.

595 Furthermore, the results of the studies carried out in the context of the ALGECO2 project (IGME,
596 2010) in the area of the Almazán Basin, indicate that the carbonate aquifer reaches a depth of about
597 1200 m. The geothermal gradient for the Almazán Basin is about 30 °C/Km (Fernández et al., 1998)
598 and, thus, considering an average air temperature of about 14 - 15 °C in this area (López et al., 2007),
599 the estimated temperature at these depths would be 52 °C, in close agreement with the average
600 temperature obtained from the combined techniques used in this study.

601 **6. CONCLUSIONS**

602 The waters of the low temperature Alhama-Jaraba geothermal system, hosted in carbonate rocks and
603 one of the largest naturally flowing thermal systems in Europe, have been characterised in this study,
604 and various chemical geothermometrical techniques have been tested.

605 The thermal waters in the Jaraba springs are of Ca-Mg-HCO₃-type whilst they are more SO₄-Cl type in
606 Alhama. The range of emerging temperatures in the Alhama springs is quite narrow, between 30 and
607 32.4 °C, while in Jaraba the temperatures range between 21 and 32 °C, due to the effects of mixing
608 with shallower and cooler waters. Variable CO₂-outgassing processes affect different springs at both
609 sites, promoting changes in the pH values of the waters. In summary, the Alhama-Jaraba system, as a
610 whole, brings together almost all drawbacks and possible difficulties for the application of the
611 geothermometrical methods in this type of low temperature geothermal system: problems related to
612 the existence of secondary processes during the ascent of the thermal waters and problems related to
613 the effective mineral equilibria in the reservoir at low temperatures.

614 The effects of the secondary processes identified can be minimised with 1) a careful selection of the
615 adequate samples for the geothermometrical calculations (e.g. discarding those samples affected by
616 mixing) and/or 2) using the reconstruction methodologies available when applying the
617 multicomponent geothermometrical methods (e.g. adding CO₂ to reverse the effects of CO₂-outgassing
618 during the ascent of the thermal waters).

619 The mineralogical/lithological characteristics of the aquifer importantly constrain the mineral
620 equilibria at depth and, therefore, the results obtained with the classical geothermometers or with the
621 multicomponent geothermometry. Cation geothermometers have been successfully used in some
622 carbonate-evaporitic geothermal systems with presence of detrital rocks in the aquifer. These detrital
623 rocks are also present in the Alhama-Jaraba system but the lower residence times, the lower
624 temperature at depth and/or the more disperse distribution of siliciclastic materials in the aquifer
625 prevent the waters from attaining the mineral equilibria on which these geothermometers are based
626 (e.g. albite and K-feldspar). This has also been confirmed in the results of the geothermometrical
627 modelling.

628 The aquifer studied is dominated by carbonates with only a slight evaporitic character reflected by the
629 low abundance of gypsum/anhydrite in the rocks and by the disequilibrium of the waters with respect
630 to these phases. Due to this disequilibrium, the SO₄-F geothermometer (specifically developed for
631 carbonate-evaporitic geothermal systems) and the equilibrium quartz (or chalcedony)-anhydrite (one
632 of the most reliable equilibria in the geothermometrical modelling), cannot be used for this system.

633 Therefore, the only possible mineral equilibria available for the geothermometrical calculations in
634 systems like the one presented here are silica polymorphs, calcite, dolomite and clay minerals. After
635 evaluating the results obtained with different silica phases, the SiO₂-quartz geothermometer appears to
636 provide consistent results in the system studied. The evaluation of the dolomite and clay mineral
637 equilibria, however, shows important uncertainties in the solubility values available related to degree
638 of crystallinity, particle size effects and/or the order/disorder phenomena.

639 Although the waters are in equilibrium with respect to calcite and dolomite, the uncertainties
640 associated with the order degree of dolomite affect the Ca-Mg geothermometer and the evaluation of
641 this equilibrium by geothermometrical modelling. To deal with these uncertainties a possible strategy
642 is the one applied in this paper, consisting of evaluating the results obtained with different dolomites
643 (with the Ca-Mg geothermometer and the geochemical modelling).

644 Finally, clay mineral equilibria in the geothermometrical modelling provide consistent results within a
645 reasonable uncertainty range, as long as proper sensitivity analysis is performed in order to evaluate
646 the effects of the thermodynamic data selected.

647 By applying all these methods, the reservoir temperature for the Alhama-Jaraba system has been
648 established to be 51 ± 14 °C, with waters in equilibrium with quartz, calcite, partially-ordered dolomite
649 and some aluminosilicate phases. This temperature is in close agreement with that deduced from the
650 results of geophysical studies in the area.

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