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ISOTOPE SYSTEMATICS OF ICELANDIC THERMAL FLUIDS

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21 **Abstract**

22 Thermal fluids in Iceland range in temperature from <10°C to >440°C and are dominated by
23 water (>97 mol%) with a chloride concentration from <10 ppm to >20,000 ppm. The isotope
24 systematics of the fluids reveal many important features of the source(s) and transport
25 properties of volatiles at this divergent plate boundary. Studies spanning over four decades
26 have revealed a large range of values for δD (-131 to +3.3‰), tritium (-0.4 to +13.8 TU),
27 $\delta^{18}O$ (-20.8 to +2.3‰), $^3He/^4He$ (3.1 to 30.4 R_A), $\delta^{11}B$ (-6.7 to +25.0‰), $\delta^{13}C_{\Sigma CO_2}$ (-27.4 to
28 +4.6‰), $^{14}C_{\Sigma CO_2}$ (+0.6 to +118 pMC), $\delta^{13}C_{CH_4}$ (-52.3 to -17.8‰), $\delta^{15}N$ (-10.5 to +3.0‰),
29 $\delta^{34}S_{\Sigma S-II}$ (-10.9 to +3.4‰), $\delta^{34}S_{SO_4}$ (-2.0 to +21.2‰) and $\delta^{37}Cl$ (-1.0 to +2.1‰) in both liquid
30 and vapor phases. Based on this isotopic dataset, the thermal waters originate from meteoric
31 inputs and/or seawater. For other volatiles, degassing of mantle-derived melts contributes to
32 He, CO₂ and possibly also to Cl in the fluids. Water-basalt interaction also contributes to CO₂
33 and is the major source of H₂S, SO₄, Cl and B in the fluids. Redox reactions additionally
34 influence the composition of the fluids, for example, oxidation of H₂S to SO₄ and reduction of
35 CO₂ to CH₄. Air-water interaction mainly controls N₂, Ar and Ne concentrations. The large
36 range of many non-reactive volatile isotope ratios, such as $\delta^{37}Cl$ and $^3He/^4He$, indicate
37 heterogeneity of the mantle and mantle-derived melts beneath Iceland. In contrast, the large
38 range of many reactive isotopes, such as $\delta^{13}C_{\Sigma CO_2}$ and $\delta^{34}S_{\Sigma S-II}$, are heavily affected by
39 processes occurring within the geothermal systems, including fluid-rock interaction,
40 depressurization boiling, and isotopic fractionation between secondary minerals and the
41 aqueous and vapor species. Variations due to these geothermal processes may exceed
42 differences observed among various crust-mantle sources, highlighting the importance and
43 effects of chemical reactions on the isotope systematics of reactive elements.

44

45 Keywords: Iceland; isotopes; thermal fluids; volatiles

46 **1. Introduction**

47

48 Volatiles are a group of elements and compounds that typically have low boiling points and
49 are commonly found within planetary crusts and the atmosphere. In thermal fluids, elements
50 that are often considered volatiles include H, He, B, C, N, O, F, S, Cl and other noble gases.
51 Collectively, they are derived from the atmosphere, mantle, and crust and often reflect
52 processes occurring within geothermal systems, such as fluid-rock interaction and thermal
53 decomposition of organic matter (e.g., Giggenbach, 1992; Porcelli et al., 2002). Their
54 chemical and isotopic composition is of interest for understanding geothermal systems and
55 processes, whereas their isotope systematics are particularly useful in tracing source(s) and
56 transport pathways of elements from the mantle and through the crust. Some volatiles, for
57 example, He and other noble gases, undergo limited interactions within geothermal systems
58 and are effective tracers of source provenance based on isotope characteristics alone. Others,
59 such as C, S, H and O, are reactive compounds and their isotope characteristics may be altered
60 during transport to the geothermal system or by reactions and processes occurring within the
61 geothermal system. In order to reveal the source(s) of such reactive volatile element isotopes,
62 these secondary processes need to be recognized and quantified.

63 Thermal fluids in Iceland provide a unique opportunity to study the source(s) and
64 reactions of volatile elements at divergent plate boundaries. Most divergent plate boundaries
65 are at oceanic bottom depths with seawater often dominating and overprinting other possible
66 sources of volatiles. The Iceland divergent plate boundary is subaerial and largely
67 characterized by thermal fluids composed of dilute meteoric water (<500 ppm Cl) making it
68 less challenging to reveal the characteristics of non-seawater volatile sources at shallow
69 levels. However, some geothermal systems in Iceland do have seawater sources, making it
70 possible to study the influence of salinity on volatile chemical and isotope features in these

71 predominantly basaltic systems. Moreover, geothermal activity is widespread, both within the
72 rift zones of Iceland and off-rift, facilitating studies on mantle volatile input to the uppermost
73 oceanic crust both associated with, and away from, recent magmatic activity.

74 Isotopes of volatile elements in thermal fluids in Iceland have been studied since the
75 1960s. Considerable effort has been made in defining the source and flow path of meteoric
76 waters, mainly using δD values (e.g., Friedmann et al., 1963; Árnason and Sigurgeirsson,
77 1968; Árnason, 1976, 1977). The role of deep mantle degassing and mantle source
78 provenance has been addressed using He isotopes (Polak et al., 1976; Torgersen et al., 1982;
79 Sano et al., 1985; Hilton et al., 1990, 1998; Marty et al., 1991; Poreda et al., 1992; Füre et al.,
80 2010). Despite some early and pioneering work related to reactive volatiles, for example the
81 work of Arnórsson and Barnes (1983) on carbon and Sakhai et al. (1980) and Torssander
82 (1986) on sulfur, less is known about their sources in the thermal fluids. However, more
83 recent work (e.g., Aggarwal et al., 2000; Barry et al., 2014; Stefánsson et al., 2015;
84 Stefánsson and Barnes, 2016; Stefánsson et al., 2016c; Thomas et al., 2016), including the
85 introduction of quantitative isotope modeling, has resulted in considerable progress in
86 understanding the sources of, and controls on, reactive volatiles in geothermal systems.

87 In this overview, we aim to summarize available data on the isotopes of volatile
88 elements of thermal fluids in Iceland. The isotopes discussed include δD and $\delta^{18}O$ for H_2O ,
89 both in the liquid and vapor phases, $^3He/^4He$ as well as other noble gases, $\delta^{15}N$, $\delta^{11}B$, $\delta^{37}Cl$,
90 $\delta^{13}C$ and ^{14}C in dissolved inorganic carbon, $\delta^{13}C$ in CH_4 , and $\delta^{34}S$ for total dissolved sulfide
91 and SO_4 in the liquid phase and H_2S in the vapor phase. The elements and their isotopes that
92 display non-reactive behavior, like He, were used to indicate sources and transport pathways
93 in the crust whereas others, like S and C, were used to provide insight into the elemental
94 sources as well as reactions upon transport within the geothermal systems. In order to reveal
95 the possible sources and reactions of these reactive volatile species, recent isotope

96 geochemical modeling approaches (Stefánsson et al., 2015; Stefánsson and Barnes, 2016;
97 Stefánsson et al., 2016c) have been applied and compared with field data.

98

99 **2. Geothermal activity in Iceland**

100

101 The regional geology of Iceland is the result of both extension and migration of the Mid-
102 Atlantic divergent plate boundary relative to the Iceland mantle plume (Fig. 1). The plate
103 boundary is migrating westwards relative to the mantle plume, causing the volcanic zones in
104 Iceland to shift eastwards (e.g., Bjarnason, 2008). The plate movements are not orthogonal,
105 causing crustal tension and development of fissuring and faulting that cut obliquely across the
106 plate boundary. Recent volcanic activity is most intensive where these extensional zones cut
107 across the plate boundary. In the Eastern and Northern Volcanic Zones and the flank zones,
108 central volcanic complexes have formed. These complexes are typically characterized by a
109 central volcano, caldera structure and a fissure swarm parallel to spreading in the Eastern
110 Zone but 5-10° oblique in the Northern Zone. In the Western Volcanic Zone, such volcanic
111 complexes are less obvious (e.g., Sæmundsson, 1974; Jóhannesson, 1980).

112 Geothermal activity in Iceland has been classified into low- and high-temperature
113 systems (Bödvarsson, 1961; Fridleifsson, 1979). The main high- and low-temperature
114 geothermal systems are summarized in Table 1 and their geographical distribution is shown in
115 Figure 1. Most of the high-temperature geothermal systems are located in central parts of the
116 belts of active volcanism and rifting. In the Eastern and Northern Volcanic Zones, the high-
117 temperature geothermal systems are typically associated with the volcanic complexes. In the
118 Western Zone, between Langjökull and Lake Thingvallavatn, no high-temperature systems
119 are present, whereas between Lake Thingvallavatn and the Reykjanes Peninsula, there are
120 several high-temperature systems.

121 Low-temperature geothermal activity is widespread in the Quaternary and Tertiary
122 formations of Iceland with the main activity mostly confined within the North American Plate
123 and the Southern Lowlands. The low-temperature activity is frequently associated with active
124 fractures and faults. Some systems are located within the active fissure swarms that run into
125 older formations, whereas others are located in the crust where build-up of stress by plate
126 movements leads to deformation and fracturing (e.g., Björnsson et al., 1990; Arnórsson et al.,
127 2008).

128

129 **3. Thermal fluids in Iceland**

130

131 Thermal fluids of low- and high-temperature geothermal systems in Iceland are commonly
132 divided into two groups: primary and secondary type fluids (Arnórsson et al., 2007). Primary
133 fluids, sometimes referred to as reservoir fluids, are those reaching the deepest level of
134 penetration and originate from meteoric water, seawater and magmatic water. Upon ascent to
135 the surface, they can undergo chemical and physical changes leading to the formation of
136 secondary geothermal fluids. The most common processes include: depressurization boiling,
137 resulting in volatile enriched vapor phase and boiled liquid; vapor condensation in shallow
138 non-thermal ground and surface water forming steam-heated water; mixing of deep CO₂ and
139 sometimes H₂S-rich gas with non-thermal ground and surface water; mixing of boiled liquid
140 with shallower non-thermal ground and surface water (Björke et al., 2015; Stefánsson et al.,
141 2016b).

142 The chemical composition of thermal fluids in Iceland is dominated by H₂O, which
143 generally accounts for >97 mol% of the total fluid (Stefánsson et al., 2016a). In Iceland,
144 primary fluids of meteoric origin are relatively low in chloride (Cl) compared to thermal
145 fluids worldwide (e.g., Ellis and Mahon, 1977). Low-temperature waters typically have Cl

146 concentrations <50 ppm and high-temperature waters typically have Cl concentrations <200
147 ppm (Ármansson, 2015; Stefánsson et al., 2016a). The reason for the low Cl concentration
148 of many Icelandic thermal fluids is related to the generally low Cl content of basaltic rocks
149 which make up the bulk of the Icelandic crust (Sigvaldason and Óskarsson, 1976; Arnórsson
150 and Andrésdóttir, 1995). Thermal water associated with silicic rocks (rhyolites) are generally
151 higher in Cl and other volatiles, for example fluids from the Torfajökull and Geysir areas
152 (Arnórsson 1985). Geothermal systems that have a seawater component, such as Reykjanes
153 and Svartsengi on the Reykjanes Peninsula and those within the Southern Lowlands, display
154 much higher Cl concentration, up to ~20,000 ppm, similar to seawater salinity values
155 (Arnórsson and Andrésdóttir, 1995; Ármansson, 2015).

156 For both high- and low-temperature geothermal systems, it has been demonstrated that
157 local chemical equilibria between the primary fluids and geothermal minerals is approached
158 for all major elements (except Cl) at temperatures as low as ~100°C (e.g., Arnórsson et al.,
159 1983). The effect of pressure variation between the surface and the base of the geothermal
160 system on fluid-mineral equilibria, however, is considered small. Therefore, the temperature
161 and supply of Cl are effectively the independent variables controlling the composition of
162 primary thermal fluids in Iceland. On the other hand, the concentrations of many other
163 volatile elements are highly variable. Non-reactive elements like, Ar and He, are considered
164 to largely represent their source characteristics and/or mixing with atmospheric-derived
165 components (e.g., Arnórsson, 1986; Furi et al., 2010), whereas the concentrations of reactive
166 volatiles such as CO₂, H₂S and H₂ may be close to gas-mineral equilibrium (e.g., Stefánsson
167 and Arnórsson, 2002). Sometimes, gas-mineral and gas-gas equilibria is not observed for
168 thermal fluids in Iceland, suggesting that the source exerts a significant control on the gas
169 input and/or slow redox reactions are occurring between gaseous species (e.g., Ármansson et
170 al., 1982; Stefánsson and Arnórsson, 2002).

171 Secondary fluids are usually formed after boiling of primary geothermal fluids and
172 subsequent mixing with non-thermal water. Vapor condensation and mixing lead to the
173 formation of steam-heated water. These secondary fluids are typically low in Cl, enriched in
174 SO₄ due to oxidation of H₂S, causing acidic pH values and formation of mud pots at the
175 surface, or enriched in CO₂ leading to formation of mildly acidic carbonate springs. The
176 boiled fraction commonly forms hot springs at the surface with high (alkaline) pH and
177 enrichment in Cl compared to the reservoir fluids (Björke et al., 2015; Stefánsson et al.,
178 2016b). It has also been suggested that the CO₂ springs have formed by mixing of deep-seated
179 CO₂ gas with shallow non-thermal water (Arnórsson and Barnes, 1983; Stefánsson et al.,
180 2016c). Hot springs formed by mixing of boiled reservoir water and shallow non-thermal
181 water are also common. These mixed waters typically form thermal springs at the surface
182 enriched in major elements relative to the non-thermal water (e.g., Arnórsson, 1985;
183 Kaasalainen and Stefánsson, 2012; Stefánsson et al., 2016b). Unlike primary geothermal
184 fluids, secondary fluids may depart significantly from fluid-mineral equilibrium, yet
185 secondary mineralization at the surface is commonly associated with secondary fluids,
186 particularly argillic alteration around steam-heated acid water (e.g., Markússon and
187 Stefánsson, 2011).

188

189 **4. Tracing source and reactions of volatiles in thermal fluids**

190

191 Volatile components in thermal fluids can be used to trace source characteristics and
192 subsequent reactions during transit from the mantle to the surface and atmosphere. Stefánsson
193 et al. (2015, 2016c) and Stefánsson and Barnes (2016) introduced a method to quantify the
194 sources and reaction of elements and isotopes in thermal fluids. The approach includes three
195 steps: (1) development of a conceptual model, (2) quantitative isotope geochemical

196 simulations of the conceptual models, and (3) comparison of data on natural thermal fluids
197 with the results of the model to identify and distinguish the various processes that may be
198 occurring.

199 The conceptual models that were simulated and compared with chemical composition
200 and isotope values observed in thermal fluids in Iceland in this contribution include: (1) fluid-
201 rock interaction with and without deep input of gas, (2) boiling, and (3) mixing between two
202 or more fluid sources. The input values for various sources are listed in Table 2 and the
203 isotope fractionation factors (α_{j-k}) and their temperature dependences used for the models are
204 given by Chacko et al. (2001), Stefánsson et al. (2015, 2016c) and Stefánsson and Barnes
205 (2016).

206 A summary of quantitative isotope modeling is given below. For non-reactive
207 elements, the isotope values, both ratio and delta value, (A^{fluid}) in the thermal fluids,
208 correspond to their sources and molar contribution to the fluids,

209

$$210 \quad A^{fluid} = \sum_s x_{i,s} A_{i,s} \quad (1)$$

211

212 where $A_{i,s}$ is the isotope value of the i -th element, component or compound and s denotes the
213 source and x is the mole fraction,

214

$$215 \quad x_{i,s} = \frac{n_{i,s}}{\sum_s n_{i,s}} \quad (2)$$

216

217 where n is the number of moles

218 Stable isotope values are commonly given as the ratio between two isotopes relative to
219 a standard, i.e., standard δ notation,

220

221
$$\delta = [(R_{sample} - R_{standard})/R_{standard}] \cdot 1000 \quad (3)$$

222

223 where R is the ratio of the abundance of a heavy to light isotope of a given component or
 224 element. In this case the isotope ratio of the thermal fluids (δ_i^{fluid}) is described by the
 225 relationship,

226

227
$$\delta_i^{fluid} = \sum_s x_{i,s} \delta_{i,s} \quad (4)$$

228

229 In order to explain the isotope or isotope ratio of the i -th element or compound in the thermal
 230 fluids, one needs to define the isotope value for the various sources.

231 For reactive elements, the total isotope value of the system is defined in a similar
 232 manner, i.e., as the value in the fluid of non-reactive elements,

233

234
$$\delta_i^{system} = \sum_s x_{i,s} \delta_{i,s} \quad (5)$$

235

236 Upon progressive reactions, the mole fraction of the s -th source can be calculated as a
 237 function of reaction progress from,

238

239
$$n_{i,s} = n_{i,s}^o + v_{i,s} \Delta \xi \quad (6)$$

240

241 where $n_{i,s}^o$ is the initial moles of the s -th source in the thermal fluid, $v_{i,s}$ is the stoichiometric
 242 number of the reaction and ξ is the extent of the reaction. For isolated thermodynamic
 243 systems, like adiabatic boiling, $n_{i,s} = n_{i,s}^o$ and δ_i^{system} is constant, whereas for other systems,

244 e.g., progressive fluid-rock interaction and gas input, $n_{i,s}$, $x_{i,s}$ and δ_i^{system} varies as a function
 245 of the extent of reaction.

246 For reactive components, isotopic fractionation due to chemical reactions (e.g.,
 247 formation of secondary minerals; liquid-vapor speciation) must be calculated as a function of
 248 reaction progress (ξ). In this case, the system or total isotope value of the i -th component
 249 (δ_i^{system}) can be defined by

250

$$251 \quad \delta_i^{system} = \sum_j x_{i,j} \delta_{i,j} \quad (7)$$

252

$$253 \quad x_{i,j} = \frac{n_{i,j}}{\sum_j n_{i,j}} \quad (8)$$

254

$$255 \quad n_{i,j} = n_{i,j}^0 + v_{i,j} \Delta \xi \quad (9)$$

256

257 where $x_{i,j}$, $\delta_{i,j}$, $n_{i,j}$, $n_{i,j}^0$ and $v_{i,j}$ are the mole fraction, isotope ratio, mole number, initial mole
 258 number and reaction stoichiometric coefficient of the j -th aqueous or vapor species or mineral
 259 of the i -th component, respectively. The isotope fractionation between various aqueous and
 260 vapor species and minerals are then calculated from,

261

$$262 \quad \delta_i^{system} = x_k \delta_k + \sum_j x_{i,j} (\alpha_{j-k} (1000 + \delta_k) - 1000) \quad (10)$$

263

$$264 \quad \delta_{i,j} = \alpha_{j-k} (1000 + \delta_k) - 1000 \quad (11)$$

265

266 where x_k and δ_k are the mole fraction and isotope ratio of the k -th reference species or mineral,
267 α_{j-k} is the fractionation factor between the j -th and k -th aqueous or vapor species or mineral
268 defined by,

$$270 \quad \alpha_{j-k} = \frac{1000 + \delta_{i,j}}{1000 + \delta_{i,k}} \quad (12)$$

271
272 The fractionation factors for different isotope exchange reactions depend on temperature and
273 hence, the isotope geochemical modeling itself. The fractionation factors used and applied as
274 well as their temperature variations are given by Chacko et al. (2001) and references therein
275 and Stefánsson et al. (2015, 2016c).

276 The isotope geochemical simulations were carried out for the following volatile
277 species: H, O, C, S, B and Cl and their results are compared with the data in the following
278 sections. A representative example of the isotope geochemical modeling results is shown in
279 Figure 2 for CO₂ as a function of progressive fluid-rock interaction with and without gas
280 addition. More examples are given by Stefánsson et al. (2015, 2016c) and Stefánsson and
281 Barnes (2016).

282

283 **5. Source and reactions of volatile element isotopes in thermal fluids in Iceland**

284

285 *5.1. Water and δD and $\delta^{18}O$ values*

286 Oxygen and hydrogen isotopes are commonly used in geothermal studies to identify the
287 source(s) of thermal fluids and to define the physical and chemical properties of the
288 geothermal reservoir. The pioneering work of Craig (1963), Friedmann et al. (1963) and
289 Árnason and Sigurgeirsson (1968) followed by Árnason (1976, 1977) led to the
290 extensive work on δD values of precipitation and non-thermal and thermal water in

291 Iceland in the 1960s and 70s, followed by subsequent regionally restricted studies on δD
292 and $\delta^{18}\text{O}$ (Ólafsson and Riley, 1978; Arnórsson, 1985; Darling and Ármannsson, 1989;
293 Sveinbjörnsdóttir et al., 1986; Ármannsson et al., 2014; Pope et al., 2015; Stefánsson et al.,
294 2016c). Tritium has also been measured in some low-temperature thermal waters (Stefánsson
295 et al., 2005).

296 The relationship between δD and $\delta^{18}\text{O}$ values for low-temperature water closely
297 follows the global meteoric water line (GMWL) (Fig. 3) ($n = 1011$). The range of values is
298 large, with δD values from -131 to $+3.3$ ‰ and $\delta^{18}\text{O}$ values from -20.8 to $+2.3$ ‰. This wide
299 range is considered to indicate both meteoric and seawater sources of low-temperature waters
300 in Iceland.

301 Based on δD values of local springs, rivers, and winter snow layers within glaciers,
302 Árnason (1976) constructed a detailed map showing the average δD values for annual
303 precipitation in Iceland (Fig. 4). The δD value of the precipitation decreases with increasing
304 distance from the coast, altitude and from the southern to the northern coast of Iceland. The
305 lowest δD values are lower than -100 ‰ at the northern extent of the Vatnajökull icecap, and
306 the highest δD values are about -50 ‰ at the southwest coast.

307 An important feature of the δD values of many geothermal fluids in Iceland is that
308 they differ from the local precipitation. However, based on the δD value of modern-day
309 precipitation, it is possible to project the possible source of the water from the highland to
310 lowland areas, taking into account the orientation of fissures and fractures. In this way,
311 Árnason (1977) suggested that the source water feeding many geothermal systems in the
312 south and north of Iceland are the corresponding adjacent highlands regions (Fig. 4).

313 Many low-temperature geothermal areas have δD and $\delta^{18}\text{O}$ values lower than those of
314 the nearby lowland and highland areas. In some cases, the values are lower than observed for
315 present-day precipitation throughout Iceland. It has been suggested that the origin of these

316 low values, at least for some areas, is the presence of old groundwater of meteoric origin
317 recharged during the last glaciation when air temperatures were lower than today and the
318 precipitation isotopically lighter (e.g., Árnason, 1976; Arnórsson and Andrésdóttir, 1995;
319 Sveinbjörnsdóttir et al., 2001). An example of this phenomenon is the Skagafjörður region in
320 northern Iceland (Fig. 5). Modern local springs and streams (<60 yrs old), dated using tritium
321 analysis, have δD and $\delta^{18}O$ values similar to the local precipitation, with lower values at high
322 elevation and higher values at low elevation close to coastal areas (Sveinbjörnsdóttir et al.
323 1999, 2001; Stefánsson et al., 2005). In the valley floor of Skagafjörður, old, reacted water
324 with much lower δD and $\delta^{18}O$ values compared with the values for modern local and
325 sometimes highland precipitation are sometimes observed. This water is considered to
326 represent times when the air temperature was cooler and precipitation was isotopically lighter,
327 i.e., last glacial times ~12,000 years ago, here referred to as “ice age” water. Such waters are
328 found where low hydrologic flow may be expected in valley bottoms at altitudes close to sea
329 level.

330 The high-temperature geothermal systems exhibit a trend similar to low-temperature
331 systems, with δD and $\delta^{18}O$ values often being lower than the present day local precipitation.
332 The cause is also thought to be groundwater flow from high to low altitudes. In addition, the
333 high-temperature fluids have undergone both boiling and fluid-rock interaction (Fig. 6).
334 Progressive fluid-rock interaction shifts the oxygen isotope composition to higher $\delta^{18}O$ values
335 relative to the GMWL. This shift is due to fluid-rock interaction with host rocks having $\delta^{18}O$
336 values higher than the source water (Fig. 6A). Incorporation of oxygen by secondary
337 geothermal minerals, like quartz, epidote and chlorite, may also affect the absolute $\delta^{18}O$ value
338 of the thermal water at high rock to fluid ratios, but this effect is of minor importance
339 compared to changes in $\delta^{18}O$ values due to primary rock leaching. In contrast, the effect of
340 fluid-rock interaction on δD values are less well understood. The effect is usually assumed to

341 be minimal, except in the case of very high rock to water ratios (e.g., Pope et al., 2015).
342 Alternatively, dissolution of altered crustal material containing clay minerals with low δD
343 values may also result in changes in δD values of the thermal water due to fluid-rock
344 interaction (e.g., Pope et al., 2015). Additionally, closed system depressurization boiling may
345 also leads to modification of δD and $\delta^{18}O$ values from the reservoir to surface with the vapor
346 phase becoming isotopically lighter and the corresponding boiled water becoming isotopically
347 heavier. Such a trend between vapor and liquid is often observed, for example at Krafla, NE
348 Iceland (Fig. 6B).

349

350 *5.2. Helium and $^3\text{He}/^4\text{He}$*

351 Russian scientists were the first to analyze He isotopes in thermal fluids from Iceland.
352 Kononov and Polak (1975) and Polak et al. (1976) reported He isotope analyses of
353 geothermal fluids and gases from throughout Iceland. This work was followed by a few
354 additional analyses by Hauksson and Goddard (1981) and Torgersen and Jenkins (1982).
355 These initial results demonstrated significant variability in the isotopic composition of helium
356 with $^3\text{He}/^4\text{He}$ ratios as high as 23.8 R_A off-rift (Polak et al., 1976), where R_A is the air $^3\text{He}/^4\text{He}$
357 value of 1.4×10^{-6} . Significantly, Iceland, along with Hawaii and Yellowstone, were quickly
358 identified as distinct regions of magmatic degassing with a high $^3\text{He}/^4\text{He}$ ratio and associated
359 with deep-mantle plumes under hotspots (e.g., Craig et al., 1978).

360 Later studies by Sano et al. (1985) and Marty et al. (1991), but particularly the detailed
361 studies of Hilton et al. (1990) and Poreda et al (1992), confirmed this high $^3\text{He}/^4\text{He}$ signal in
362 Iceland, both within the active rift zone and off-rift, relative to the constant depleted MORB
363 mantle (DMM) $^3\text{He}/^4\text{He}$ of $\sim 8 R_A$ sampled along deep oceanic ridges (e.g., Graham, 2002).
364 The high $^3\text{He}/^4\text{He}$ ratios in the older crust were interpreted to have resulted from the release of
365 magmatic volatiles due to incipient mantle melting rather than dispersion by groundwater

366 flow from the active rift zone (Hilton et al., 1998). Currently, the most detailed survey of the
367 He isotope systematics of Icelandic thermal fluids is the study of Fűri et al. (2010) who
368 reported data from a total of 50 individual geothermal localities.

369 The $^3\text{He}/^4\text{He}$ ratios in thermal fluids from both low- and high-temperature areas across
370 Iceland are shown in Figure 7 ($n = 272$). The highest helium isotope ratios ($>24 R_A$) are found
371 not only in central Iceland (VON) but also in Vestfirđir (the West Fjords), over 100 km west
372 of the present-day active rift zones. In Vestfirđir, $^3\text{He}/^4\text{He}$ ratios are highly diverse and reach
373 values $> 30 R_A$ (Hilton et al., 1998). Notably, the few measurements that have been carried
374 out in eastern Iceland show considerably lower values than those reported from Vestfirđir. A
375 cluster of samples, located in low-temperature areas in the Southern Lowlands, have high
376 $^3\text{He}/^4\text{He}$ ratios which are mostly characterized by values $>14 R_A$, and in some locations >20
377 R_A . Helium isotope values appear to decrease towards the west as the Reykjanes Peninsula
378 (SW) is approached. In the northern part of the Northern Volcanic Zone, $^3\text{He}/^4\text{He}$ values are
379 similar to those observed for the DMM (Hilton et al., 1990).

380

381 *5.3. Nitrogen and noble gases other than He*

382 Limited data are available for nitrogen and the noble gases other than He. Sano et al. (1985)
383 reported both Ne and Ar isotope compositions of six gas samples from Krafla, Námajfall,
384 Hveragerđi, Geysir, Krýsuvík and Reykjanes. Their reported that range in Ar isotope ratios
385 ($^{40}\text{Ar}/^{36}\text{Ar}$) was very limited, ranging from air-like (~ 299) values to 305. Similar values of
386 295 to 313 were reported by Óskarsson et al. (2015b) for thermal fluids at Reykjanes. One
387 anomalous sample displayed $^{40}\text{Ar}/^{36}\text{Ar}$ values lower than air. Given the dominance of
388 meteoric- and seawater-derived fluids in Icelandic thermal fluids, and the relative abundance
389 of argon in air ($\sim 1\%$), the occurrence of $^{40}\text{Ar}/^{36}\text{Ar}$ ratio greater than air in these samples this
390 somewhat surprising. No significant Ne isotope anomalies relative to air were found among

391 the samples studied by Sano et al. (1985). However, a more recent study by Fűri et al. (2010)
392 was able to show that although Ne in thermal fluids was dominated by an atmospheric
393 component, samples from Vestfirđir displayed a small excess of nucleogenic ^{21}Ne , likely
394 produced *in situ* and released to circulating fluids. In contrast, geothermal fluids from the rift
395 zone did not reveal such nucleogenic ^{21}Ne excesses, but rather displayed clear evidence for a
396 contribution of a mantle-derived (solar) neon component (Fűri et al., 2010).

397 Sano et al. (1985) also reported Kr and Xe isotope compositions for five out of the
398 seven samples analyzed for Ne and Ar isotopes. In agreement with their Ne results, and
399 within their quoted experimental accuracy, the isotopic compositions of Kr and Xe were
400 found to be indistinguishable from those of atmospheric Kr and Xe. Additionally, Sano et al.
401 (1985) found no evidence for excess ^{129}Xe .

402 Three studies have reported data on nitrogen isotopes ($\delta^{15}\text{N}$) for Icelandic geothermal
403 fluids. In the aforementioned study, Sano et al., (1985) reported a limited range in $\delta^{15}\text{N}$ values
404 from -2.7 to +3.0‰. Marty et al. (1991) reported $\delta^{15}\text{N}$ values in 13 well and fumarole samples
405 from the Hengill and Hveragerđi regions. In contrast to the Sano et al. (1985) study, Marty et
406 al. (1991) found a significantly greater range in $\delta^{15}\text{N}$ values from -10.5 to -0.2‰. A similar
407 range of $\delta^{15}\text{N}$ values were also reported for thermal fluids at Reykjanes from -4.8 to -1.5 ‰
408 (Óskarsson et al., 2015b). A few of these samples thus display $\delta^{15}\text{N}$ values lower than the
409 postulated DMM end-member value of $-5 \pm 2\text{‰}$ and outside the range in $\delta^{15}\text{N}$ values of -2.3
410 to +5.7‰ found to characterize the Icelandic mantle N isotope distribution, based on $\delta^{15}\text{N}$
411 analyses of subglacial basalts (Halldórsson et al., 2016b).

412

413 5.4. Boron and $\delta^{11}\text{B}$

414 Boron is considered to be a mobile element during fluid-rock interaction of mafic rocks
415 (Arnórsson and Andrésdóttir, 1995). However, it has been demonstrated to be reactive to

416 some degree and incorporated onto and/or into aluminum silicates and it partitions between
417 liquid and vapor phases upon boiling (e.g., Ellis, 1970; Michard, 1991; Leeman et al., 1992).
418 The boron isotope composition of thermal waters in Iceland is therefore considered to mainly
419 reflect the source of boron in these waters, but the effects of reactions cannot be neglected.
420 Boron isotopes have been measured in low- and high-temperature waters in Iceland
421 (Aggarwal et al., 2000) (n = 27). The $\delta^{11}\text{B}$ values range from -6.7‰ in the Krafla system to
422 +25.0‰ in a warm spring from the Southern Lowlands. By comparing results from isotope
423 geochemical modeling, in this case represented by end-member component mixing as there
424 are no reactions involved, with data on natural thermal fluids, it is evident that the source of B
425 in the fluids is the source water, i.e., meteoric water or a mixture of meteoric water with traces
426 of seawater together with leaching of basaltic rocks to various degrees (Fig. 8). High-
427 temperature fluids, for example at Krafla and Hengill, are dominated by rock leaching and
428 have Cl/B ratios and $\delta^{11}\text{B}$ values very similar to local basalts. In contrast, low-temperature
429 fluids, for example in the Southern Lowlands and Snæfellsnes, have much higher Cl/B ratios
430 and $\delta^{11}\text{B}$ values more similar to the source water. The $\delta^{11}\text{B}$ values of these thermal waters,
431 dominated by rock leaching (Cl/B ratio >200), range from -6.7 to -1.5‰, somewhat more
432 positive than those observed for the presumed $\delta^{11}\text{B}$ value of basaltic rocks of -1.5 to -16.9‰
433 (Gurenko and Chaussidon, 1997; Aggarwal et al., 2000; Rose-Koga and Sigmarsson, 2008;
434 Brounce et al. 2012). Enrichment in ^{11}B evident in Icelandic thermal waters, may result from
435 mineral alteration and uptake by B and/or partitioning of B between the vapor and liquid
436 phase upon boiling, resulting in the liquid phase becoming isotopically heavier than the vapor
437 phase (Leeman et al., 1992), i.e. indicating the possible reactive nature of B under geothermal
438 conditions.

439

440 *5.5. Chlorine and $\delta^{37}\text{Cl}$*

441 The chlorine isotope composition of Icelandic thermal fluids is considered to reflect the
442 source(s) of Cl for the thermal fluids. Chlorine concentrations and $\delta^{37}\text{Cl}$ values of the fluids
443 from these low- and high-temperature systems range from 5.2 to 20,800 ppm and from -1.0 to
444 +2.1‰ (n = 54), respectively (Kaufmann and Arnórsson, 1986; Stefánsson and Barnes, 2016).
445 Fluids from most geothermal systems exhibit a limited range of $\delta^{37}\text{Cl}$ values of about -0.5 to
446 +1.0‰, whereas some samples, in particular those from Krafla, have significantly higher
447 $\delta^{37}\text{Cl}$ values, up to +2.1‰. Isotope geochemical modeling shows that the measured $\delta^{37}\text{Cl}$
448 values in the fluids can be explained by leaching of Cl from basaltic rocks by meteoric source
449 water or seawater or mixtures thereof (Stefánsson and Barnes, 2016). Natural thermal fluids
450 of meteoric origin have a similar range in Cl concentrations, Cl/B ratios, and $\delta^{37}\text{Cl}$ values as
451 Icelandic basalts and fluids modeled with fluid-rock interaction (Fig. 9) (Stefánsson and
452 Barnes, 2016). The range in $\delta^{37}\text{Cl}$ values of the natural fluids can be explained as reflecting
453 the large range of $\delta^{37}\text{Cl}$ values observed for Icelandic basalt from -0.6 to +1.4‰ (Halldórsson
454 et al., 2016a). Highly positive $\delta^{37}\text{Cl}$ values in some samples from Krafla are likely due to
455 additional Cl sourced from HCl (gas) via magma degassing (e.g., Sharp et al., 2010).
456 Modeling results show that hydrothermal processes, such as secondary mineral formation,
457 aqueous and vapor speciation, and boiling, have minimal effects on the chlorine isotope
458 composition of the thermal fluids, yet as in the case of B, more data are needed on the
459 partitioning of Cl into secondary minerals and the associated Cl isotope fractionation.

460

461 5.6. Carbon dioxide, $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and $^{14}\text{C}_{\Sigma\text{CO}_2}$

462 The concentrations of total dissolved inorganic carbon (ΣCO_2) in thermal liquid and vapor
463 range from <5 ppm to ~4100 ppm and <50 ppm to ~750,000 ppm, respectively (Stefánsson et
464 al., 2016a). For the high-temperature vapor from wells and fumaroles, the $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values are
465 -1.6 to -9.0‰, whereas boiled high-temperature and low-temperature liquid waters have

466 $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values between -27.4 to +4.6‰ (Arnórsson and Barnes, 1983; Sano et al., 1985;
467 Marty et al., 1991; Poreda et al., 1992; Barry et al., 2014; Stefánsson et al., 2016c) (n = 645).

468 The relationship between $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and ΣCO_2 reveal a distinctive trend that is thought
469 to reflect the carbon source and reactions occurring within the geothermal systems (Fig. 10).
470 For thermal fluids with >100 ppm ΣCO_2 , the $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values both for low- and high-
471 temperature fluids converge to a value of about -5 to -2‰ in both liquid and vapor phases.
472 Results of isotope geochemical models reveal that these values can only be explained by
473 partitioning of CO_2 gas into the thermal fluids with $p_{\text{CO}_2(\text{g})} > 1$ bar with $\delta^{13}\text{C}$ value similar to
474 that predicted for the pre-eruptive melt beneath Iceland (e.g., Metrich et al., 1991; Barry et al.,
475 2014). Progressive fluid-rock interaction and leaching of CO_2 from the rock neither explain
476 the ΣCO_2 concentration nor $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values observed for these fluids. Boiling also cannot
477 explain these values. This process results in partitioning of the majority of the CO_2 into the
478 vapor phase, resulting in the vapor phase having similar $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values as the reservoir fluid
479 but with higher CO_2 concentrations. The boiled liquid, however, becomes progressively more
480 alkaline, resulting in changes in aqueous speciation which, together with isotope fractionation,
481 leads to the boiled liquid becoming initially isotopically lower with respect to $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and
482 eventually isotopically higher upon progressive boiling (Fig. 11).

483 For thermal fluids with low ΣCO_2 concentrations, multiple carbon sources have been
484 suggested (Stefánsson et al., 2016c). First, most thermal water characterized by low ΣCO_2
485 (<100 ppm) and alkaline pH values (>8.5) can be explained by interaction of water of
486 meteoric origin with degassed basalt typical of the Icelandic upper crust (Barry et al., 2014).
487 The water-rock interaction results in an increased pH value of the groundwater, deprotonation
488 of $\text{CO}_2(\text{aq})$ to HCO_3^- and CO_3^{2-} and formation of calcite, resulting in decreased $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ of the
489 groundwater with increasing pH. The large scatter observed for $\delta^{13}\text{C}$ of basalt, from -25 to -5
490 ‰ (Barry et al., 2014) also contributes to the variability of $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in these waters.

491 Secondly, some thermal waters having alkaline pH values and low ΣCO_2 concentrations are
492 characterized by higher $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values compared to those previously discussed. Such trends
493 can be explained by input of mantle CO_2 at low CO_2 pressure ($<10^{-5} - 10^{-4}$ bar). The second
494 trend becomes evident when observing the $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and $^{14}\text{C}_{\Sigma\text{CO}_2}$ content of the low ΣCO_2
495 thermal water (Fig. 12).

496 The distribution of $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in the high- and low-temperature fluids in southern and
497 western Iceland is shown in Figure 13. Three major features are observed that reflect different
498 sources of CO_2 within the rift and off-rift zones. Within the rift zone and associated with
499 volcanic centers like Reykjanes, Svartsengi, Krýsuvík and Hengill, $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values are
500 typically >-5 ‰ and the ΣCO_2 concentrations are >100 ppm suggesting mantle gas as the
501 major source of CO_2 . The gas is formed by either deep or shallow magma degassing, or both.
502 Off-rift, the $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values are usually much lower, between -20 and -7 ‰, suggesting
503 water-rock interaction being the dominant source of CO_2 in these waters with the range of
504 $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values being controlled by CO_2 and $\delta^{13}\text{C}$ variation in the basalts in Iceland (Barry et
505 al., 2014) and due to fractionation between secondary minerals and aqueous species upon
506 fluid-rock interaction (Stefánsson et al., 2016c). However, at some locations off-rift in the
507 Southern Lowlands, for example at the Grímsnes (Southern Lowlands) and Snæfellsnes
508 Peninsulas, mantle-like $\delta^{13}\text{C}$ values are observed. According to geochemical modeling (Fig.
509 12), the source of the CO_2 in these thermal waters is the same as within the rift, i.e., CO_2
510 degassing of melt originating in the upper mantle and the lower crust and the percolation of
511 CO_2 through the crust and partitioning into shallower thermal groundwater systems
512 (Stefánsson et al., 2016c).

513 The off-rift $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ mantle values correlate to some extent with the $^3\text{He}/^4\text{He}$ ratios.
514 For example, within the rift zone at Reykjanes to Hengill, high $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values are typically
515 associated with $^3\text{He}/^4\text{He}$ ratio of $>14 R_A$. Slightly higher $^3\text{He}/^4\text{He}$ ratios are observed towards

516 east in the Southern Lowlands, with the exception of the areas of high $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values that
517 are also characterized by high $^3\text{He}/^4\text{He}$ values of $>20 R_A$, for example at Grímsnes, this
518 considered to indicate deep degassing. These trends are thought to indicate a deep mantle
519 source of volatiles within some off-rift areas in Iceland, whereas other areas are characterized
520 by insignificant deep gas input but are dominated by shallow fluid-rock processes.

521

522 *5.7. Methane and $\delta^{13}\text{C}_{\text{CH}_4}$*

523 Limited data exist on the $\delta^{13}\text{C}_{\text{CH}_4}$ values of geothermal fluids in Iceland. Sano et al. (1995)
524 and Poreda et al. (1992) reported values for several high- and low-temperature areas, with
525 $\delta^{13}\text{C}_{\text{CH}_4}$ values between -39.6 and -17.8 ‰ (n = 21). In addition, only a few $\delta^{13}\text{C}_{\text{CH}_4}$ values of
526 -52.3 to -21.0 ‰ have been reported for fluids discharging from submarine systems north of
527 Iceland, at Grímsey and Kolbeinsey (Botz et al., 1999; Riedel et al., 2001). The source of
528 methane in these systems is unclear. The high-temperature geothermal systems may provide
529 all the ingredients that are necessary for abiogenic methane production, such as (ultra)mafic
530 rocks, heat and CO_2 . However, to date, there is a lack of suitable criteria that allow
531 identification of the occurrence of abiogenesis, if any at all. Methane and its higher chain
532 homologues from Kidd Creek mine (Sherwood Lollar et al., 2002, 2008) and Lost City
533 hydrothermal vents (Proskurowski et al., 2008) have been ascribed to be of abiogenic origin
534 simply because the corresponding n-alkanes exhibited carbon isotope composition that
535 contrast those observed for typical thermogenic sources where the n-alkanes derive from the
536 thermal decomposition of organic matter. This criterion can only be applied if the n-alkanes
537 derive from a common source, but the genetic relationship between methane and its higher
538 chain homologues often remains unclear. Fiebig et al. (2007) suggested that the attainment of
539 isotopic equilibrium between discharged CH_4 and inorganically-derived CO_2 could point to

540 abiogenic formation of methane from CO₂. However, it is often very difficult to assess if
541 isotopic equilibrium was attained at depth.

542 Poreda et al. (1992) observed that $\delta^{13}\text{C}_{\text{CH}_4}$ of fumarolic and well discharges appears to
543 decrease with increasing CH₄/³He concentration ratios. In addition, they documented that
544 apparent carbon isotopic equilibration temperatures often disagree with measured reservoir
545 temperatures, consistent with the findings of Sano et al. (1985) for the Krafla geothermal
546 system. The notion that isotope equilibrium between CO₂ and CH₄ is not attained in the
547 corresponding hydrothermal systems is in agreement with the observation of Stefánsson and
548 Arnórsson (2002) that CO₂, H₂ and CH₄ are not in overall chemical equilibrium for thermal
549 fluids in Iceland, even at high temperatures (>250°C). Poreda et al. (1992) suggested that
550 methane beneath Iceland might derive from at least two sources: (1) the mantle or CH₄
551 contained in basaltic rocks and (2) decomposing organic matter. The same conclusion was
552 derived by Botz et al. (1999) based on the interpretation of $\delta^{13}\text{C}$ values of n-alkanes,
553 hydrocarbon distribution ratios and CH₄/³He concentration ratios in thermal fluids at
554 Kolbeinsey and Grímsey. However, it is still unknown whether the upper mantle really
555 contains methane (e.g., Etiope and Sherwood Lollar, 2013.). Botz et al. (1999) also pointed to
556 the potential importance of secondary processes (superimposed oxidation of hydrocarbons
557 after formation/mixing, secondary cracking of short chain n-alkanes) in controlling
558 hydrocarbon concentration ratios and isotope values.

559

560 *5.8. Sulfur and $\delta^{34}\text{S}$*

561 Sulfur is among the major elements constituting thermal fluids in Iceland. It is found in
562 various oxidation states: sulfide in the liquid and vapor phases and as sulfate in the liquid
563 phase. Other oxidation states, including polysulfide and thiosulfate, have also been identified
564 in trace concentrations (Kaasalainen and Stefánsson, 2011). With respect to sulfur isotopes,

565 Sakai et al (1980) and Torssander (1986) measured the $\delta^{34}\text{S}$ values of sulfide and sulfate in
566 vapor and liquid phases of geothermal systems, both high- and low-temperature, whereas
567 Marty et al. (1991) measured $\delta^{34}\text{S}$ values of sulfide in the vapor phase for some high-
568 temperature areas. Stefánsson et al. (2015) conducted a detailed study of the high-temperature
569 geothermal system at Krafla, NE Iceland, in order to trace the source of sulfur and reactions
570 of sulfide and sulfate in the thermal fluids using multiple sulfur isotopes, $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$,
571 together with sulfur chemistry and isotope geochemical modeling.

572 Low-temperature water samples have been analyzed for $\delta^{34}\text{S}$ from two locations,
573 Reykholtisdalur (W Iceland) and the Southern Lowlands. The total dissolved sulfide ($\Sigma \text{S}^{-\text{II}}$)
574 and SO_4 concentration of the waters are <0.01-12.4 ppm and 12.0-152.4 ppm, respectively,
575 with corresponding $\delta^{34}\text{S}$ values of -10.9 to +0.6‰ and +2.9 to +10.1 ‰, respectively
576 (Torssander, 1986) (n = 37). These values are considered to reflect multiple sources of sulfur,
577 as well as fractionation related to water-rock interaction. First, thermal water of meteoric
578 origin interacts with the sulfate in the basalts resulting in increased SO_4 concentrations and
579 decreased $\delta^{34}\text{S}_{\text{SO}_4}$ values approaching that of SO_4 in basalts (-1.8 to +4.1‰) (Torssander,
580 1989). Moreover, such water may mix to various extent with seawater, shifting the SO_4
581 concentration and $\delta^{34}\text{S}_{\text{SO}_4}$ to more positive values (Fig. 14). Such seawater mixing is observed
582 in the Southern Lowlands. In thermal waters inland, the source of SO_4 is dominated by rock
583 leaching, whereas closer to the coast, Cl and SO_4 concentrations increase and the ratio of
584 Cl/ SO_4 and the $\delta^{34}\text{S}_{\text{SO}_4}$ values approach that of seawater (Fig. 15). With respect to $\Sigma \text{S}^{-\text{II}}$,
585 much more negative $\delta^{34}\text{S}$ values are observed (-10.9 to +0.6‰) (Torssander, 1986) (n =19)
586 similar and lower than the $\delta^{34}\text{S}_{\Sigma-\text{II}}$ values in basalt of -2.0 to +0.1‰ (Torssander, 1989).
587 Comparison of the natural data with isotope geochemical modeling suggests that rock
588 leaching of sulfide by the thermal fluids is the main source of dissolved sulfide in the water,

589 whereas the most negative $\delta^{34}\text{S}_{\text{S-II}}$ values are possibly caused by boiling and sulfide mineral
590 formation upon fluid-rock interaction (Fig. 16).

591 The predominant form of sulfur in high-temperature thermal fluids is dissolved
592 sulfide. The values for $\delta^{34}\text{S}_{\text{S-II}}$ in the liquid and vapor phases range from -2.5 to +2.0‰ and -
593 2.0 to +3.4‰, respectively ($n = 129$), whereas in the liquid phase $\delta^{34}\text{S}_{\text{SO}_4}$ lies between -2.0 to
594 21.2‰ (Shakai et al., 1980; Torssander, 1986; Stefánsson et al., 2015) ($n=54$). According to
595 Stefánsson et al. (2015), the source of dissolved sulfide in these fluids is leaching of basalt,
596 with insignificant H_2S (or SO_2) magma gas input. The higher values in the vapor relative to
597 the liquid are the results of boiling and associated changes in aqueous and gases speciation,
598 and isotope fractionation between these aqueous and gaseous species. Extensive fluid-rock
599 interaction and quantitative pyrite formation, is an unlikely effect as this would cause the
600 $\delta^{34}\text{S}_{\text{S-II}}$ values to become significantly lower in the reservoir fluids relative to the basalt. This
601 has not been observed for the high-temperature thermal fluids in Iceland. For SO_4 , the wide
602 range of values suggest a basalt source together with seawater for the seawater-fed systems
603 like those found at Reykjanes and Svartsengi. Based on the $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ relationship for
604 sulfate in fluids at Krafla, oxidation of $\delta^{34}\text{S}_{\text{S-II}}$ to SO_4 was suggested to be the source. Such a
605 trend, however, does not indicate equilibrium between $\delta^{34}\text{S}_{\text{S-II}}$ and SO_4 ; in fact, chemical
606 equilibrium is not observed between sulfur species in thermal fluids in Iceland (Stefánsson
607 and Arnórsson, 2002; Stefánsson et al., 2015).

608

609 **6. The source of volatiles in thermal fluids at the Icelandic divergent plate boundary**

610

611 The isotope systematics of volatiles have revealed many important features of the sources and
612 reactions of thermal fluids at the Icelandic divergent plate boundary (Fig. 17). Based on data
613 on δD , tritium and $\delta^{18}\text{O}$ values for H_2O , $^3\text{He}/^4\text{He}$ and other noble gases, $\delta^{11}\text{B}$, $\delta^{13}\text{C}_{\text{CO}_2}$ and

614 $^{14}\text{C}_{\text{CO}_2}$, $\delta^{13}\text{C}_{\text{CH}_4}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}_{\text{S-II}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{37}\text{Cl}$ it has been demonstrated that the source
615 of the water in the thermal fluids is either meteoric water or seawater or a mixture of both. For
616 other volatiles, the major sources include the atmosphere (e.g., N_2 , Ar and Ne), degassing of
617 the mantle through the crust and/or from degassing basalt melt at shallower levels (e.g., He,
618 CO_2 , N_2 and Cl), and leaching of basalts (e.g., CO_2 , H_2S , SO_4 , Cl and B). Redox reactions
619 may also play a role in the oxidation of H_2S to SO_4 and reduction of CO_2 to CH_4 , as well as
620 decomposition of organic matter contributing to the CH_4 source. The range of isotope values
621 of non-reactive volatile elements (e.g., $\delta^{37}\text{Cl}$ and $^3\text{He}/^4\text{He}$), is considered to indicate
622 heterogeneity of the mantle and melts beneath Iceland. The range of isotope values for some
623 reactive volatile elements ($\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and $\delta^{34}\text{S}_{\text{S-II}}$), are affected by processes occurring within
624 the geothermal systems including boiling and fluid-rock interaction with changes in the
625 isotope ratios due to these secondary processes exceeding the variations observed between the
626 various sources, highlighting the importance and effects of chemical reactions on the isotope
627 systematics of reactive volatiles.

628

629 **7. Volatile element fluxes**

630

631 The fluxes of volatile elements have received less attention compared to their chemistry and
632 isotope ratios in geothermal fluids in Iceland. Based on He isotopes and CO_2 concentrations
633 and isotope ratios, the fluxes of He and CO_2 have been estimated both for high-temperature
634 geothermal systems within the rift zone as well as off-rift in Iceland (e.g., Hilton et al. 1990;
635 Barry et al., 2014; Stefánsson et al., 2016c) and for CH_4 for selected high-temperature
636 geothermal systems (Etiope et al., 2007) (Table 3). For comparison, we estimated the fluxes
637 of some other volatiles, i.e., H_2 , H_2S , Cl, B and N_2 , based on their elemental to CO_2 ratio and
638 the estimated CO_2 flux (Table 3).

639 The volatile element fluxes are much greater for active high-temperature geothermal
640 systems and during major eruptions than off rift. For example, the CO₂ flux is in the range of
641 500-3000 ×10⁵ mol/km²/yr for the high-temperature geothermal systems, whereas, it is 5-
642 10×10⁵ mol/km²/yr on average for the whole island. The total average CO₂ flux for Iceland
643 corresponds to 5-10×10¹⁰ mol/yr in total (Barry et al., 2014; Stefánsson et al., 2016c). During
644 major eruptions much larger CO₂ fluxes are observed temporarily. For example, 30-40×10¹⁰
645 mol/yr were emitted to the atmosphere on a yearly basis during the last two major eruptions in
646 Iceland, the Eyjafjallajökull and Holuhraun eruptions in 2010 and 2014-15 (Gíslason et al.,
647 2015). These values are a considerable proportion of the global total CO₂ flux of 295-
648 2300×10¹⁰ mol/yr (e.g., Kerrick, 2001; Morner and Etiope, 2002). The volatile elemental flux
649 of the Iceland mantle plume and plate boundary system may therefore be considered
650 significant on a global scale or <0.1-2%.

651

652 **8. Future directions**

653

654 The present work has summarized and emphasized the current state of knowledge of the
655 isotope systematics of Iceland from a geothermal fluid perspective. However, it is also of use
656 to identify issues with the present database and possible new directions of research activity to
657 assist improving understanding of the sources of volatiles and their interaction history within
658 geothermal systems.

659 There is a comprehensive dataset now available for δ¹⁸O and δD in thermal and non-
660 thermal fluids in Iceland and it is well constrained that the major source of H₂O to be
661 meteoric and/or seawater. However, little work has been done obtaining data on δ¹⁸O and δD
662 in hydrothermally altered rocks and the effects of fluid-rock interaction on the δ¹⁸O and δD
663 systematics. Moreover, our understanding of juvenile (i.e., mantle-derived) water contribution

664 is limited, the latter being important with the fact that H₂O is the dominant volatile emitted
665 during volcanic eruptions in Iceland and that characterization of the isotope values of such
666 water is important for understanding deep recycling of water and the origin of water on Earth
667 (e.g., Hallis et al., 2015).

668 There is a comprehensive database now available for the He isotope composition of
669 Icelandic geothermal fluids. The present database contains approximately 300 individual
670 ³He/⁴He analyses that provide a detailed, albeit spatially-restricted, picture of the Icelandic
671 mantle. However, there are additional ³He/⁴He analyses of volcanic glasses erupted
672 subglacially as well as mafic minerals, such as olivines and pyroxenes. These He isotope
673 results need to be integrated with those of the geothermal fluids to give an even a more
674 comprehensive overview of the He isotope systematics of the Icelandic mantle. This is
675 important to resolve discrepancies between sample types from the same region would help
676 identify geothermal systems where a strong crustal or air-derived He component is present. In
677 addition, it would allow for greater scrutiny of the spatial distribution of high ³He/⁴He ratios
678 (> 20 R_A for example) to better map the impingement history of the Icelandic plume along
679 this major section of the divergent Mid Atlantic plate boundary. In the former case,
680 understanding mantle-crust interaction from a He isotope perspective is likely to help explain
681 variations in other isotope systematics, such as N for example. On-going studies (Harðardóttir
682 et al., 2017) are directed at compiling a He isotope database for the whole of Iceland, using all
683 sample types (geothermal fluids and volcanic lavas) with the aim of tackling these
684 outstanding issues.

685 Moreover, the concentrations and isotope ratios of heavier noble gases (Ne, Xe, Kr)
686 and other non-reactive elements, like Br, and I, may further constrain the sources of material
687 in the mantle-crust system and the contribution of various type of fluids, as well as to
688 facilitate quantification of fundamental processes occurring in geothermal systems. The

689 discovery of primordial (chondritic) xenon that differs from atmospheric xenon has been
690 made using Icelandic subglacial basalts (Mukhopadhyay, 2012) and bubbling gas springs
691 from the Eifel in Germany (Caracausi et al., 2016). These discoveries highlight the need for
692 high-precision Xe (and Kr) isotope analyses of Icelandic geothermal fluids. Relative
693 abundance systematics of all the noble gases have also significant potential to elucidate the
694 boiling-mixing process at play in the roots of geothermal systems in Iceland. This is related to
695 their variable solubility which affects their relative abundances at a given degree of boiling.
696 Also, given the highly heterogeneous nature of nitrogen in the hybrid Iceland plume source,
697 and strong evidence for the presence of recycled crustal N-component(s) which have been
698 integrated into and/or entrained by this source (Halldórsson et al., 2016a), future studies
699 elucidating the $\delta^{15}\text{N}$ systematics in Icelandic geothermal fluids will likely yield further insight
700 into the nature of these components and processes that control nitrogen in such fluids.

701 As for carbon isotope, extensive work has been carried out on the $\delta^{13}\text{C}$ and ^{14}C on CO_2
702 in low-temperature and non-thermal fluids off-rift whereas more data are needed for high-
703 temperature fluids, both the liquid and vapor phases, to better constrain the effects of boiling
704 and phase separation. Data on carbon isotopes composition in alteration products is also much
705 needed. For other carbon compounds including, CH_4 and light hydrocarbons, very limited
706 data are available both for $\delta^{13}\text{C}$ and δD values. Such data are vital to understanding the source
707 and reactions of hydrocarbons in crustal environments at divergent plate boundaries and the
708 possible origin of deep hydrocarbons.

709 The sulfur isotope values of SO_4 and H_2S in thermal fluids has been well studied
710 during the last ~30 years. However, very limited data are available on multiple sulfur isotope
711 ratios of thermal fluids, as well as on sulfur isotope ratios of igneous rocks, melt inclusions,
712 and alteration products. Additionally, fundamental problems in older extraction methods of
713 sulfur from silicate matrices have recently been reported (Labidi et al., 2012), questioning the

714 reliability of the Icelandic sulfur isotope dataset. Such information, particularly when a large
715 database involving high-precision sulfur isotope data for Icelandic lavas becomes available,
716 may provide critical information needed to trace source(s) of sulfur and distinguishing
717 between sulfur originated from rock dissolution, degassing of melt and oxidation and
718 reduction reactions (e.g., Stefánsson et al., 2015). On-going studies (Gunnarsson-Robin et al.,
719 2017) are directed at compiling and evaluating a large database of multiple sulfur isotope
720 values for Iceland thermal fluids.

721 Currently, limited data are available for both Cl (n= 54) and B (n = 27) isotope ratios
722 in thermal fluids in Iceland. These elements are generally considered to be non-reactive with
723 their isotope ratios reflecting the source characteristics. However, isotope fractionation may
724 occur during various processes, including boiling, magma-gas partitioning, fluid-rock
725 interaction and incorporation into alteration minerals, as well as primary mantle-derived
726 values, needed to be better constrained with respect to Cl and B isotopes. Isotopic
727 fractionation during these various processes needs to be better constrained. Moreover, the
728 data reported by Aggarwal et al. (2000) and used here, are based on TIMS analysis, i.e. an
729 analytical technique that has been shown to sometimes exhibit a bias of up to ~4‰ for some
730 natural material (Aggarwal and You, 2016). Further work is therefore needed on $\delta^{11}\text{B}$ in
731 Icelandic fluids including comparison of different analytical techniques to verify the B isotope
732 values and better understanding the effects of aqueous speciation, fluid-mineral interaction
733 and boiling on the $\delta^{11}\text{B}$ systematics.

734 The isotope characteristics of some of the major elements in the Earth's crust are
735 poorly known (see e.g., Teng et al., 2017). For example, Si, Fe, Ca and Mg isotope ratios
736 have been poorly explored and exploited within the field of fluid-rock interaction in
737 hydrothermal systems. These isotope systems may potentially providing critical information

738 regarding conditions and reaction mechanisms of a major part of alteration minerals
739 associated with hydrothermal systems and their relation to the chemistry of thermal fluid.

740 Finally, the understanding of isotope fractionation is poorly constrained for
741 multicomponent and multiphase systems and between various aqueous and gaseous species
742 and minerals at hydrothermal temperatures and pressures. Equilibrium fractionation factors
743 and the kinetics of isotope exchange for many important chemical systems are simply missing
744 and have to be determined from experimental work and/or quantum chemical calculations.
745 Such data are vital for the further development of isotope geochemistry. But, without data on
746 natural samples only limited interpretation are possible of natural processes occurring in
747 hydrothermal systems.

748

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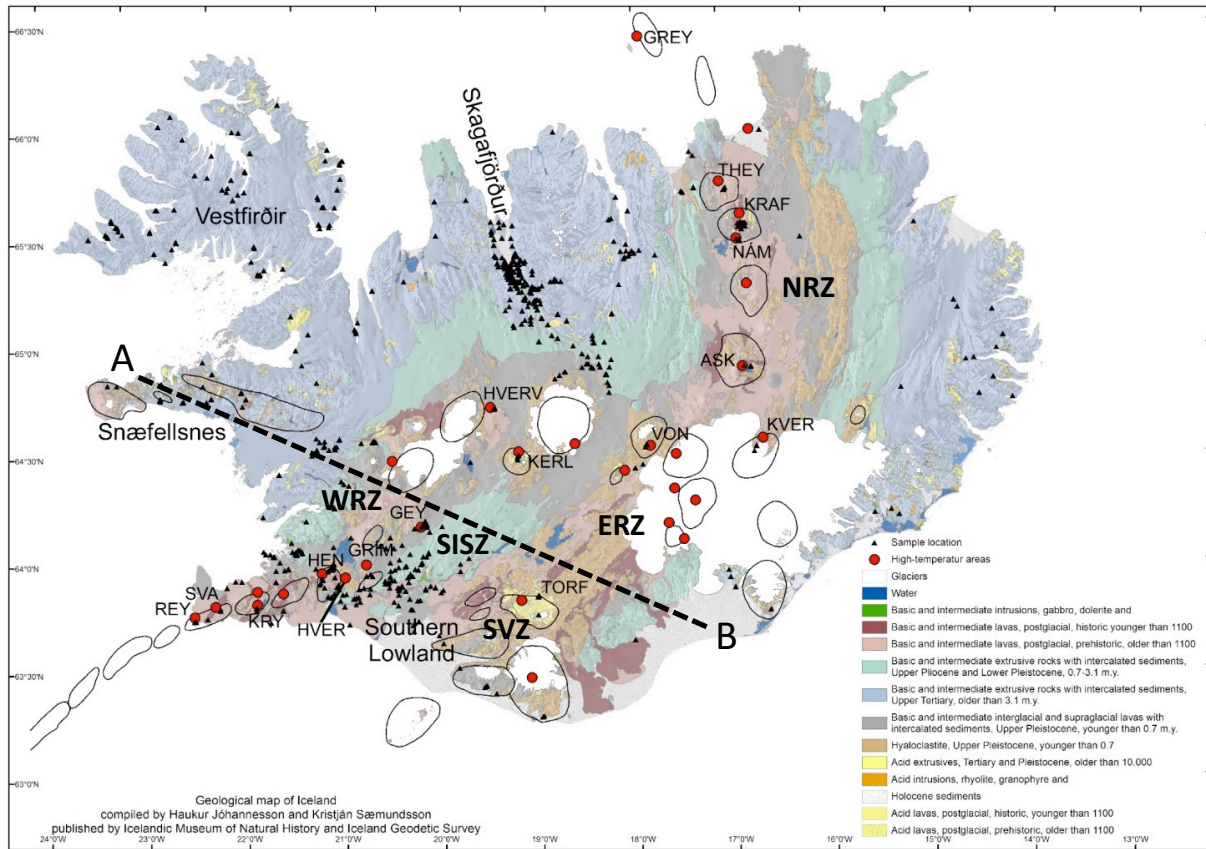
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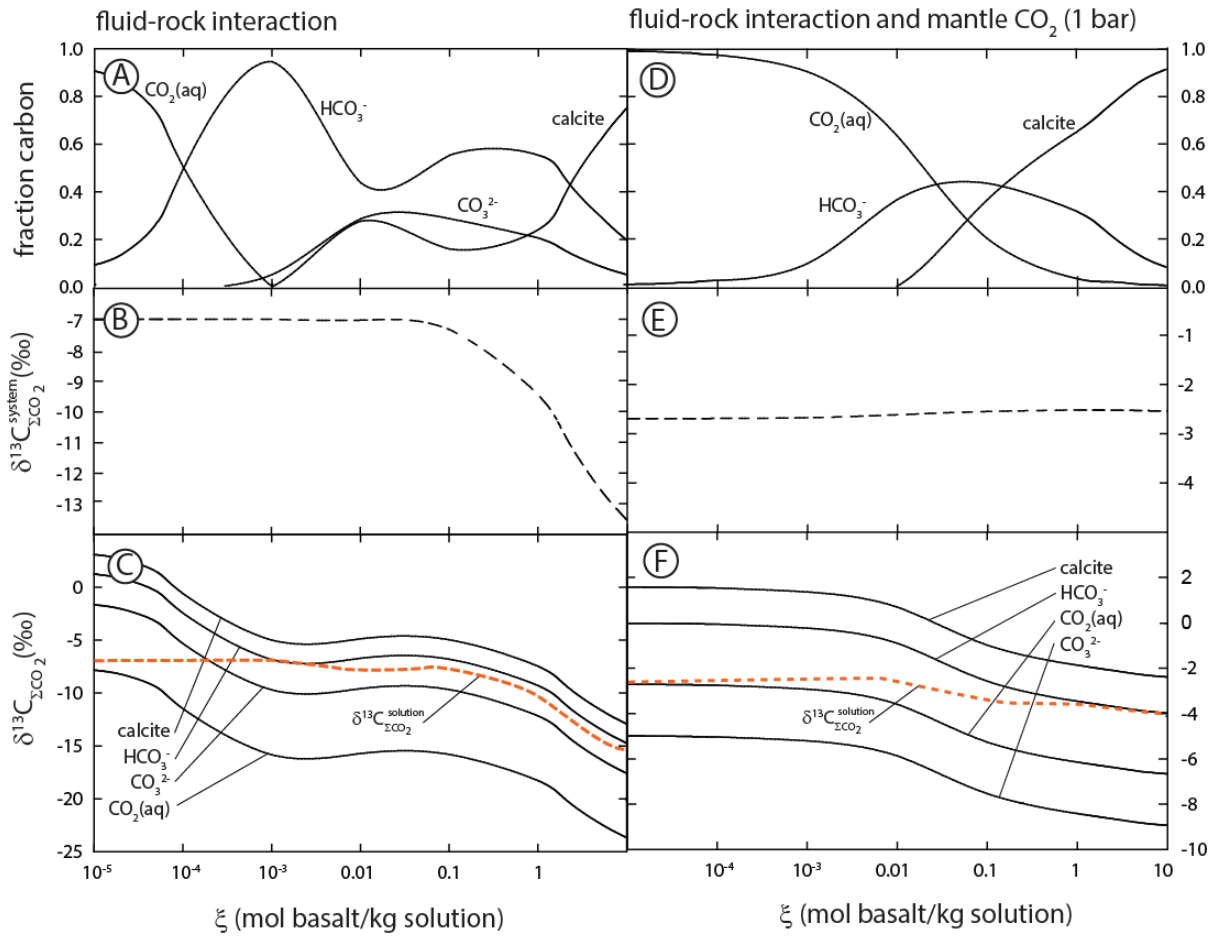
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1071 **Figure caption**



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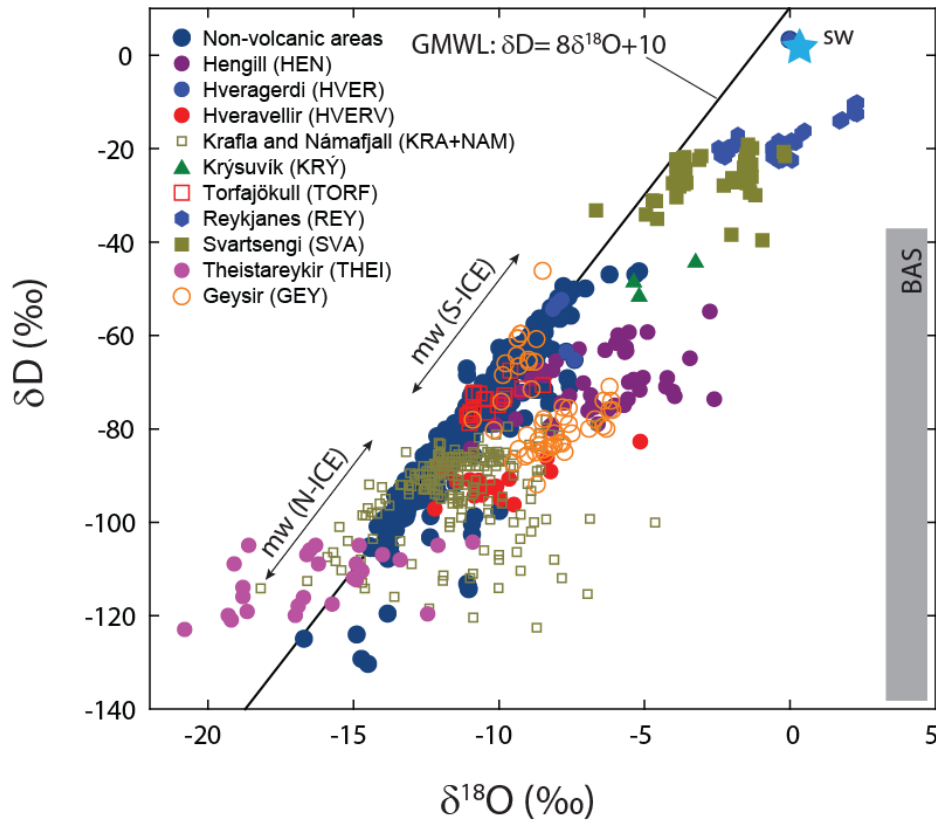
1073 **Fig. 1.** Geology and geothermal activity in Iceland and location of fluid samples discussed in
 1074 this study. Based on the geology map of Iceland, 2nd ed., Natural Museum of Iceland
 1075 (1:600.000-NJ-1600v-berg_2. ed.). The names on the map correspond to those reported in the
 1076 study as listed in Table 1. WRZ = Western Rift Zone; SISZ: South Iceland Seismic Zone;
 1077 SVZ: South Volcanic Zone; ERZ: East Rift Zone; NRZ: North Rift Zone. The A-B line refers
 1078 to the cross section shown in Figure 17.



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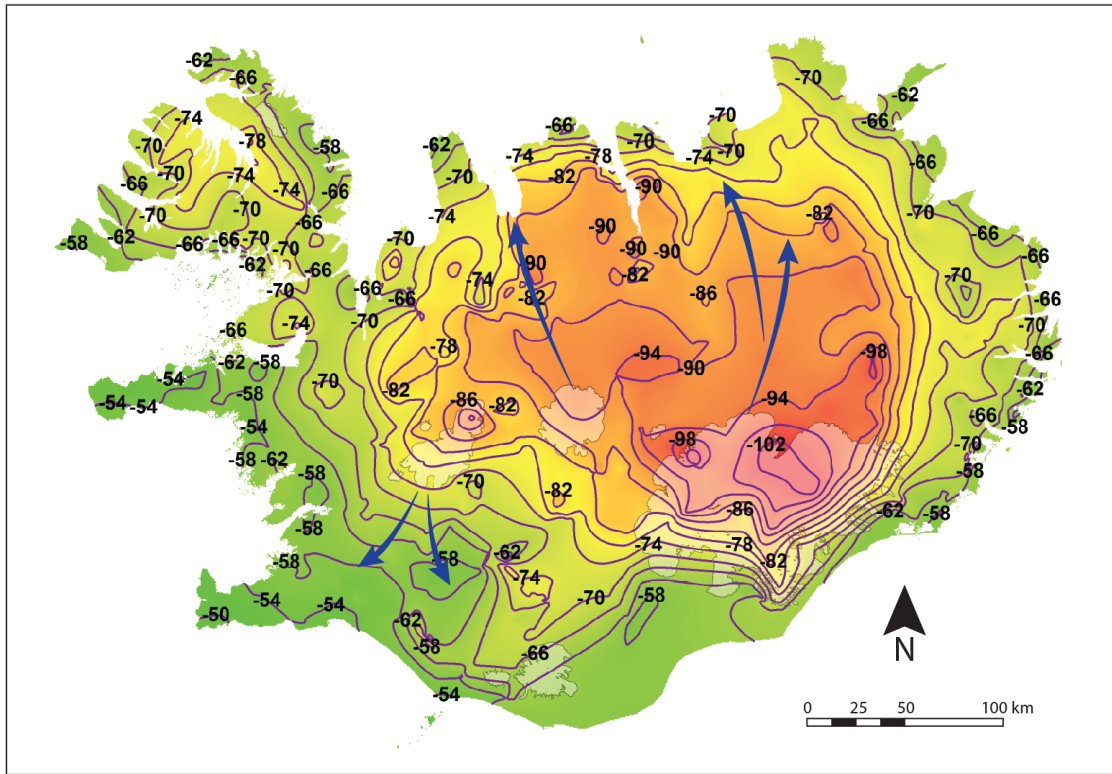
1080 **Fig. 2.** An example of the isotope geochemical model results for CO₂ as function, progressive
 1081 fluid-rock interaction (ξ) without (A-C) and with (D-F) CO₂ gas addition. The calculations
 1082 were carried out at 100°C. Shown are the fractions of CO₂ species and minerals (A and D),
 1083 the $\delta^{13}\text{C}$ of the system that may change upon progressive fluid-rock interaction due to the
 1084 ratios and isotope values of the different sources (B and E) and the isotope ratios of various
 1085 dissolved species and minerals (C and F). The results of such isotope geochemical modeling
 1086 can then be compared with the observed isotope ratios in order to distinguish possible sources
 1087 and reactions occurring within geothermal systems.

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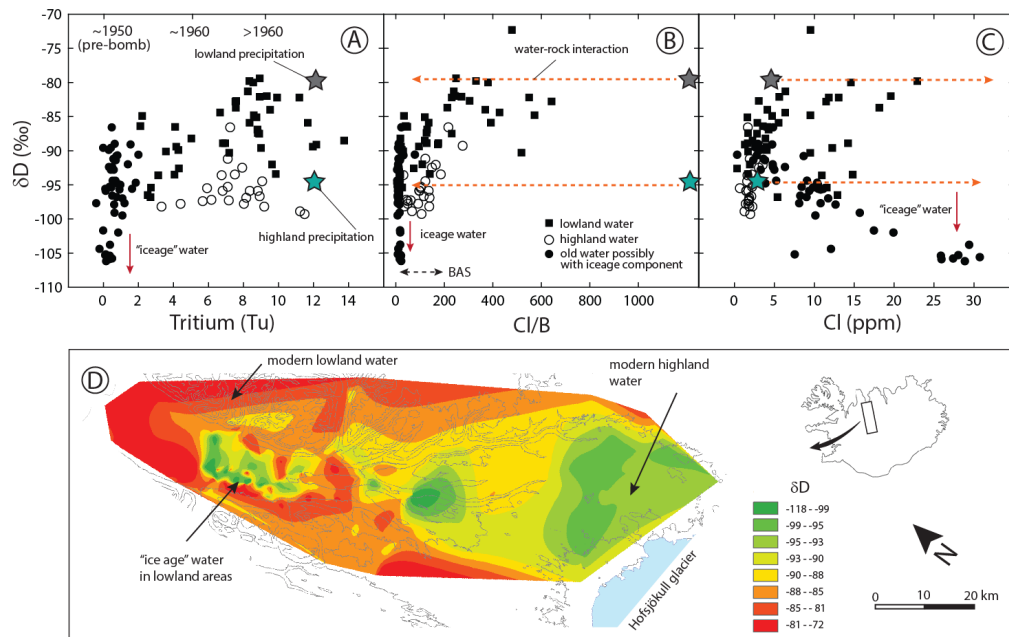
1090 **Fig. 3.** The relationship between δD and $\delta^{18}O$ values for thermal fluids in Iceland. For low-
 1091 temperature systems, the values in the liquid phase are shown; whereas for high-temperature
 1092 systems both values of the vapor and liquid phases are shown. Most systems display low-
 1093 salinity with the source of the thermal water considered to be meteoric water. Two systems,
 1094 Reykjanes and Svartsengi, have seawater or seawater-meteoric water mixtures as the source
 1095 fluid. It is evident that geothermal systems situated on the north side (mw-N-ICE) of Iceland
 1096 have lower δD and $\delta^{18}O$ values than those on the south side (mw-S-ICE). This is consistent
 1097 with the isotope values of the precipitation of the recharge areas feeding the geothermal
 1098 systems (Fig. 4). Many of the high-temperature areas are shifted towards higher $\delta^{18}O$ values
 1099 relative to the global meteoric water line (GMWL) due to fluid-rock interaction. The values
 1100 for thermal fluids are from Ólafsson and Riley (1978), Arnórsson (1985), Darling and
 1101 Ármannsson (1989), Sveinbjörnsdóttir et al. (1986), Ármannsson et al. (2014), Pope et al.
 1102 (2015), Stefánsson et al. (2016c) and the values for basalt are from Pope et al. (2013) and
 1103 references therein.



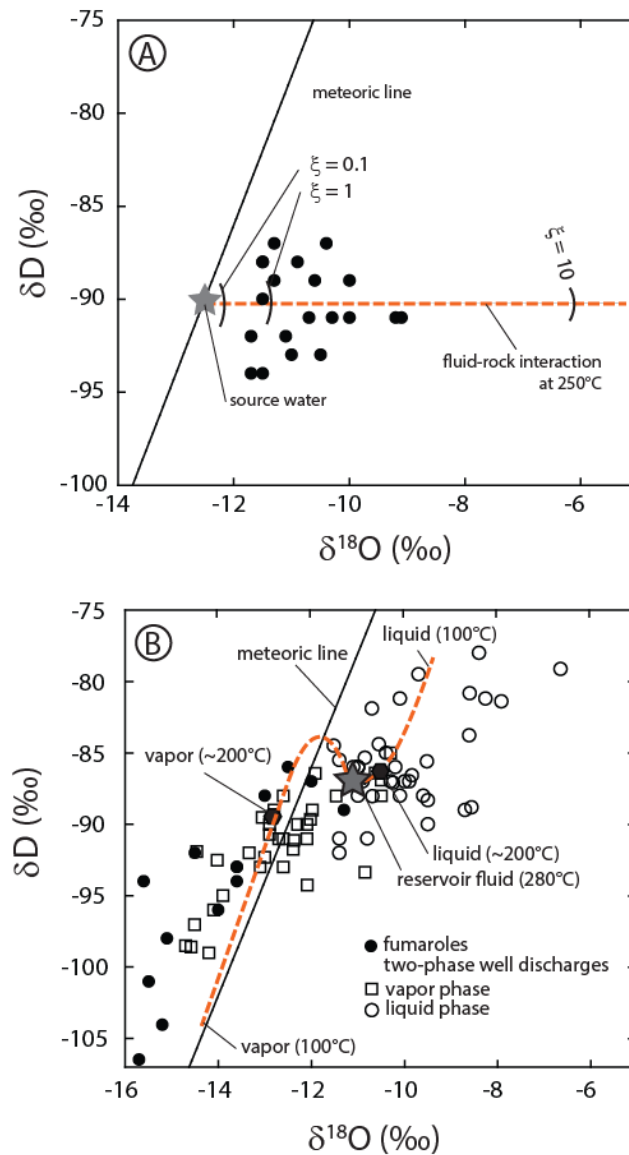
1105 **Fig. 4.** Map showing the distribution of δD values of precipitation in Iceland. Also shown are
1106 the possible recharge areas of general groundwater flow feeding the geothermal systems.
1107 Based on \acute{A} rnason (1976, 1977).

1109

1110



1111
 1112 **Fig. 5.** Thermal and non-thermal water in Skagafjörður, north Iceland, show clear trends of
 1113 different source and age. A) Based on the δD and tritium relationship, many of the waters of
 1114 the lowlands and highlands of the Skagafjörður region are of modern age (<50 yrs. old) and
 1115 closely reflect the δD value of the local precipitation. Some older water displays much lower
 1116 δD values than local precipitation. This is considered to indicate the presence of an old and
 1117 isotopically lighter water, possibly formed during or at the end of the last glaciation when
 1118 temperatures in Iceland were colder and the precipitation was lighter. B) and C) The young
 1119 waters are often similar to the Cl concentration observed in precipitation (Sigurdsson and
 1120 Einarsson, 1986) and have high Cl/B molar ratios, suggesting insignificant to slight water-
 1121 rock interaction, whereas the old water possibly containing an “ice age” component often
 1122 have Cl/B close to the basaltic rock ratio (Arnórsson and Andrésdóttir, 1995; Halldórsson et
 1123 al., 2016a) indicating significant water-rock interaction. D) Geographically, the modern water
 1124 is located in the highlands and on the mountain sides of the Skagafjörður region, whereas the
 1125 old and low δD water is typically situated in the lowlands of the Skagafjörður valley plains
 1126 where groundwater flow may be considered to be low. The data for δD , tritium, Cl and B are
 1127 taken from Arnórsson et al. (2002) and Stefánsson et al. (2005, 2016c).



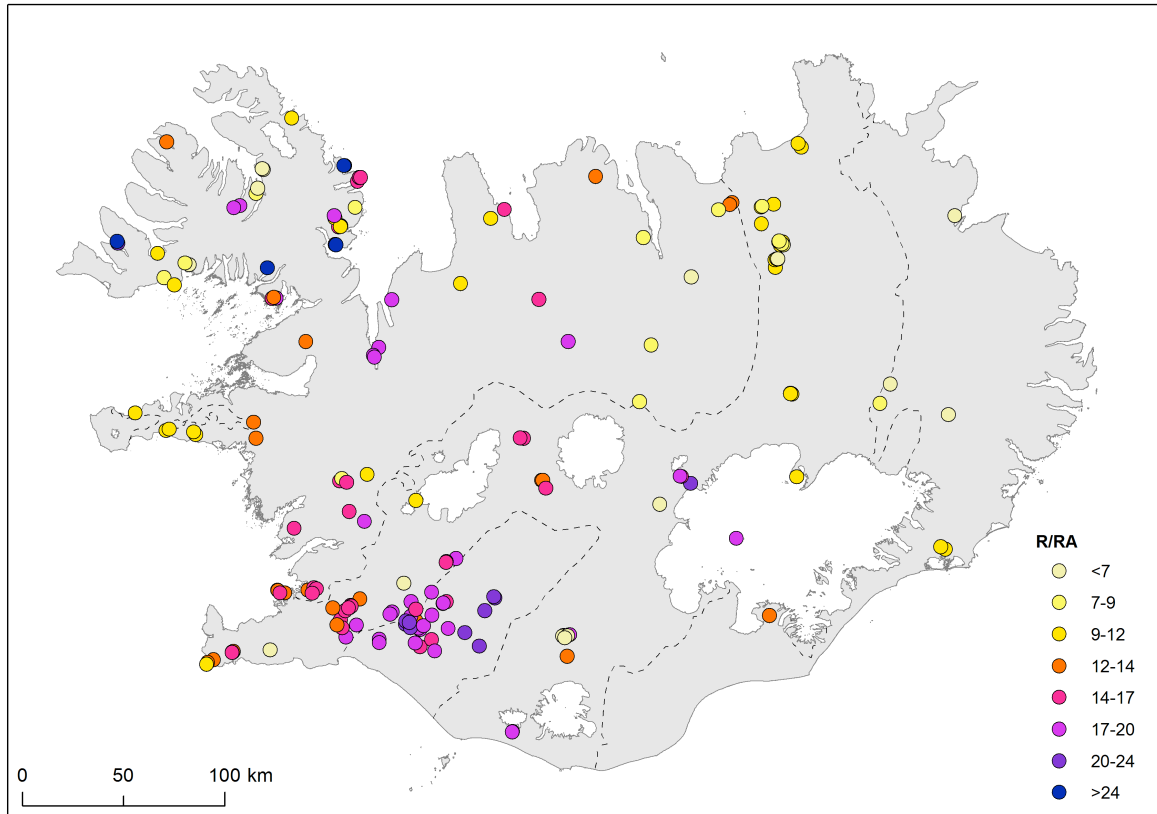
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1130 **Fig. 6.** A) The effects of fluid-rock interaction on δD and $\delta^{18}O$ values of thermal fluids of
 1131 meteoric origin at 250°C in contact with basaltic rock; also shown are Krafla reservoir fluids.
 1132 Upon progressive fluid-rock interaction (ξ) given as moles of basalt dissolved per kg of water,
 1133 basaltic rocks are dissolved and secondary minerals forms. As the rock to water ratio
 1134 increases the $\delta^{18}O$ value of the water progressively becomes rock dominated; however
 1135 secondary mineral formation makes the total $\delta^{18}O$ value of the fluid lower than expected due
 1136 to fractionation between the fluid and secondary minerals. This shift towards heavier $\delta^{18}O$
 1137 values is reflected in the high-temperature thermal reservoir waters, for example at Krafla. B).

1138 The effects of adiabatic boiling on δD and $\delta^{18}O$ values of Krafla reservoir geothermal fluids.
1139 Upon adiabatic boiling of typical reservoir fluids with temperatures of 280°C to 100°C at the
1140 surface, the δD and $\delta^{18}O$ values of the liquid phase become higher, whereas the vapor initial
1141 becomes higher and then lower upon progressive boiling for δD and lower for $\delta^{18}O$. This
1142 trend is clearly observed for fluid at Krafla, NE Iceland. In addition, the $\delta^{18}O$ values of vapor
1143 phase H_2O can be modified by oxygen exchange between CO_2 and H_2O during ascent (e.g.,
1144 Chiodini et al., 2000). Data on fluid composition at Krafla are taken from Darling and
1145 Ármannsson (1989), Sveinbjörnsdóttir et al. (2015) and Pope et al. (2015).

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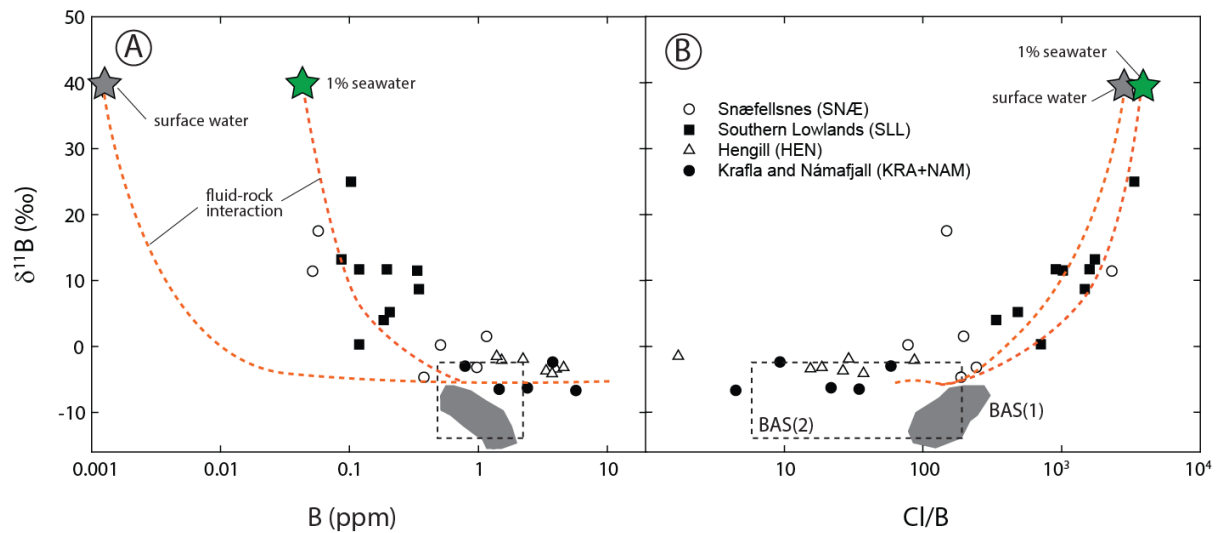
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 1149 **Fig. 7.** Distribution of $^3\text{He}/^4\text{He}$ ratios in high- and low-temperature geothermal fluids from
 1150 across Iceland. The map is based on reported values by Kononov and Polak (1975), Polak et
 1151 al. (1976), Torgersen et al. (1982), Sano et al. (1985), Hilton et al. (1990, 1998), Marty et al.
 1152 (1991), Poreda et al. (1992) and Furi et al. (2010).

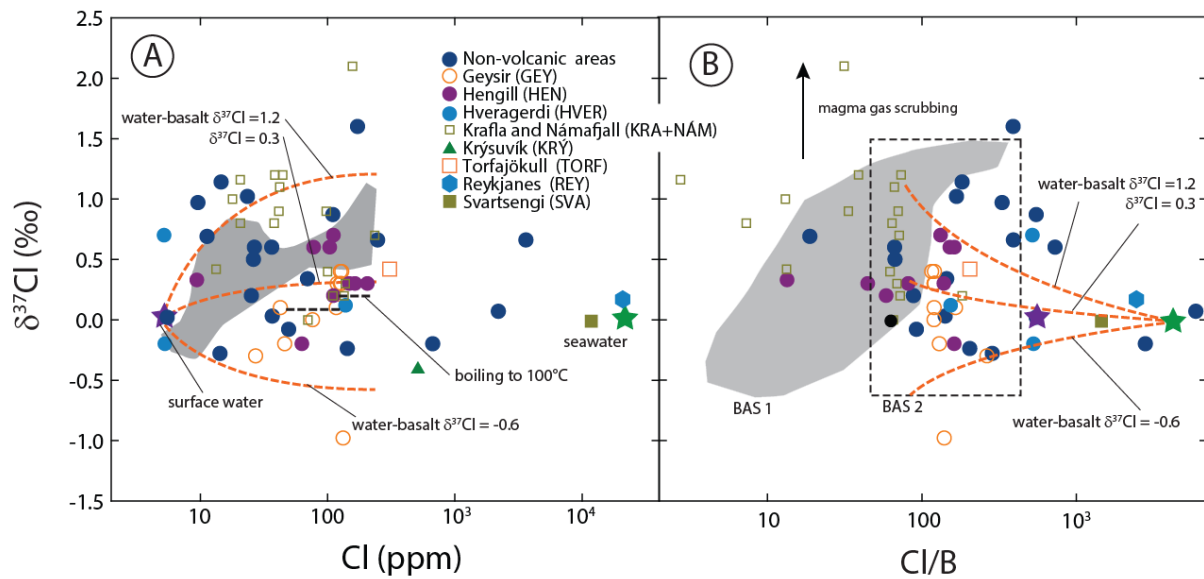
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1155 **Fig. 8.** Boron concentration versus $\delta^{11}\text{B}$ (A) and Cl/B ratios versus $\delta^{11}\text{B}$ (B) for thermal fluids
 1156 in Iceland. The low-temperature waters show trends of progressive water-rock interaction of
 1157 either meteoric water or meteoric water mixed with traces of seawater (<1%), the latter
 1158 typically observed in the Southern Lowlands of Iceland (Arnórsson and Andrésdóttir, 1995)
 1159 where high-temperature fluids are closer to the basalt values, suggesting significant leaching.
 1160 The B concentration, Cl/B ratios and $\delta^{11}\text{B}$ values are shown for two sets of data: gray field
 1161 (BAS1) is based on Gurenko and Chaussidon (1997), Aggarwal et al. (2000), Rose-Koga and
 1162 Sigmarsson (2008) and Brounce et al. (2012), whereas the dashed box (BAS2) is based on
 1163 the $\delta^{11}\text{B}$ values reported by these same referencnes, and the B and Cl concentration reported by
 1164 Arnórsson and Andrésdóttir (1995) and Halldórsson et al. (2016a).

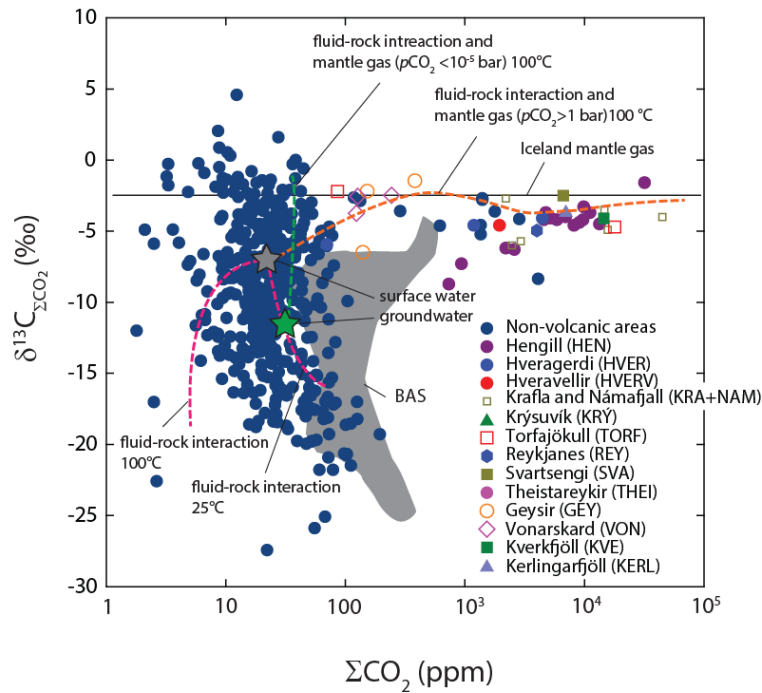
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1168 **Fig. 9.** Chlorine concentration versus $\delta^{37}\text{Cl}$ values (A) and Cl/B ratios versus $\delta^{37}\text{Cl}$ values (B)
 1169 for thermal fluids from Iceland. Based on data reported by Kaufmann and Arnórsson (1986)
 1170 and Stefánsson and Barnes (2016). Modelling results (dashed orange line) show expected
 1171 fluid compositions for progressive water-rock interaction with Iceland basalts of three
 1172 different $\delta^{37}\text{Cl}$ values (0.3‰ = average basalt; 1.2‰ = maximum value; -0.6‰ = minimum
 1173 value). A) The $\delta^{37}\text{Cl}$ values of the natural waters largely overlap with the basalt field,
 1174 suggesting the basalt as a Cl source to the thermal fluids. Cl concentrations and $\delta^{37}\text{Cl}$ values
 1175 of Icelandic basalts are shown in the gray field (Halldórsson et al., 2016a). B) $\delta^{37}\text{Cl}$ values
 1176 and Cl/B ratios of natural thermal waters can also be explained by progressive interaction of
 1177 meteoric water and/or seawater with the host basalts. High $\delta^{37}\text{Cl}$ values at Krafla suggest the
 1178 addition of magmatic HCl(g) gas scrubbing into the geothermal reservoir. Two different
 1179 basalt fields are shown: 1) BAS1 (gray field) is defined by the average B concentration of
 1180 Icelandic basalts (1.2 ppm; Arnórsson and Andrésdóttir, 1995) and the Cl concentration and
 1181 $\delta^{37}\text{Cl}$ values of Icelandic basaltic glasses (Halldórsson et al., 2016a); 2) BAS2 (dashed box) is
 1182 defined by the $\delta^{37}\text{Cl}$ values reported by Halldórsson et al. (2016a) and the range in Cl/B ratios
 1183 measured by Arnórsson and Andrésdóttir (1995).

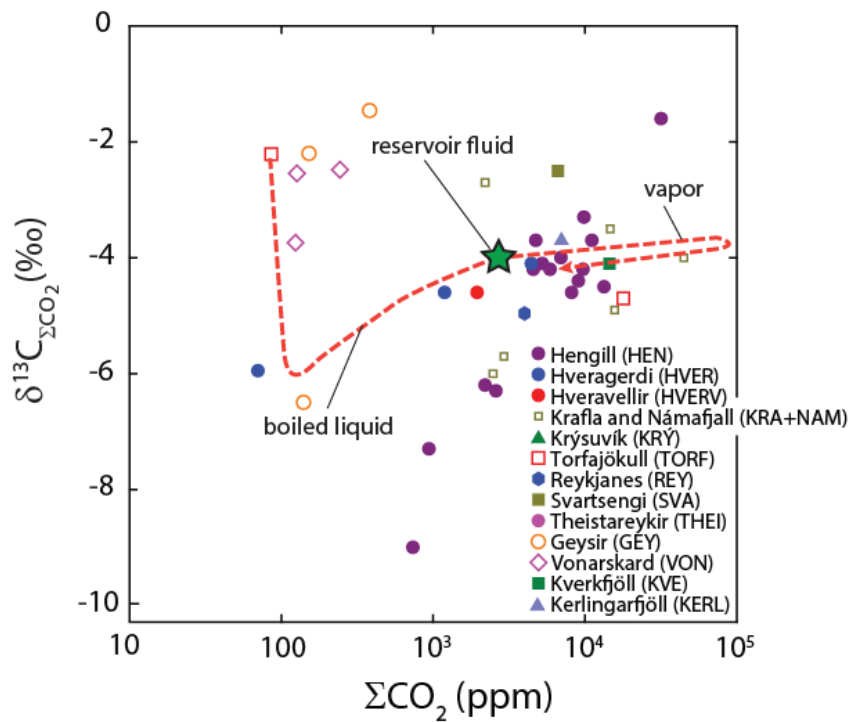
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1186 **Fig. 10.** The relationship between $\delta^{13}C_{\Sigma CO_2}$ and ΣCO_2 for thermal fluids in Iceland
 1187 (Stefansson et al., 2016c). Also shown are the distribution of subglacial basalts in Iceland
 1188 (Barry et al. 2014) and the results of the three isotope geochemical models. Comparison of
 1189 the natural data and the model results suggest that fluids with elevated ΣCO_2 concentration
 1190 (>100 ppm) and $\delta^{13}C_{\Sigma CO_2}$ values of -7 to -2% are explained by fluid-rock interaction and gas
 1191 partitioning into the thermal water at depth. The gas has similar $\delta^{13}C_{\Sigma CO_2}$ values as the pre-
 1192 eruptive melt of the Icelandic upper mantle and lower crust and having pressures of $p_{CO_2} \Rightarrow$
 1193 1bar. Most thermal waters having low ΣCO_2 concentration (<100 ppm) are characterized by
 1194 fluid-rock interaction. The observed range of $\delta^{13}C_{\Sigma CO_2}$ values is due to the range of values for
 1195 basalts in Iceland (Barry et al., 2014) and because of fractionation between carbonate minerals
 1196 formed and aqueous speciation (Stefansson et al., 2016c). Some thermal waters having low
 1197 ΣCO_2 concentration and high $\delta^{13}C_{\Sigma CO_2}$ values of >-5 cannot be explained by fluid-rock
 1198 interaction alone. Instead, geochemical modeling suggests either or both interaction of
 1199 intrusive rocks having higher $\delta^{13}C_{\Sigma CO_2}$ values and higher ΣCO_2 concentration and/or gas
 1200 input into the system at low pressures ($p_{CO_2} = 10^{-4}$ to 10^{-6} bar).

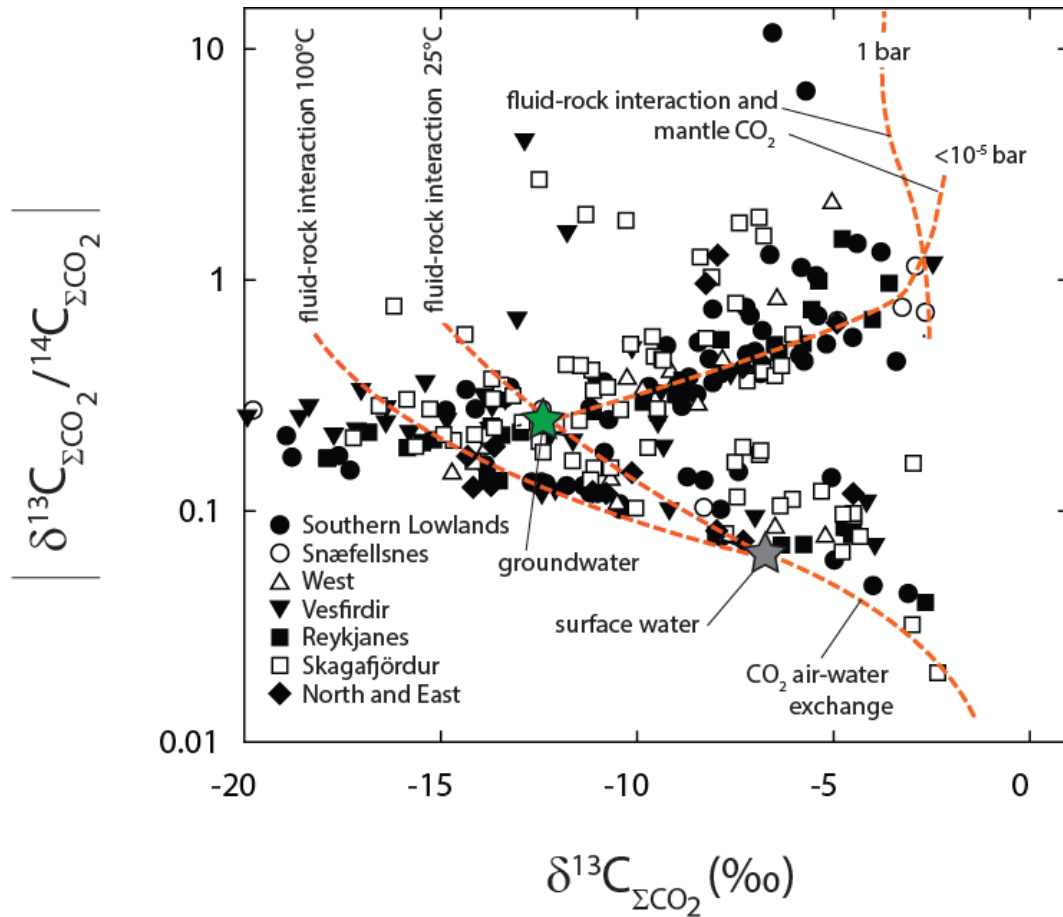
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1203 **Fig. 11.** The effects of adiabatic boiling on the ΣCO_2 concentration and $\delta^{13}\text{CO}_2$ values for the
 1204 high-temperature fluid. According to isotope geochemical modeling results, the vapor
 1205 becomes enriched and the boiled liquid depleted in ΣCO_2 relative to the reservoir fluid
 1206 initially at 280°C and allowed to boil in steps to 100°C. Most of the CO_2 enters the vapor
 1207 phase resulting in insignificant changes in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ value of the vapor upon boiling and thus
 1208 a similar value for the reservoir fluid. In contrast, the boiled liquid becomes initially
 1209 isotopically lighter, followed by an increase to heavier values. This trend is the result of
 1210 changes in aqueous speciation of ΣCO_2 and temperature effects on the fractionation factors
 1211 between dissolved inorganic aqueous species. The plot demonstrates that geothermal vapor is
 1212 likely to closely represent the reservoir $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values, whereas boiled liquid does not. The
 1213 data are from Arnórsson and Barnes (1983), Sano et al. (1985), Marty et al. (1991), Poreda et
 1214 al. (1992) and Barry et al (2014).

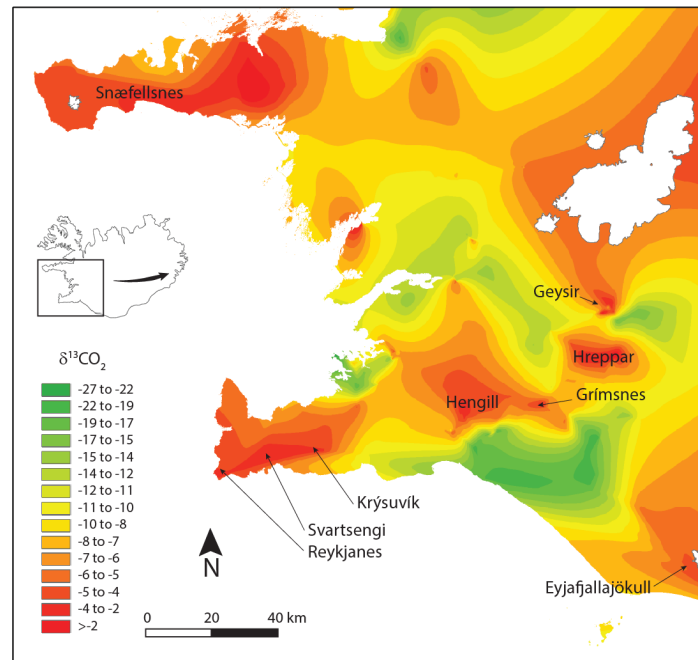
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1217 **Fig 12.** The relationship between $|\delta^{13}\text{C}_{\Sigma\text{CO}_2} / ^{14}\text{C}_{\Sigma\text{CO}_2}|$ and $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ for Icelandic non-
 1218 thermal groundwater and low-temperature water. Also shown are the results of the three
 1219 isotope geochemical models: (1) fluid-rock interaction with typical degassed basalt, (2) fluid-
 1220 rock interaction with intrusive basalt and (3) fluid-rock interaction and deep gas input. Three
 1221 major trends are observed that indicate multiple sources of CO_2 in the thermal water: (1)
 1222 atmospheric CO_2 through air-water interaction, (2) dissolution of basalts at surface and
 1223 shallow depths and largely degassed with CO_2 followed by calcite formation, and (3) input of
 1224 deep-seated CO_2 gas with p_{CO_2} of $<10^{-5}$ to 1 bar having the $\delta^{13}\text{C}$ value of the Icelandic mantle
 1225 (e.g., Metrich et al., 1991; Barry et al., 2014). This deep-seated gas is thought to indicate deep
 1226 degassing through the Icelandic crust off-axis, with the gas originating from the upper mantle
 1227 and lower crust. The data are taken from Stefánsson et al. (2016c).

1228



1229

1230 **Fig. 13.** The distribution of $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in thermal waters in western and southern Iceland.

1231 Three major features are observed: 1) within the rift and associated with volcanic centers like

1232 Reykjanes, Svartsengi, Krýsuvík and Hengill, high $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values suggest a mantle source

1233 of CO_2 ; 2) off-rift, the $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values are usually much lower, suggesting water-rock

1234 interaction being the dominant source of CO_2 in these waters; and 3) in some locations in the

1235 Southern Lowlands (Grímsnes) and Snæfellsnes, mantle $\delta^{13}\text{C}$ values are observed. Data from

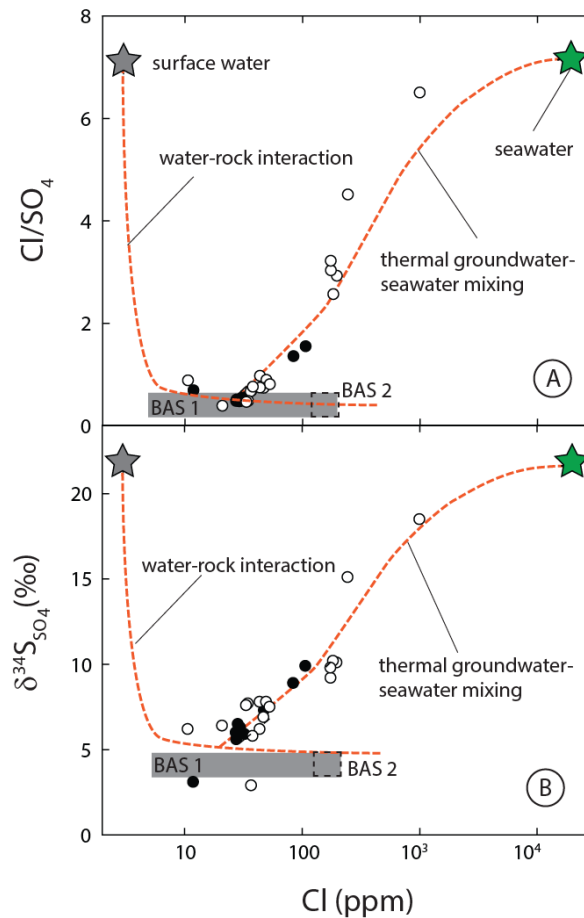
1236 Arnórsson and Barnes (1983), Sano et al. (1985), Marty et al. (1991), Poreda et al. (1992),

1237 Sveinbjörnsdóttir et al. (1995), Hilton et al. (1998), Barry et al. (2014) and Stefánsson et al.

1238 (2016c).

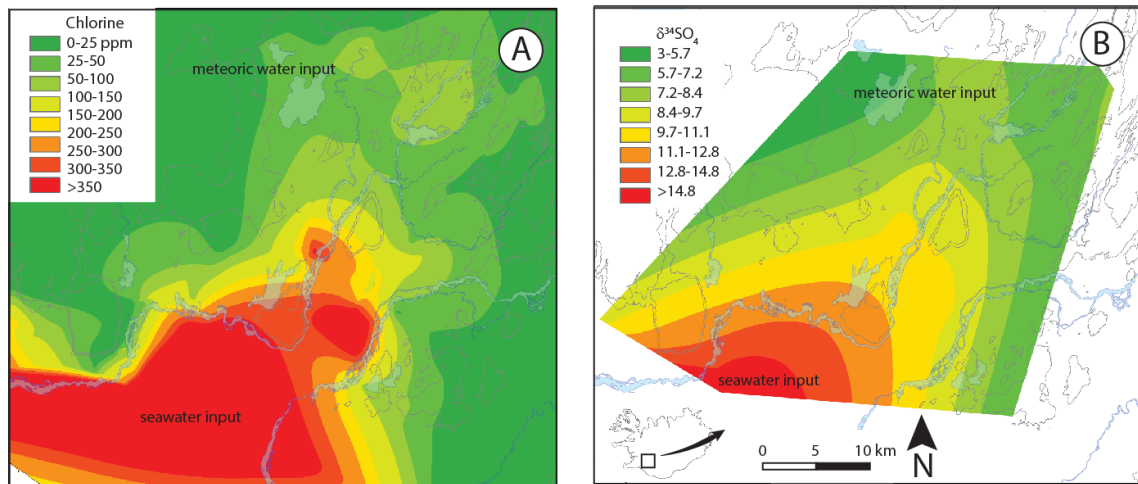
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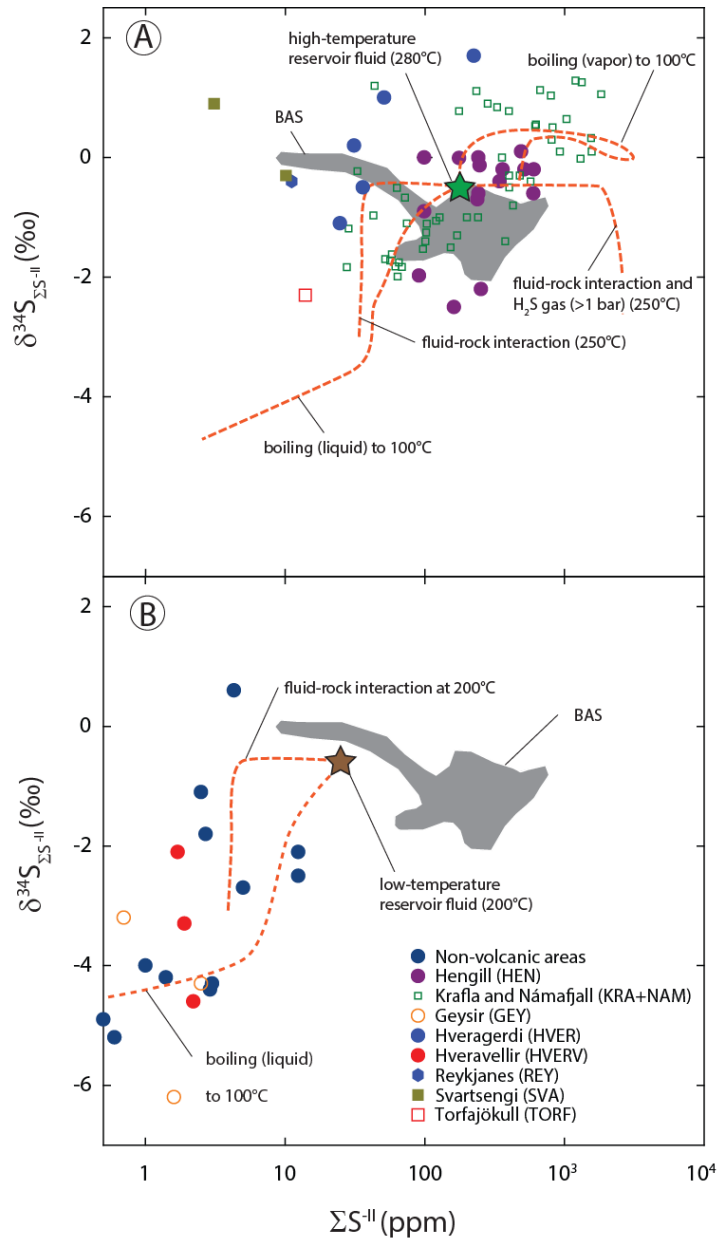
1242 **Fig. 14.** The relationship between Cl/SO_4 and Cl (A) and $\delta^{34}\text{S}_{\text{SO}_4}$ and Cl (B) in low-
 1243 temperature water in the Southern Lowlands (open circles) and West Iceland (dots). Also
 1244 shown are the results of geochemical modeling involving surface water interaction with
 1245 basaltic rocks and mixing between thermal groundwater with ~ 30 ppm Cl and seawater.
 1246 Comparison of the models and the data demonstrate that the source of SO_4 in these waters is
 1247 leaching of SO_4 from the rocks and mixing with seawater, particularly in coastal areas. The
 1248 thermal water data are from Torssander (1986). Two different basalt fields are shown: 1)
 1249 BAS1 (gray field) is defined by $\delta^{34}\text{S}_{\text{SO}_4}$ values of Icelandic basalts (Torssander, 1989) and
 1250 the Cl concentration basaltic glasses (Halldórsson et al., 2016a); 2) BAS2 (dashed box) is
 1251 defined by the $\delta^{34}\text{S}_{\text{SO}_4}$ values of Icelandic basalts (Torssander, 1989) and the range in Cl
 1252 concentrations reported by Arnórsson and Andrésdóttir (1995).



1253
 1254 **Fig. 15.** The geographical distribution of Cl concentrations (A) and $\delta^{34}\text{SO}_4$ values (B) of low-
 1255 temperature thermal water in the Southern Lowlands. Seawater input is observed towards the
 1256 coast with increasing Cl concentration and increasing $\delta^{34}\text{SO}_4$ values. The thermal water data
 1257 are taken from Stefánsson et al. (2016a) and Torssander (1986).

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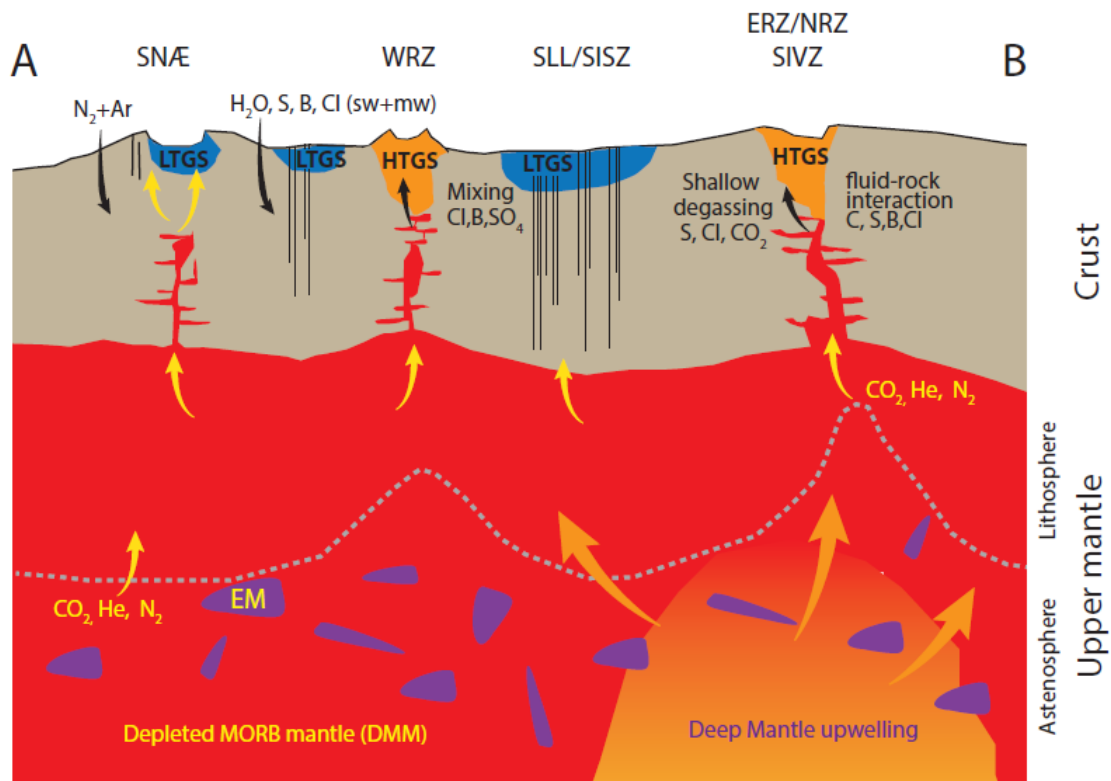
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1261 **Fig. 16.** The relationship between the concentration of dissolved sulfide (ΣS^{-II}) and $\delta^{34}S^{-II}$ for
 1262 high-temperature fluids (A) and low-temperature water (B). Water at Geysir and Hveravellir
 1263 have also been included in (B) as these have many similarities with low-temperature systems.
 1264 For high-temperature systems, boiling leads to enrichment of ΣS^{-II} and ^{34}S in the vapor phase,
 1265 whereas the boiled liquid phase becomes depleted in ΣS^{-II} and ^{34}S . This is caused by changes
 1266 in vapor and aqueous speciation and accompanied isotope fractionation (Stefánsson et al.,
 1267 2015). Intensive fluid-rock interaction causes the reservoir fluid to have progressively lower
 1268 $\delta^{34}S^{-II}$ values and lower ΣS^{-II} , where fluid-rock interaction and H_2S gas input results in

1269 increased $\Sigma\text{S}^{\text{II}}$ fluid concentration and progressively lower $\delta^{34}\text{S}^{\text{II}}$ values in thermal fluids.
1270 This suggests that rock-leaching with no or minor H_2S magma gas addition is the source of
1271 $\delta^{34}\text{S}^{\text{II}}$ in high-temperature fluids. For low-temperature systems, the reservoir $\Sigma\text{S}^{\text{II}}$
1272 concentrations are lower than for high-temperature water. A similar trend is observed with
1273 boiling and water-rock interaction as for high-temperature fluids with the source of sulfur
1274 being rock leaching. The data on fluid composition are from Sakai et al. (1980), Torssander
1275 (1986) and Stefánsson et al. (2015) and the data on basalts are from Torssander (1989).
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1279 **Fig. 17.** Summary of major sources and processes affecting volatile elements in Icelandic
 1280 thermal fluids traced by their isotope characteristics. The A-B cross section referred to Figure
 1281 1 and marks a section from Snæfellsnes (SNÆ), through West Rift Zone (WRZ), the Southern
 1282 Lowlands (SLL) and the South Iceland Seismic Zone (SISZ) to the South Iceland Volcanic
 1283 Zone, East Rift Zone (ERZ) and North Rift Zone (NRZ). LTGS and HTGS stands for low-
 1284 temperature and high-temperature geothermal systems, respectively. It should be noted that
 1285 the figure is not in scale. EM: enriched mantle, LTGS: low-temperature geothermal systems
 1286 and HTGS: high-temperature geothermal systems.

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